



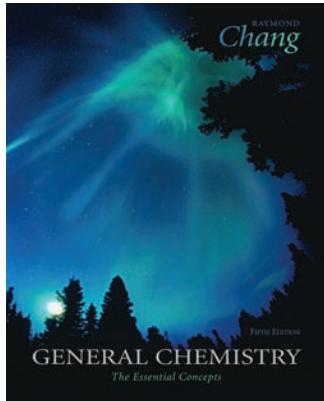
RAYMOND  
*Chang*

FIFTH EDITION

# GENERAL CHEMISTRY

*The Essential Concepts*

# GENERAL CHEMISTRY



## ABOUT THE COVER

Molecules in the upper atmosphere are constantly being bombarded by high-energy particles from the sun. As a result, these molecules either break up into atoms and/or become ionized. Eventually, the electronically excited species return to the ground state with the emission of light, giving rise to the phenomenon called *aurora borealis* (in the Northern Hemisphere) or *aurora australis* (in the Southern Hemisphere).

Raymond  
**CHANG**

Williams College

# GENERAL CHEMISTRY

*The Essential Concepts*

FIFTH EDITION



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## GENERAL CHEMISTRY: THE ESSENTIAL CONCEPTS, FIFTH EDITION

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Professor Chang has served on the American Chemical Society Examination Committee, the National Chemistry Olympiad Examination Committee, and the Graduate Record Examinations (GRE) Committee. He is an editor of *The Chemical Educator*. Professor Chang has written books on physical chemistry, industrial chemistry, and physical science. He has also coauthored books on the Chinese language, children's picture books, and a novel for young readers.

For relaxation, Professor Chang maintains a forest garden, plays tennis, and practices the violin.





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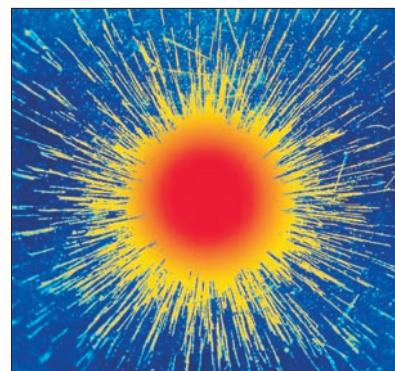
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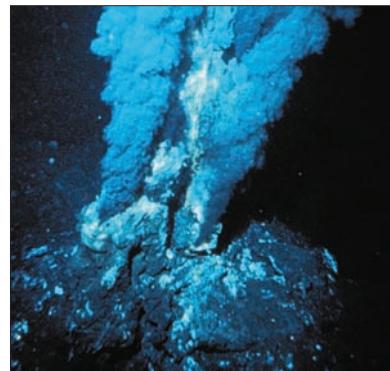
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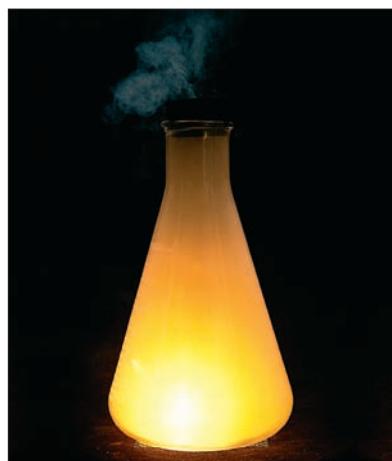
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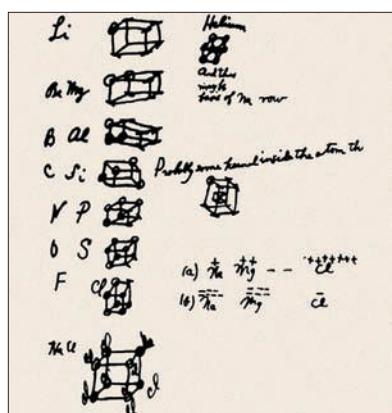
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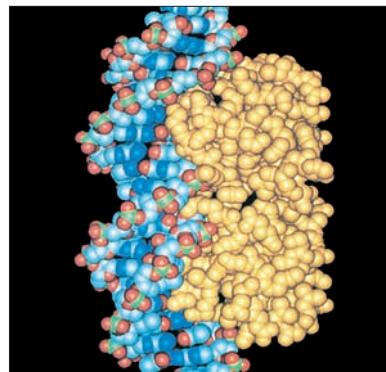
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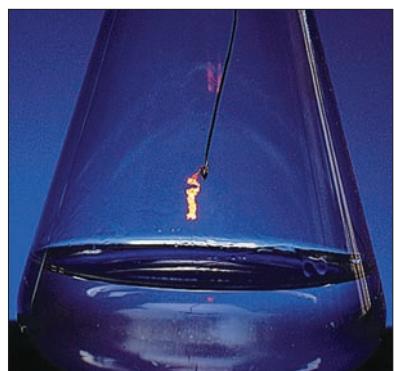
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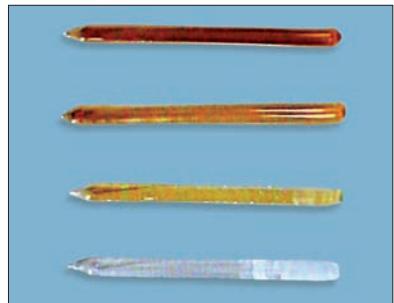
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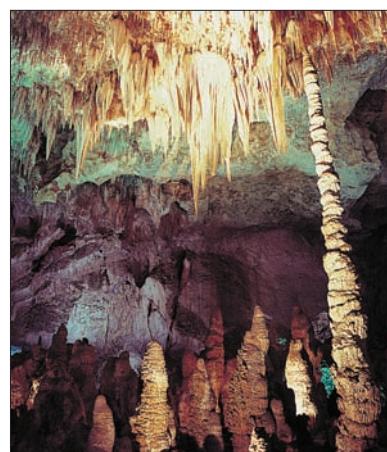


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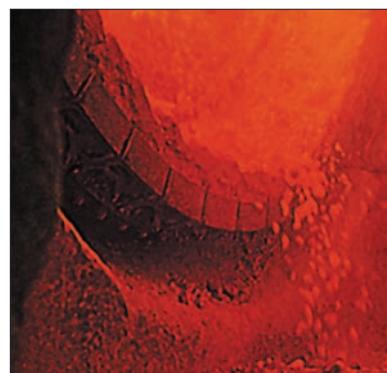
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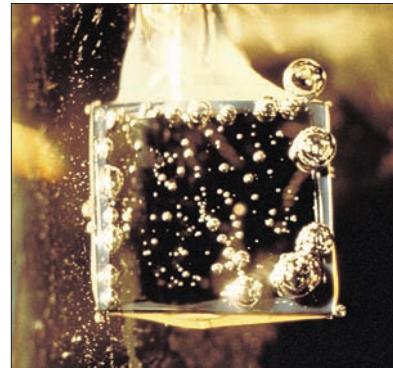
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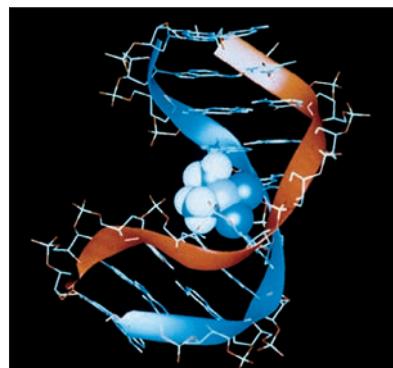
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The animations below are correlated to **General Chemistry** within each chapter in two ways. The first is the Interactive Activity Summary found in the opening pages of

every chapter. Then within the chapter are icons informing the student and instructor that an animation is available for a specific topic and where to find the animation for viewing on our Chang *General Chemistry* ARIS website. For the instructor, the animations are also available on the Chemistry Animations Library DVD.

## Chang Animations

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- Acid-base titrations (17.3)
- Acid ionization (16.5)
- Activation energy (14.4)
- Alpha, beta, and gamma rays (2.2)
- Alpha-particle scattering (2.2)
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## Simulations

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- Ideal gas law (Chapter 5)
- Kinetics (Chapter 14)
- Equilibrium (Chapter 15)
- Titration (Chapter 17)
- Electrochemistry (Chapter 19)
- Nuclear (Chapter 21)



In this fifth edition of *General Chemistry: The Essential Concepts*, I have continued the tradition of presenting only the material that is essential to a one-year general chemistry course. As with previous editions, I have included all the core topics that are necessary for a solid foundation in general chemistry without sacrificing depth, clarity, or rigor.

*General Chemistry* covers these topics in the same depth and at the same level as 1100-page texts. Therefore, this book is not a condensed version of a big text. I have written it so that an instructor can cover 95 percent of the content, instead of the two-thirds or three-quarters that in my experience is typical of the big books. My hope is that this concise-but-thorough approach will appeal to efficiency-minded instructors and will please value-conscious students. The responses I have received from users over the years convince me that there is a strong need for such a text.

## What's New in This Edition?

Many sections have been revised and updated based on the comments from reviewers and users. Some examples are:

- An introduction to organic compounds has been added to Section 2.8.
- Ionic bonding has been added to Section 9.2.
- Section 14.3 now also discusses zero-order reactions in addition to first- and second-order reactions.
- Section 16.3 compares the definition of pH using concentration and activity.
- Many new problems have been added under the Special Problems section in each chapter.
- The ARIS electronic homework system is available for the fifth edition. ARIS will enhance the student learning experience, administer assignments, track student progress, and administer an instructor's course. The students can locate the animations and interactives noted in the text margins in ARIS. Quizzing and homework assigned by the instructor is available in the ARIS electronic homework program.

## Art

As always, I strive for a clean but visual design. For example, the following diagram shows the conversion of molecular hydrogen chloride to hydrochloric acid.



I have also added new molecular art to line drawings and photos and to a number of end-of-chapter problems. In addition, we have updated the photo program to complement the visual layout of the design. Finally, we have updated the format of the periodic table throughout the text.

All key equations and answers to many Worked Examples have been shaded for easy visual access. The key equations are also listed at the end of each chapter.

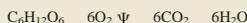
$$\text{bond order} = \frac{1}{2} \left( \frac{\text{number of electrons in bonding MOs}}{\text{number of electrons in antibonding MOs}} \right) \quad (10.2)$$

## Problems

The development of problem-solving skills has always been a major objective of this text. For example, in Section 3.8 the general approach for solving stoichiometry problems is broken down in a numbered step-by-step process. Immediately following is Example 3.13 using this approach. Example 3.14 then requires the students to use this same type of process on their own.

**Example 3.13**

The food we eat is degraded, or broken down, in our bodies to provide energy for growth and function. A general overall equation for this very complex process represents the degradation of glucose ( $C_6H_{12}O_6$ ) to carbon dioxide ( $CO_2$ ) and water ( $H_2O$ ):



If 856 g of  $C_6H_{12}O_6$  is consumed by a person over a certain period, what is the mass of  $CO_2$  produced?

**Strategy** Looking at the balanced equation, how do we compare the amount of  $C_6H_{12}O_6$  and  $CO_2$ ? We can compare them based on the *mole ratio* from the balanced equation. Starting with grams of  $C_6H_{12}O_6$ , how do we convert to moles of  $C_6H_{12}O_6$ ? Once moles of  $CO_2$  are determined using the mole ratio from the balanced equation, how do we convert to grams of  $CO_2$ ?

**Solution** We follow the preceding steps and Figure 3.8.

*Step 1:* The balanced equation is given in the problem.

*Step 2:* To convert grams of  $C_6H_{12}O_6$  to moles of  $C_6H_{12}O_6$ , we write

$$856 \text{ g } C_6H_{12}O_6 \times \frac{1 \text{ mol } C_6H_{12}O_6}{180.2 \text{ g } C_6H_{12}O_6} = 4.750 \text{ mol } C_6H_{12}O_6$$

*Step 3:* From the mole ratio, we see that 1 mol  $C_6H_{12}O_6$   $\approx$  6 mol  $CO_2$ . Therefore, the number of moles of  $CO_2$  formed is

$$4.750 \text{ mol } C_6H_{12}O_6 \times \frac{6 \text{ mol } CO_2}{1 \text{ mol } C_6H_{12}O_6} = 28.50 \text{ mol } CO_2$$

*Step 4:* Finally, the number of grams of  $CO_2$  formed is given by

$$28.50 \text{ mol } CO_2 \times \frac{44.01 \text{ g } CO_2}{1 \text{ mol } CO_2} = 1.25 \times 10^3 \text{ g } CO_2$$

After some practice, we can combine the conversion steps

grams of  $C_6H_{12}O_6$   $\longrightarrow$  moles of  $C_6H_{12}O_6$   $\longrightarrow$  moles of  $CO_2$   $\longrightarrow$  grams of  $CO_2$   
into one equation:

$$\text{mass of } CO_2 = 856 \text{ g } C_6H_{12}O_6 \times \frac{1 \text{ mol } C_6H_{12}O_6}{180.2 \text{ g } C_6H_{12}O_6} \times \frac{6 \text{ mol } CO_2}{1 \text{ mol } C_6H_{12}O_6} \times \frac{44.01 \text{ g } CO_2}{1 \text{ mol } CO_2}$$

$$= 1.25 \times 10^3 \text{ g } CO_2$$

**Check** Does the answer seem reasonable? Should the mass of  $CO_2$  produced be larger than the mass of  $C_6H_{12}O_6$  reacted, even though the molar mass of  $CO_2$  is considerably less than the molar mass of  $C_6H_{12}O_6$ ? What is the mole ratio between  $CO_2$  and  $C_6H_{12}O_6$ ?

**Practice Exercise** Methanol ( $CH_3OH$ ) burns in air according to the equation



If 209 g of methanol are used up in a combustion process, what is the mass of  $H_2O$  produced?

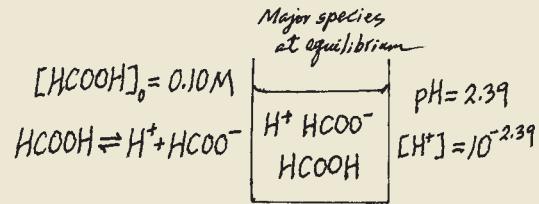
Marginal references enable students to apply new skills to other, similar problems at the end of the chapter. Each Worked Example is followed by a Practice Exercise that asks the students to solve a similar problem on their own. The answers to the Practice Exercises are provided after the end-of-chapter problems in each chapter.

As an instructor, I often tell my students that a good learning tool is to sketch out the inner workings of a problem. In some of the Worked Examples, I have included this type of drawing (for example, see Example 16.9 on p. 545). It is what a scientist would do as he or she works out a problem.

**Example 16.9**

The pH of a 0.10 M solution of formic acid ( $HCOOH$ ) is 2.39. What is the  $K_a$  of the acid?

**Strategy** Formic acid is a weak acid. It only partially ionizes in water. Note that the concentration of formic acid refers to the initial concentration, before ionization has started. The pH of the solution, on the other hand, refers to the equilibrium state. To calculate  $K_a$ , then, we need to know the concentrations of all three species:  $[H^+]$ ,  $[HCOO^-]$ , and  $[HCOOH]$  at equilibrium. As usual, we ignore the ionization of water. The following sketch summarizes the situation.



**Solution** We proceed as follows.

*Step 1:* The major species in solution are  $HCOOH$ ,  $H^+$ , and the conjugate base  $HCOO^-$ .

*Step 2:* First we need to calculate the hydrogen ion concentration from the pH value

$$\begin{aligned} pH &= -\log[H^+] \\ 2.39 &= -\log[H^+] \end{aligned}$$

Taking the antilog of both sides, we get

$$[H^+] = 10^{-2.39} = 4.1 \times 10^{-3} \text{ M}$$

Next we summarize the changes:

	$HCOOH(aq)$	$\rightleftharpoons$	$H^+(aq)$	$+$	$HCOO^-(aq)$
Initial (M):	0.10		0.00		0.00
Change (M):	$-4.1 \times 10^{-3}$		$+4.1 \times 10^{-3}$		$+4.1 \times 10^{-3}$
Equilibrium (M):	$(0.10 - 4.1 \times 10^{-3})$		$4.1 \times 10^{-3}$		$4.1 \times 10^{-3}$

Note that because the pH and hence the  $H^+$  ion concentration is known, it follows that we also know the concentrations of  $HCOOH$  and  $HCOO^-$  at equilibrium.

*Step 3:* The ionization constant of formic acid is given by

$$\begin{aligned} K_a &= \frac{[H^+][HCOO^-]}{[HCOOH]} \\ &= \frac{(4.1 \times 10^{-3})(4.1 \times 10^{-3})}{(0.10 - 4.1 \times 10^{-3})} \\ &= 1.8 \times 10^{-4} \end{aligned}$$

**Check** The  $K_a$  value differs slightly from the one listed in Table 16.3 because of the rounding-off procedure we used in the calculation.

**Practice Exercise** The pH of a 0.060 M weak monoprotic acid is 3.44. Calculate the  $K_a$  of the acid.

## Pedagogy

The Interactive Activity Summary shows the available media to further enhance students' ability to understand a concept.

The *Essential Concepts* in each chapter opener summarizes the main topics to be discussed in the chapter.

**CHAPTER**

# 10

**Chemical Bonding II: Molecular Geometry and Hybridization of Atomic Orbitals**

**CHAPTER OUTLINE**

- 10.1 Molecular Geometry 313
- Molecules in Which the Central Atom Has No Lone Pairs · Molecules in Which the Central Atom Has One or More Lone Pairs · Geometry of Molecules with More Than One Central Atom · Guidelines for Applying the VSEPR Model
- 10.2 Dipole Moments 322
- 10.3 Valence Bond Theory 325
- 10.4 Hybridization of Atomic Orbitals 328
  - $\sigma$  Hybridization ·  $\sigma$  Hybridization ·  $\sigma^2$  Hybridization · Procedure for Hybridizing Atomic Orbitals · Hybridization of  $p$ , and  $d$  Orbitals
- 10.5 Hybridization in Molecules Containing Double and Triple Bonds 331
- 10.6 Molecular Orbital Theory 340
  - Bonding and Antibonding Molecular Orbitals · Molecular Orbital Configurations

**ESSENTIAL CONCEPTS**

**Molecular Geometry** Molecular geometry refers to the three-dimensional arrangement of atoms in a molecule. For relatively small molecules, in which the central atom contains two to six bonding pairs, molecular geometry provides the basis for the shell-electron-pair repulsion (VSEPR) model. This model is based on the assumption that chemical bonds and lone pairs tend to remain as far apart as possible to minimize repulsion.

**Dipole Moments** In a diatomic molecule the difference in the electronegativity of the two atoms determines the dipole and a dipole moment. The dipole moment of a molecule made of three or more atoms depends both on the polarity of the bonds and molecular geometry. Dipole moment measurements can help us distinguish between different possible geometries of a molecule.

**Hybridization of Atomic Orbitals** Hybridization is the quantum mechanical description of chemical bonding. Atomic orbitals are hybridized, or mixed, to form hybrid orbitals. These orbitals then interact with other atomic orbitals to form chemical bonds. Various molecular geometries can be generated by different hybridizations. The hybridization concept accounts for the exception to the octet rule and also explains the formation of double and triple bonds.

**Molecular Orbital Theory** Molecular orbital theory describes bonding in terms of the combination of atomic orbitals to form bonding that is associated with the molecule as a whole. Molecular orbitals stable if the sum of electrons in bonding molecular orbitals is greater than that in antibonding molecular orbitals. We write electron configurations for molecular orbitals as we do for atomic orbitals, using the Pauli exclusion principle and Hund's rule.

**Interactive Activity Summary**

1. Animation: VSEPR (10.1)  
 2. Interactivity: Determining Molecular Shape (10.1)  
 3. Animation: Polarity of Molecules (10.2)  
 4. Interactivity: Molecular Polarity (10.2)  
 5. Animation: Hybridization (10.4)  
 6. Interactivity: Determining Orbital Hybridization (10.4)  
 7. Animation: Sigma and Pi Bonds (10.5)  
 8. Interactivity: Energy Levels of Bonding—Homonuclear Diatomic Molecules (10.6)

4.2 Precipitation Reactions 97

in which  $\text{CH}_3\text{COO}^-$  is called the acetate ion. (In this book we will use the term *dissociation* for ionic compounds and *ionization* for acids and bases.) By writing the formula of acetic acid as  $\text{CH}_3\text{COOH}$  we indicate that the ionizable proton is in the  $\text{COOH}$  group. The double arrow ( $\rightleftharpoons$ ) in an equilibrium reaction is *reversible*; that is, the reaction may occur in either direction. Initially, a number of  $\text{H}_3\text{O}^+$  and  $\text{CH}_3\text{COO}^-$  molecules break up to yield  $\text{CH}_3\text{COO}^-$  and  $\text{H}_3\text{O}^+$  ions. As time goes on, some of the  $\text{CH}_3\text{COO}^-$  and  $\text{H}_3\text{O}^+$  ions recombine to form  $\text{CH}_3\text{COOH}$  molecules. Eventually, a state is reached in which the acid molecules break up as fast as the ions recombine. Such a *chemical state*, in which no net change can be observed (although continuous activity is taking place on the molecular level), is called *chemical equilibrium*. Acetic acid, then, is a weak electrolyte because its ionization in water is incomplete. By contrast, in a hydrochloric acid solution, the  $\text{H}^+$  and  $\text{Cl}^-$  ions have no tendency to recombine to form molecular  $\text{HCl}$ . We use the single arrow to represent complete ionization.

In Sections 4.2–4.4 we will study three types of reactions in the aqueous medium (precipitation, acid-base, and oxidation-reduction) that are of great importance to industrial, environmental, and biological processes. They also play a role in our daily experience.

**4.2 Precipitation Reactions**

One common type of reaction that occurs in aqueous solution is the *precipitation reaction*, which results in the formation of an insoluble product, or precipitate. A *precipitate* is an insoluble solid that separates from the solution. Precipitation reactions usually involve ionic compounds. For example, when an aqueous solution of lead(II) nitrate [ $\text{Pb}(\text{NO}_3)_2$ ] is added to an aqueous solution of potassium iodide ( $\text{KI}$ ), a yellow precipitate of lead iodide ( $\text{PbI}_2$ ) is formed:

$$\text{Pb}(\text{NO}_3)_2(aq) + 2\text{KI}(aq) \rightarrow \text{PbI}_2(s) + 2\text{KNO}_3(aq)$$

Potassium nitrate remains in solution. Figure 4.3 shows this reaction in progress. The preceding reaction is an example of a *metathesis reaction* (also called a double displacement reaction), a reaction that involves the exchange of parts between two

**Figure 4.2** Formation of yellow  $\text{PbI}_2$  precipitate as a solution of  $\text{Pb}(\text{NO}_3)_2$  is added to a solution of  $\text{KI}$ .

**Figure 4.3** Formation of yellow  $\text{PbI}_2$  precipitate as a solution of  $\text{Pb}(\text{NO}_3)_2$  is added to a solution of  $\text{KI}$ .

**Figure 4.4** Formation of yellow  $\text{PbI}_2$  precipitate as a solution of  $\text{Pb}(\text{NO}_3)_2$  is added to a solution of  $\text{KI}$ .

Marginal notes provide additional information to students regarding quick facts, referring students to a section in which the concept will be further detailed or linking back to a section they can use to review the material.

There is a plethora of molecular art in the margin, enabling students to “see” the molecule under discussion.

The periodic table icon in the margin illustrates the properties of elements according to their positions in the periodic table.

Also in the margin, students will find the icon highlighting the media (animations and interactives) that can be used to understand the concept presented.

The end of the chapter provides further study aids with the Key Equations, Summary of Facts and Concepts, and also the Key Words. They give students a quick snapshot of the chapter in review.

## Media

The Interactive Activity Summary in the chapter opening pages enables students and instructors to see at a glance the media that can be incorporated into the learning process. Within the text, an icon shows students where the concept in the animation or interactive is introduced. The icon directs students to the ARIS website for viewing. For instructors, there are also directions for finding the animation or interactive in the instructor materials.



### Animations

We have created six new animations to accompany the library of animations that support the fifth edition. The animations visually bring to life the areas in chemistry that are difficult to understand by reading alone. The animations are marked by an icon and located within ARIS for student use.

### Interactives

Two sets of interactives are available with *General Chemistry*. The interactives enable students to manipulate several variables. Students can “see” how changes affect the topic being studied. The seven topics include stoichiometry, the gas laws, kinetics, equilibrium, acid/base reactions, nuclear reactions and radioactivity, and the electrochemical cell. The other set of interactives are simple and fun learning tools that encompass a broad range of topics. All of these interactives are marked by the Interactive Activity icon.

## Instructor Resources

### Annotated Instructor’s Edition

By Raymond Chang. The Annotated Instructor’s Edition includes all resources available to instructors marked by icons located in the margins of the text. Information is

**RAYMOND Chang**

**Fifth Edition**

**GENERAL CHEMISTRY**  
*The Essential Concepts*

**Home** | **Self Study**

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provided with regard to the integration of media (animations, interactives, ARIS) and instructions as to where the instructor will find the various media. The difficulty level of the end-of-chapter problems and the various chemical disciplines to which the problems are related to is indicated. Information on quality demonstration videos, tips for instructors, and the icons marking the digital assets available on the ARIS Presentation Center are provided.

## ARIS

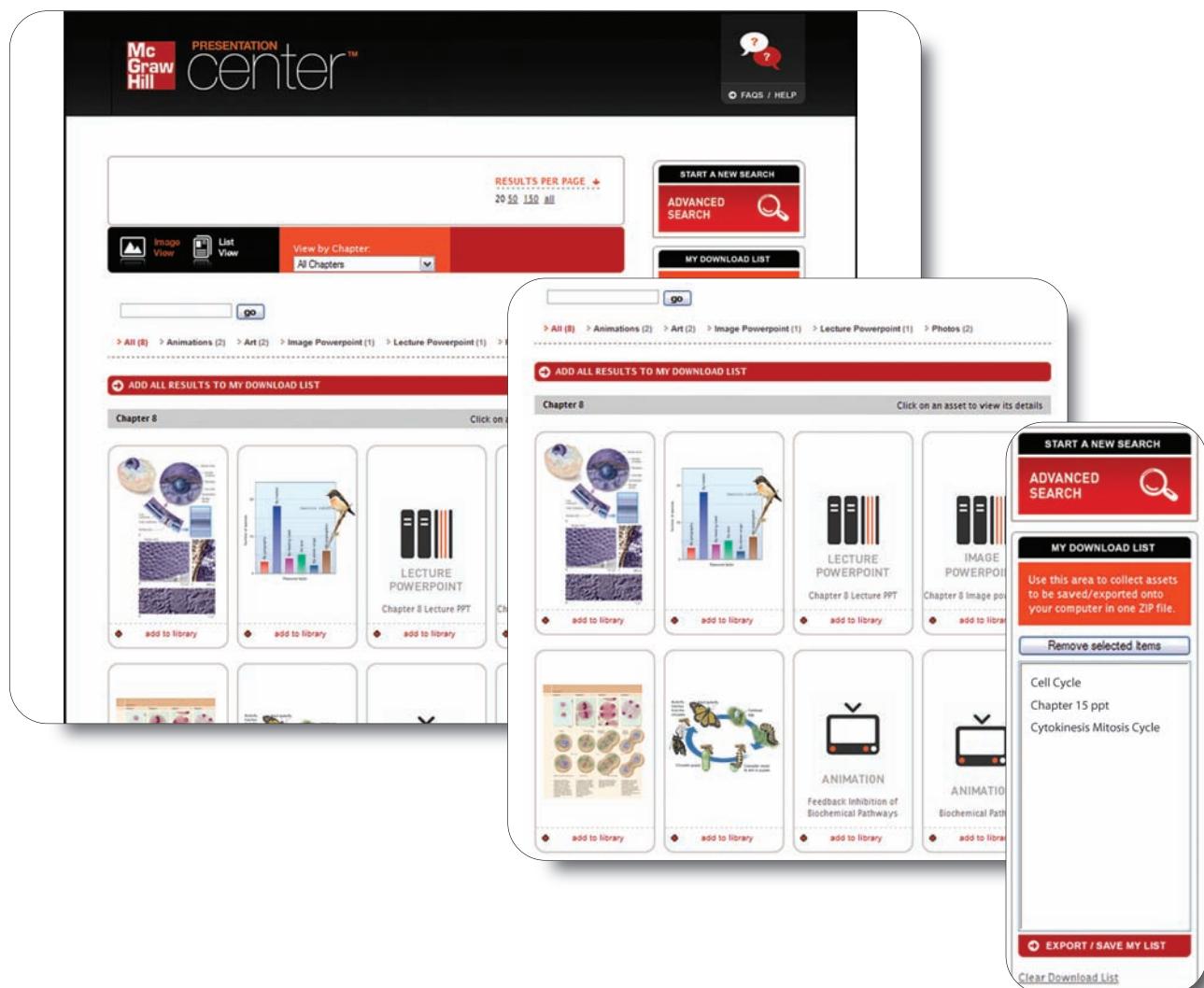
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Go to [www.aris.mhhe.com](http://www.aris.mhhe.com) to learn more, or go directly to *General Chemistry* ARIS site at [www.mhhe.com/chang](http://www.mhhe.com/chang).

### Presentation Center

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## Instructor's Testing and Resource CD-ROM

The **Test Bank** is written by John Adams (University of Missouri) and the **Instructor's Solution Manual** by Brandon J. Cruickshank (Northern Arizona University) and Raymond Chang. The Test Bank contains over 2000 multiple choice and short-answer questions. The questions, which are graded in difficulty, are comparable to the problems in the text. The Test Bank is formatted for integration into the following course management systems: WebCT and Blackboard.

The Instructor's Testing and Resource CD-ROM also contains the electronic file of the **Instructor's Solution Manual**. The solutions to all of the end-of-chapter problems are given in the manual. This manual is included on the Instructor's Testing and Resource CD-ROM.

## Overhead Transparencies

Approximately 260 full-color text illustrations are reproduced on acetate for overhead projection.

## eInstruction

McGraw-Hill has partnered with eInstruction to provide the *RF* (radio frequency) *Classroom Performance System* (CPS), to bring interactivity into the classroom. CPS is a wireless response system that gives the instructor and students immediate feedback from the entire class. The wireless response pads are essentially remotes that are easy to use and engage students. CPS enables you to motivate student preparation, interactivity, and active learning so you can receive immediate

feedback and know what students understand. A text-specific set of questions, formatted for PowerPoint, is available via download from the Instructor area of the ARIS textbook website.

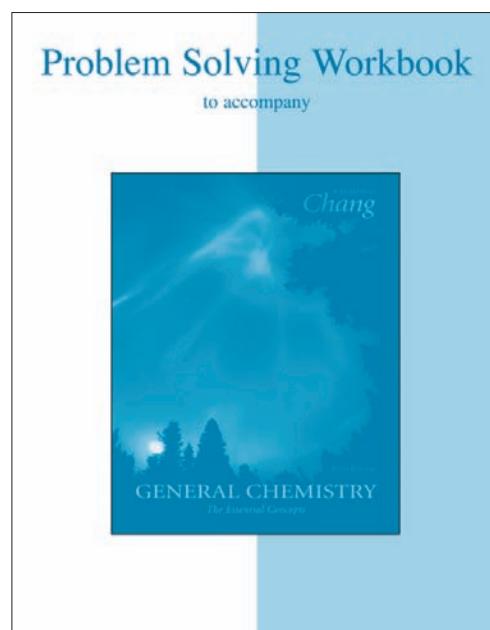
## Cooperative Chemistry Laboratory Manual

By Melanie Cooper (Clemson University). This innovative guide features open-ended problems designed to simulate experience in a research lab. Working in groups, students investigate one problem over a period of several weeks, so that they might complete three or four projects during the semester, rather than one preprogrammed experiment per class. The emphasis here is on experimental design, analysis problem solving, and communication.

## Student Resources

### Problem-Solving Workbook with Solutions

By Brandon J. Cruickshank (Northern Arizona University) and Raymond Chang is a success guide written for use with *General Chemistry*. It aims to help students hone their analytical and problem-solving skills by presenting detailed approaches to solving chemical problems. Solutions for all of the text's even-numbered problems are included.



## ARIS

For students, ARIS contains the animations and interactivities listed in the Interactive Activity list at the beginning of each chapter. ARIS also features interactive quizzes for each chapter of the text. This program enables students to complete their homework online, as assigned by their instructors.



## Chang Chemistry Resource Card

Our resource card is an easy, quick source of information on general chemistry. The student will find the periodic table, basic tables, and key equations within reach without having to consult the text.

## Schaum's Outline of College Chemistry

By Jerome Rosenberg, Michigan State University, and Lawrence Epstein, University of Pittsburgh. This helpful study aid provides students with hundreds of solved and supplementary problems for the general chemistry course.

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Raymond Chang

# A NOTE TO THE STUDENT

General chemistry is commonly perceived to be more difficult than most other subjects. There is some justification for this perception. For one thing, chemistry has a very specialized vocabulary. At first, studying chemistry is like learning a new language. Furthermore, some of the concepts are abstract. Nevertheless, with diligence you can complete this course successfully, and you might even enjoy it. Here are some suggestions to help you form good study habits and master the material in this text.

- Attend classes regularly and take careful notes.
- If possible, always review the topics discussed in class the same day they are covered in class. Use this book to supplement your notes.
- Think critically. Ask yourself if you really understand the meaning of a term or the use of an equation. A good way to test your understanding is to explain a concept to a classmate or some other person.
- Do not hesitate to ask your instructor or your teaching assistant for help.

The fifth edition tools for *General Chemistry* are designed to enable you to do well in your general chemistry course. The following guide explains how to take full advantage of the text, technology, and other tools.

- Before delving into the chapter, read the chapter *outline* and the chapter *introduction* to get a sense of the important topics. Use the outline to organize your notetaking in class.
- Use the *Interactive Activity Icon* as a guide to review challenging concepts in motion. The animations and interactives are valuable in presenting a concept and allowing the student to manipulate or choose steps so full understanding can take place.
- At the end of each chapter you will find a summary of facts and concepts, key equations, and a list of key words, all of which will help you review for exams.

- Definitions of the key words can be studied in context on the pages cited in the end-of-chapter list or in the glossary at the back of the book.
- ARIS houses an extraordinary amount of resources. Go to [www.mhhe.com/physsc/chemistry/chang](http://www.mhhe.com/physsc/chemistry/chang) and click on the appropriate cover to explore chapter quizzes, animations, interactivities, simulations, and more.
- Careful study of the worked-out examples in the body of each chapter will improve your ability to analyze problems and correctly carry out the calculations needed to solve them. Also take the time to work through the practice exercise that follows each example to be sure you understand how to solve the type of problem illustrated in the example. The answers to the practice exercises appear at the end of the chapter, following the homework problems. For additional practice, you can turn to similar homework problems referred to in the margin next to the example.
- The questions and problems at the end of the chapter are organized by section.
- For even more practice problems, use *ChemSkill Builder*. *ChemSkill Builder* is a problem-solving tutorial with hundreds of problems that include feedback.
- The back inside cover shows a list of important figures and tables with page references. This index makes it convenient to quickly look up information when you are solving problems or studying related subjects in different chapters.

If you follow these suggestions and stay up-to-date with your assignments, you should find that chemistry is challenging, but less difficult and much more interesting than you expected.

*Raymond Chang*

A hydrogen-filled balloon exploding when heated with a flame. The hydrogen gas reacts with oxygen in air to form water. Chemistry is the study of the properties of matter and the changes it undergoes.



## Introduction

### CHAPTER OUTLINE

- 1.1** The Study of Chemistry 2  
How to Study Chemistry
- 1.2** The Scientific Method 2
- 1.3** Classifications of Matter 4  
Substances and Mixtures • Elements and Compounds
- 1.4** Physical and Chemical Properties of Matter 7
- 1.5** Measurement 8  
SI Units • Mass and Weight • Volume • Density • Temperature Scales
- 1.6** Handling Numbers 13  
Scientific Notation • Significant Figures • Accuracy and Precision
- 1.7** Dimensional Analysis in Solving Problems 18  
A Note on Problem Solving

### ESSENTIAL CONCEPTS

**The Study of Chemistry** Chemistry is the study of the properties of matter and the changes it undergoes. Elements and compounds are substances that take part in chemical transformation.

**Physical and Chemical Properties** To characterize a substance, we need to know its physical properties, which can be observed without changing its identity, and chemical properties, which can be demonstrated only by chemical changes.

**Measurements and Units** Chemistry is a quantitative science and requires measurements. The measured quantities (for example, mass, volume, density, and temperature) usually have units associated with them. The units used in chemistry are based on the international system (SI) of units.

**Handling Numbers** Scientific notation is used to express large and small numbers, and each number in a measurement must indicate the meaningful digits, called significant figures.

**Doing Chemical Calculations** A simple and effective way to perform chemical calculations is dimensional analysis. In this procedure, an equation is set up in such a way that all the units cancel except the ones for the final answer.



### Interactive Activity Summary

- 1. Interactivity: Substances and Mixtures (1.3)
- 2. Interactivity: Elements (1.3)
- 3. Interactivity: SI Base Units (1.5)
- 4. Interactivity: Unit Prefixes (1.5)
- 5. Interactivity: Density (1.5)
- 6. Interactivity: Accuracy and Precision (1.6)
- 7. Interactivity: Dimensional Analysis Method (1.7)

## 1.1 The Study of Chemistry

Whether or not this is your first course in chemistry, you undoubtedly have some preconceived ideas about the nature of this science and about what chemists do. Most likely, you think chemistry is practiced in a laboratory by someone in a white coat who studies things in test tubes. This description is fine, up to a point. Chemistry is largely an experimental science, and a great deal of knowledge comes from laboratory research. In addition, however, today's chemist may use a computer to study the microscopic structure and chemical properties of substances or employ sophisticated electronic equipment to analyze pollutants from auto emissions or toxic substances in the soil. Many frontiers in biology and medicine are currently being explored at the level of atoms and molecules—the structural units on which the study of chemistry is based. Chemists participate in the development of new drugs and in agricultural research. What's more, they are seeking solutions to the problem of environmental pollution along with replacements for energy sources. And most industries, whatever their products, have a basis in chemistry. For example, chemists developed the polymers (very large molecules) that manufacturers use to make a wide variety of goods, including clothing, cooking utensils, artificial organs, and toys. Indeed, because of its diverse applications, chemistry is often called the “central science.”

### How to Study Chemistry

Compared with other subjects, chemistry is commonly perceived to be more difficult, at least at the introductory level. There is some justification for this perception. For one thing, chemistry has a very specialized vocabulary. At first, studying chemistry is like learning a new language. Furthermore, some of the concepts are abstract. Nevertheless, with diligence you can complete this course successfully—and perhaps even pleasurable. Listed here are some suggestions to help you form good study habits and master the material:

- Attend classes regularly and take careful notes.
- If possible, always review the topics you learned in class the *same* day the topics are covered in class. Use this book to supplement your notes.
- Think critically. Ask yourself if you really understand the meaning of a term or the use of an equation. A good way to test your understanding is for you to explain a concept to a classmate or some other person.
- Do not hesitate to ask your instructor or your teaching assistant for help.

You will find that chemistry is much more than numbers, formulas, and abstract theories. It is a logical discipline brimming with interesting ideas and applications.

## 1.2 The Scientific Method

All sciences, including the social sciences, employ variations of what is called the **scientific method**—*a systematic approach to research*. For example, a psychologist who wants to know how noise affects people's ability to learn chemistry and a chemist interested in measuring the heat given off when hydrogen gas burns in air follow roughly the same procedure in carrying out their investigations. The first step is carefully defining the problem. The next step includes performing experiments, making careful observations, and recording information, or *data*, about the system—the part

of the universe that is under investigation. (In these examples, the systems are the group of people the psychologist will study and a mixture of hydrogen and air.)

The data obtained in a research study may be both *qualitative*, consisting of general observations about the system, and *quantitative*, comprising numbers obtained by various measurements of the system. Chemists generally use standardized symbols and equations in recording their measurements and observations. This form of representation not only simplifies the process of keeping records, but also provides a common basis for communications with other chemists. Figure 1.1 summarizes the main steps of the research process.

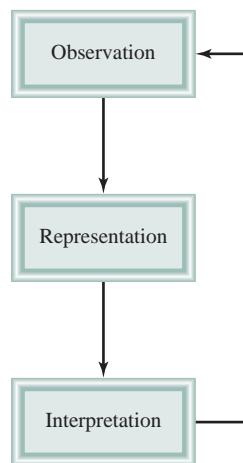
When the experiments have been completed and the data have been recorded, the next step in the scientific method is interpretation, meaning that the scientist attempts to explain the observed phenomenon. Based on the data that were gathered, the researcher formulates a *hypothesis*, or *tentative explanation for a set of observations*. Further experiments are devised to test the validity of the hypothesis in as many ways as possible, and the process begins anew.

After a large amount of data has been collected, it is often desirable to summarize the information in a concise way, as a law. In science, a *law* is a concise verbal or mathematical statement of a relationship between phenomena that is always the same under the same conditions. For example, Sir Isaac Newton's second law of motion, which you may remember from high school science, says that force equals mass times acceleration ( $F = ma$ ). What this law means is that an increase in the mass or in the acceleration of an object always increases the object's force proportionally, and a decrease in mass or acceleration always decreases the force.

Hypotheses that survive many experimental tests of their validity may evolve into theories. A *theory* is a unifying principle that explains a body of facts and/or those laws that are based on them. Theories, too, are constantly being tested. If a theory is disproved by experiment, then it must be discarded or modified so that it becomes consistent with experimental observations. Proving or disproving a theory can take years, even centuries, in part because the necessary technology is not available. Atomic theory, which we will study in Chapter 2, is a case in point. It took more than 2000 years to work out this fundamental principle of chemistry proposed by Democritus, an ancient Greek philosopher.

Scientific progress is seldom, if ever, made in a rigid, step-by-step fashion. Sometimes a law precedes a theory; sometimes it is the other way around. Two scientists may start working on a project with exactly the same objective, but may take drastically different approaches. They may be led in vastly different directions. Scientists are, after all, human beings, and their modes of thinking and working are very much influenced by their backgrounds, training, and personalities.

The development of science has been irregular and sometimes even illogical. Great discoveries are usually the result of the cumulative contributions and experience of many workers, even though the credit for formulating a theory or a law is usually given to only one individual. There is, of course, an element of luck involved in scientific discoveries, but it has been said that "chance favors the prepared mind." It takes an alert and well-trained person to recognize the significance of an accidental discovery and to take full advantage of it. More often than not, the public learns only of spectacular scientific breakthroughs. For every success story, however, there are hundreds of cases in which scientists spent years working on projects that ultimately led to a dead end. Many positive achievements came only after many wrong turns and at such a slow pace that they went unheralded. Yet even the dead ends contribute something to the continually growing body of knowledge about the physical universe. It is the love of the search that keeps many scientists in the laboratory.



**Figure 1.1**

The three levels of studying chemistry and their relationships. Observation deals with events in the macroscopic world; atoms and molecules constitute the microscopic world. Representation is a scientific shorthand for describing an experiment in symbols and chemical equations. Chemists use their knowledge of atoms and molecules to explain an observed phenomenon.

# 化 学

The Chinese characters for chemistry mean “the study of change.”

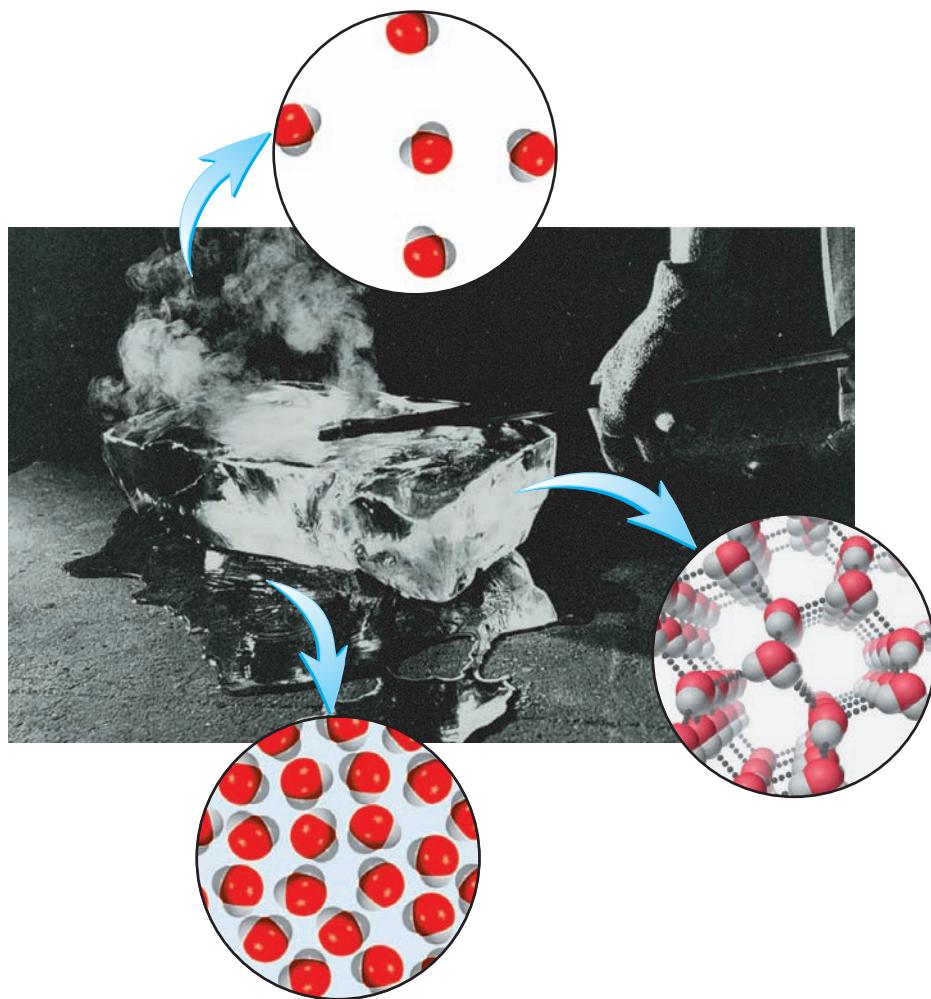
## 1.3 Classifications of Matter

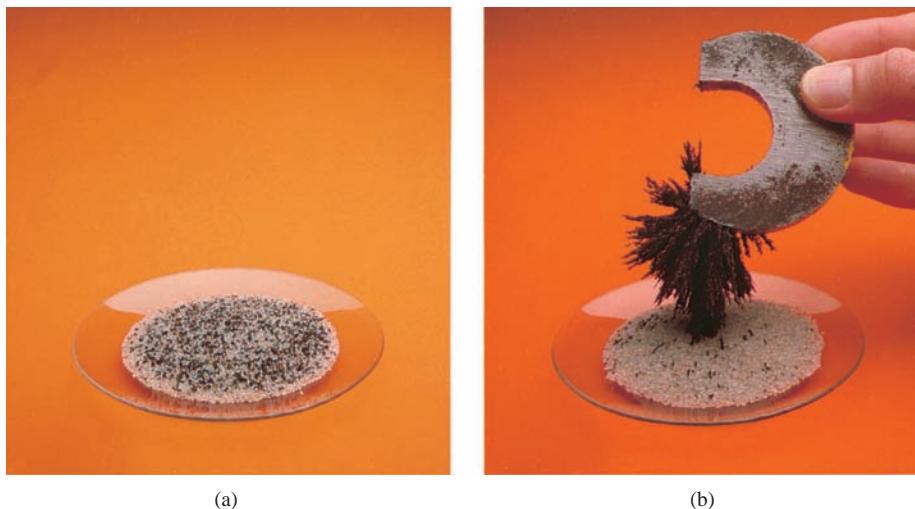
**Matter** is anything that occupies space and has mass, and **chemistry** is the study of matter and the changes it undergoes. All matter, at least in principle, can exist in three states: solid, liquid, and gas. Solids are rigid objects with definite shapes. Liquids are less rigid than solids and are fluid—they are able to flow and assume the shape of their containers. Like liquids, gases are fluid, but unlike liquids, they can expand indefinitely.

The three states of matter can be interconverted without changing the composition of the substance. Upon heating, a solid (for example, ice) will melt to form a liquid (water). (The temperature at which this transition occurs is called the *melting point*.) Further heating will convert the liquid into a gas. (This conversion takes place at the *boiling point* of the liquid.) On the other hand, cooling a gas will cause it to condense into a liquid. When the liquid is cooled further, it will freeze into the solid form. Figure 1.2 shows the three states of water. Note that the properties of water are unique among common substances in that the molecules in the liquid state are more closely packed than those in the solid state.

**Figure 1.2**

The three states of matter. A hot poker changes ice into water and steam.



**Figure 1.3**

(a) The mixture contains iron filings and sand. (b) A magnet separates the iron filings from the mixture. The same technique is used on a larger scale to separate iron and steel from nonmagnetic objects such as aluminum, glass, and plastics.

## Substances and Mixtures

A **substance** is matter that has a definite or constant composition and distinct properties. Examples are water, silver, ethanol, table salt (sodium chloride), and carbon dioxide. Substances differ from one another in composition and can be identified by their appearance, smell, taste, and other properties. At present, over 20 million substances are known, and the list is growing rapidly.

A **mixture** is a combination of two or more substances in which the substances retain their distinct identities. Some examples are air, soft drinks, milk, and cement. Mixtures do not have constant composition. Therefore, samples of air collected in different cities would probably differ in composition because of differences in altitude, pollution, and so on.

Mixtures are either homogeneous or heterogeneous. When a spoonful of sugar dissolves in water, the *composition of the mixture*, after sufficient stirring, is the same throughout the solution. This solution is a **homogeneous mixture**. If sand is mixed with iron filings, however, the sand grains and the iron filings remain visible and separate (Figure 1.3). This type of mixture, in which the *composition is not uniform*, is called a **heterogeneous mixture**. Adding oil to water creates another heterogeneous mixture because the liquid does not have a constant composition.

Any mixture, whether homogeneous or heterogeneous, can be created and then separated by physical means into pure components without changing the identities of the components. Thus, sugar can be recovered from a water solution by heating the solution and evaporating it to dryness. Condensing the water vapor will give us back the water component. To separate the iron-sand mixture, we can use a magnet to remove the iron filings from the sand, because sand is not attracted to the magnet (see Figure 1.3b). After separation, the components of the mixture will have the same composition and properties as they did to start with.

## Elements and Compounds

A substance can be either an element or a compound. An **element** is a substance that cannot be separated into simpler substances by chemical means. At present, 114 elements have been positively identified. (See the list inside the front cover of this book.)



**Interactivity:**  
Substances and Mixtures  
ARIS, Interactives



**Interactivity:**  
Elements  
ARIS, Interactives

**TABLE 1.1** Some Common Elements and Their Symbols

Name	Symbol	Name	Symbol	Name	Symbol
Aluminum	Al	Fluorine	F	Oxygen	O
Arsenic	As	Gold	Au	Phosphorus	P
Barium	Ba	Hydrogen	H	Platinum	Pt
Bromine	Br	Iodine	I	Potassium	K
Calcium	Ca	Iron	Fe	Silicon	Si
Carbon	C	Lead	Pb	Silver	Ag
Chlorine	Cl	Magnesium	Mg	Sodium	Na
Chromium	Cr	Mercury	Hg	Sulfur	S
Cobalt	Co	Nickel	Ni	Tin	Sn
Copper	Cu	Nitrogen	N	Zinc	Zn

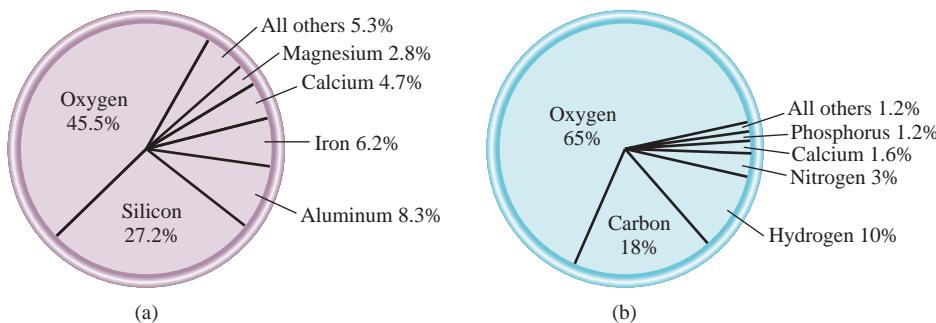
Chemists use alphabetical symbols to represent the names of the elements. The first letter of the symbol for an element is *always* capitalized, but the second letter is *never* capitalized. For example, Co is the symbol for the element cobalt, whereas CO is the formula for carbon monoxide, which is made up of the elements carbon and oxygen. Table 1.1 shows some of the more common elements. The symbols for some elements are derived from their Latin names—for example, Au from *aurum* (gold), Fe from *ferrum* (iron), and Na from *natrium* (sodium)—although most of them are abbreviated forms of their English names.

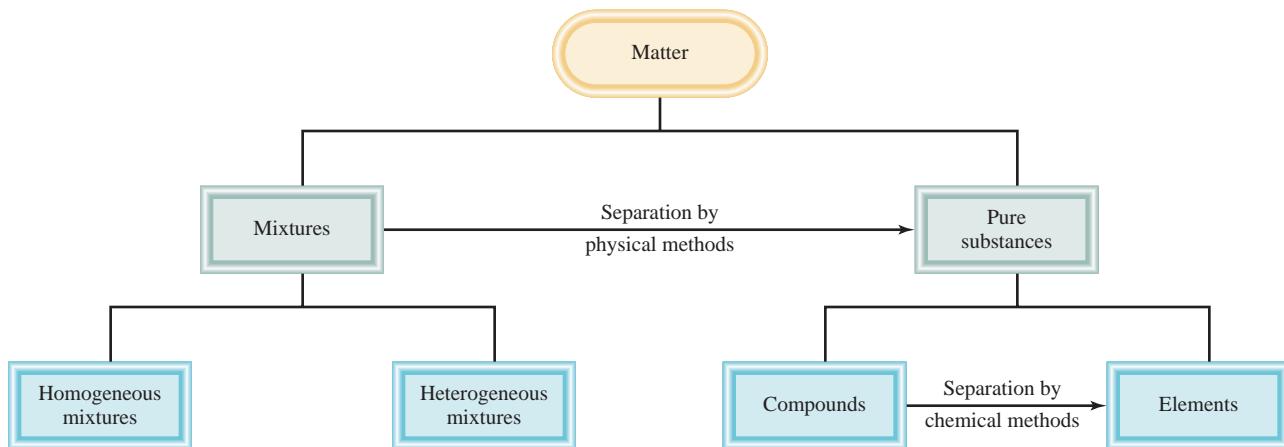
Figure 1.4 shows the most abundant elements in Earth's crust and in the human body. As you can see, only five elements (oxygen, silicon, aluminum, iron, and calcium) comprise over 90 percent of Earth's crust. Of these five elements, only oxygen is among the most abundant elements in living systems.

Most elements can interact with one or more other elements to form compounds. We define a **compound** as a substance composed of two or more elements chemically united in fixed proportions. Hydrogen gas, for example, burns in oxygen gas to form water, a compound whose properties are distinctly different from those of the starting materials. Water is made up of two parts of hydrogen and one part of oxygen. This composition does not change, regardless of whether the water comes from a faucet in the United States, the Yangtze River in China, or the ice caps on Mars. Unlike mixtures, compounds can be separated only by chemical means into their pure components.

**Figure 1.4**

(a) Natural abundance of the elements in percent by mass. For example, oxygen's abundance is 45.5 percent. This means that in a 100-g sample of Earth's crust there are, on the average, 45.5 g of the element oxygen.  
 (b) Abundance of elements in the human body in percent by mass.





**Figure 1.5**  
*Classification of matter.*

The relationships among elements, compounds, and other categories of matter are summarized in Figure 1.5.

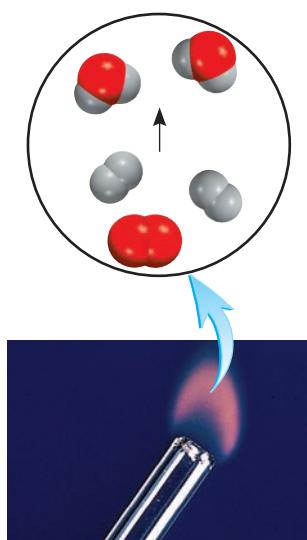
## 1.4 Physical and Chemical Properties of Matter

Substances are identified by their properties as well as by their composition. Color, melting point, boiling point, and density are physical properties. A **physical property** can be measured and observed without changing the composition or identity of a substance. For example, we can measure the melting point of ice by heating a block of ice and recording the temperature at which the ice is converted to water. Water differs from ice only in appearance and not in composition, so this is a physical change; we can freeze the water to recover the original ice. Therefore, the melting point of a substance is a physical property. Similarly, when we say that helium gas is lighter than air, we are referring to a physical property.

On the other hand, the statement “Hydrogen gas burns in oxygen gas to form water” describes a **chemical property** of hydrogen because to observe this property we must carry out a chemical change, in this case burning. After the change, the original substances, hydrogen and oxygen gas, will have vanished and a chemically different substance—water—will have taken their place. We cannot recover hydrogen and oxygen from water by a physical change such as boiling or freezing.

Every time we hard-boil an egg, we bring about a chemical change. When subjected to a temperature of about 100°C, the yolk and the egg white undergo reactions that alter not only their physical appearance but their chemical makeup as well. When eaten, the egg is changed again, by substances in the body called *enzymes*. This digestive action is another example of a chemical change. What happens during such a process depends on the chemical properties of the specific enzymes and of the food involved.

All measurable properties of matter fall into two categories: extensive properties and intensive properties. The measured value of an **extensive property** depends on how much matter is being considered. Mass, length, and volume are extensive properties. More matter means more mass. Values of the same extensive property can be added together. For example, two copper pennies have a combined mass that is the sum of the masses of each penny, and the total volume occupied by the water in two beakers is the sum of the volumes of the water in each of the beakers.



Hydrogen burning in air to form water.

The measured value of an *intensive property* does not depend on the amount of matter being considered. Temperature is an intensive property. Suppose that we have two beakers of water at the same temperature. If we combine them to make a single quantity of water in a larger beaker, the temperature of the larger amount of water will be the same as it was in two separate beakers. Unlike mass and volume, temperature and other intensive properties such as melting point, boiling point, and density are not additive.

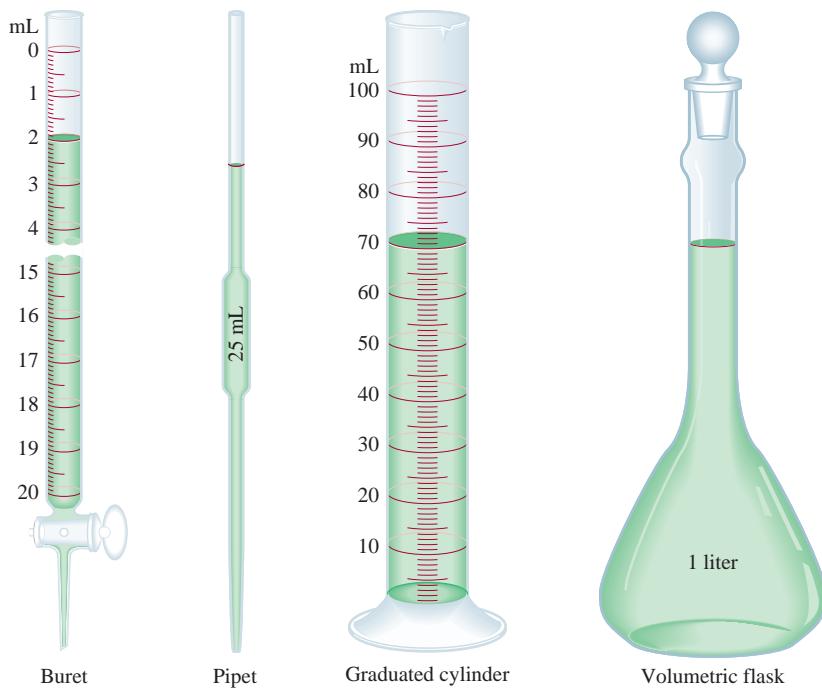
## 1.5 Measurement

The study of chemistry depends heavily on measurement. For instance, chemists use measurements to compare the properties of different substances and to assess changes resulting from an experiment. A number of common devices enable us to make simple measurements of a substance's properties: The meterstick measures length; the buret, the pipet, the graduated cylinder, and the volumetric flask measure volume (Figure 1.6); the balance measures mass; the thermometer measures temperature. These instruments provide measurements of *macroscopic properties*, which can be determined directly. *Microscopic properties*, on the atomic or molecular scale, must be determined by an indirect method, as we will see in Chapter 2.

A measured quantity is usually written as a number with an appropriate unit. To say that the distance between New York and San Francisco by car along a certain route is 5166 is meaningless. We must specify that the distance is 5166 kilometers. In science, units are essential to stating measurements correctly.



**Figure 1.6**  
Some common measuring devices found in a chemistry laboratory. These devices are not drawn to scale relative to one another. We will discuss the uses of these measuring devices in Chapter 4.



**TABLE 1.2** SI Base Units

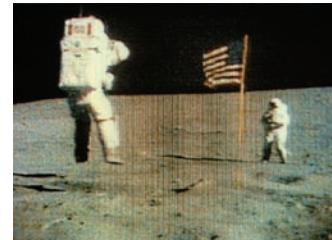
Base Quantity	Name of Unit	Symbol
Length	meter	m
Mass	kilogram	kg
Time	second	s
Electrical current	ampere	A
Temperature	K	
Amount of substance	mole	mol
Luminous intensity	candela	cd

system called the *International System of Units* (abbreviated *SI*, from the French *System International d'Unités*). Table 1.2 shows the seven SI base units. All other SI units of measurement can be derived from these base units. Like metric units, SI units are modified in decimal fashion by a series of prefixes, as shown in Table 1.3. We use both metric and SI units in this book.

Measurements that we will utilize frequently in our study of chemistry include time, mass, volume, density, and temperature.

## Mass and Weight

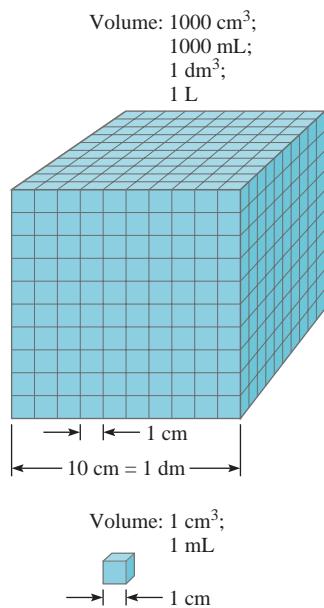
**Mass** is a measure of the quantity of matter in an object. The terms “mass” and “weight” are often used interchangeably, although, strictly speaking, they refer to different quantities. In scientific terms, **weight** is the force that gravity exerts on an object. An apple that falls from a tree is pulled downward by Earth’s gravity. The mass of the apple is constant and does not depend on its location, but its weight does. For example, on the surface of the moon the apple would weigh only one-sixth what it does on Earth, because of the smaller mass of the moon. This is why astronauts



An astronaut jumping on the surface of the moon.

**TABLE 1.3** Prefixes Used with SI Units

Prefix	Symbol	Meaning	Example
tera-	T	1,000,000,000,000, or $10^{12}$	1 terameter (Tm) = $1 \times 10^{12}$ m
giga-	G	1,000,000,000, or $10^9$	1 gigameter (Gm) = $1 \times 10^9$ m
mega-	M	1,000,000, or $10^6$	1 megameter (Mm) = $1 \times 10^6$ m
kilo-	k	1,000, or $10^3$	1 kilometer (km) = $1 \times 10^3$ m
deci-	d	1/10, or $10^{-1}$	1 decimeter (dm) = 0.1 m
centi-	c	1/100, or $10^{-2}$	1 centimeter (cm) = 0.01 m
milli-	m	1/1,000, or $10^{-3}$	1 millimeter (mm) = 0.001 m
micro-	$\mu$	1/1,000,000, or $10^{-6}$	1 micrometer ( $\mu$ m) = $1 \times 10^{-6}$ m
nano-	n	1/1,000,000,000, or $10^{-9}$	1 nanometer (nm) = $1 \times 10^{-9}$ m
pico-	p	1/1,000,000,000,000, or $10^{-12}$	1 picometer (pm) = $1 \times 10^{-12}$ m



**Figure 1.7**  
Comparison of two volumes,  
1 mL and 1000 mL.



were able to jump about rather freely on the moon's surface despite their bulky suits and equipment. The mass of an object can be determined readily with a balance, and this process, oddly, is called weighing.

The SI base unit of mass is the *kilogram* (kg), but in chemistry the smaller gram (g) is more convenient:

$$1 \text{ kg} = 1000 \text{ g} = 1 \times 10^3 \text{ g}$$

## Volume

**Volume** is *length (m) cubed*, so its SI-derived unit is the cubic meter (m<sup>3</sup>). Generally, however, chemists work with much smaller volumes, such as the cubic centimeter (cm<sup>3</sup>) and the cubic decimeter (dm<sup>3</sup>):

$$\begin{aligned} 1 \text{ cm}^3 &= (1 \times 10^{-2} \text{ m})^3 = 1 \times 10^{-6} \text{ m}^3 \\ 1 \text{ dm}^3 &= (1 \times 10^{-1} \text{ m})^3 = 1 \times 10^{-3} \text{ m}^3 \end{aligned}$$

Another common, non-SI unit of volume is the liter (L). A *liter* is *the volume occupied by one cubic decimeter*. Chemists generally use L and mL for liquid volume. One liter is equal to 1000 milliliters (mL) or 1000 cubic centimeters:

$$\begin{aligned} 1 \text{ L} &= 1000 \text{ mL} \\ &= 1000 \text{ cm}^3 \\ &= 1 \text{ dm}^3 \end{aligned}$$

and one milliliter is equal to one cubic centimeter:

$$1 \text{ mL} = 1 \text{ cm}^3$$

Figure 1.7 compares the relative sizes of two volumes.

## Density

**Density** is *the mass of an object divided by its volume*:

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

or

$$d = \frac{m}{V} \quad (1.1)$$

where *d*, *m*, and *V* denote density, mass, and volume, respectively. Note that density is an intensive property that does not depend on the quantity of mass present. The reason is that *V* increases as *m* does, so the ratio of the two quantities always remains the same for a given material.

The SI-derived unit for density is the kilogram per cubic meter (kg/m<sup>3</sup>). This unit is awkwardly large for most chemical applications. Therefore, grams per cubic centimeter (g/cm<sup>3</sup>) and its equivalent, grams per milliliter (g/mL), are more commonly used for solid and liquid densities. Table 1.4 lists the densities of several substances.

\* Measured at 1 atmosphere.

† Osmium (Os) is the densest element known.

**TABLE 1.4**

### Densities of Some Substances at 25°C

Substance	Density (g/cm <sup>3</sup> )
Air*	0.001
Ethanol	0.79
Water	1.00
Mercury	13.6
Table salt	2.2
Iron	7.9
Gold	19.3
Osmium <sup>†</sup>	22.6

### Example 1.1

Gold is a precious metal that is chemically unreactive. It is used mainly in jewelry, dentistry, and electronic devices. A piece of gold ingot with a mass of 301 g has a volume of 15.6 cm<sup>3</sup>. Calculate the density of gold.

**Solution** We are given the mass and volume and asked to calculate the density. Therefore, from Equation (1.1), we write

$$\begin{aligned} d &= \frac{m}{V} \\ &= \frac{301 \text{ g}}{15.6 \text{ cm}^3} \\ &= 19.3 \text{ g/cm}^3 \end{aligned}$$

**Practice Exercise** A piece of platinum metal with a density of 21.5 g/cm<sup>3</sup> has a volume of 4.49 cm<sup>3</sup>. What is its mass?



Gold bars.

**Similar problems:** 1.17, 1.18.

## Temperature Scales

Three temperature scales are currently in use. Their units are °F (degrees Fahrenheit), °C (degrees Celsius), and K (kelvin). The Fahrenheit scale, which is the most commonly used scale in the United States outside the laboratory, defines the normal freezing and boiling points of water to be exactly 32°F and 212°F, respectively. The Celsius scale divides the range between the freezing point (0°C) and boiling point (100°C) of water into 100 degrees. As Table 1.2 shows, the *kelvin* is the *SI base unit of temperature*; it is the *absolute* temperature scale. By absolute we mean that the zero on the Kelvin scale, denoted by 0 K, is the lowest temperature that can be attained theoretically. On the other hand, 0°F and 0°C are based on the behavior of an arbitrarily chosen substance, water. Figure 1.8 compares the three temperature scales.

The size of a degree on the Fahrenheit scale is only 100/180, or 5/9, of a degree on the Celsius scale. To convert degrees Fahrenheit to degrees Celsius, we write

$$?^\circ\text{C} = (?^\circ\text{F} - 32^\circ\text{F}) \times \frac{5^\circ\text{C}}{9^\circ\text{F}} \quad (1.2)$$

Note that the Kelvin scale does not have the degree sign. Also, temperatures expressed in kelvins can never be negative.

The following equation is used to convert degrees Celsius to degrees Fahrenheit:

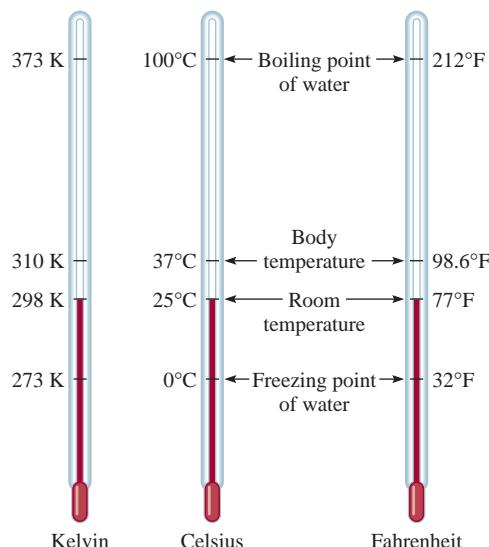
$$?^\circ\text{F} = \frac{9^\circ\text{F}}{5^\circ\text{C}} \times (?^\circ\text{C}) + 32^\circ\text{F} \quad (1.3)$$

Both the Celsius and the Kelvin scales have units of equal magnitude; that is, one degree Celsius is equivalent to one kelvin. Experimental studies have shown that absolute zero on the Kelvin scale is equivalent to  $-273.15^\circ\text{C}$  on the Celsius scale. Thus, we can use the following equation to convert degrees Celsius to kelvin:

$$? \text{ K} = (?^\circ\text{C} + 273.15^\circ\text{C}) \frac{1 \text{ K}}{1^\circ\text{C}} \quad (1.4)$$

**Figure 1.8**

*Comparison of the three temperature scales: Celsius, and Fahrenheit, and the absolute (Kelvin) scales. Note that there are 100 divisions, or 100 degrees, between the freezing point and the boiling point of water on the Celsius scale, and there are 180 divisions, or 180 degrees, between the same two temperature limits on the Fahrenheit scale. The Celsius scale was formerly called the centigrade scale.*



Solder is used extensively in the construction of electronic circuits.

### Example 1.2

- Solder is an alloy made of tin and lead that is used in electronic circuits. A certain solder has a melting point of 224°C. What is its melting point in degrees Fahrenheit?
- Helium has the lowest boiling point of all the elements at  $-452^{\circ}\text{F}$ . Convert this temperature to degrees Celsius. (c) Mercury, the only metal that exists as a liquid at room temperature, melts at  $-38.9^{\circ}\text{C}$ . Convert its melting point to kelvins.

**Solution** These three parts require that we carry out temperature conversions, so we need Equations (1.2), (1.3), and (1.4). Keep in mind that the lowest temperature on the Kelvin scale is zero (0 K); therefore, it can never be negative.

- This conversion is carried out by writing

$$\frac{9^{\circ}\text{F}}{5^{\circ}\text{C}} \times (224^{\circ}\text{C}) + 32^{\circ}\text{F} = 435^{\circ}\text{F}$$

- Here we have

$$(-452^{\circ}\text{F} - 32^{\circ}\text{F}) \times \frac{5^{\circ}\text{C}}{9^{\circ}\text{F}} = -269^{\circ}\text{C}$$

- The melting point of mercury in kelvins is given by

$$(-38.9^{\circ}\text{C} + 273.15^{\circ}\text{C}) \times \frac{1\text{ K}}{1^{\circ}\text{C}} = 234.3\text{ K}$$

Similar problems: 1.19, 1.20.

**Practice Exercise** Convert (a)  $327.5^{\circ}\text{C}$  (the melting point of lead) to degrees Fahrenheit; (b)  $172.9^{\circ}\text{F}$  (the boiling point of ethanol) to degrees Celsius; and (c)  $77\text{ K}$ , the boiling point of liquid nitrogen, to degrees Celsius.

## 1.6 Handling Numbers

Having surveyed some of the units used in chemistry, we now turn to techniques for handling numbers associated with measurements: scientific notation and significant figures.

# Scientific Notation

Chemists often deal with numbers that are either extremely large or extremely small. For example, in 1 g of the element hydrogen there are roughly

602,200,000,000,000,000,000,000

hydrogen atoms. Each hydrogen atom has a mass of only

0.0000000000000000000000000166 g

These numbers are cumbersome to handle, and it is easy to make mistakes when using them in arithmetic computations. Consider the following multiplication:

$$0.000000056 \times 0.00000000048 = 0.00000000000000002688$$

It would be easy for us to miss one zero or add one more zero after the decimal point. Consequently, when working with very large and very small numbers, we use a system called *scientific notation*. Regardless of their magnitude, all numbers can be expressed in the form

$N \times 10^n$

where  $N$  is a number between 1 and 10 and  $n$ , the exponent, is a positive or negative integer (whole number). Any number expressed in this way is said to be written in scientific notation.

Suppose that we are given a certain number and asked to express it in scientific notation. Basically, this assignment calls for us to find  $n$ . We count the number of places that the decimal point must be moved to give the number  $N$  (which is between 1 and 10). If the decimal point has to be moved to the left, then  $n$  is a positive integer; if it has to be moved to the right,  $n$  is a negative integer. The following examples illustrate the use of scientific notation:

(1) Express 568.762 in scientific notation:

$$568.762 = 5.68762 \times 10^2$$

Note that the decimal point is moved to the left by two places and  $n = 2$ .

(2) Express 0.00000772 in scientific notation:

$$0.00000772 = 7.72 \times 10^{-6}$$

Here the decimal point is moved to the right by six places and  $n = -6$ .

Keep in mind the following two points. First,  $n = 0$  is used for numbers that are not expressed in scientific notation. For example,  $74.6 \times 10^0$  ( $n = 0$ ) is equivalent to 74.6. Second, the usual practice is to omit the superscript when  $n = 1$ . Thus the scientific notation for 74.6 is  $7.46 \times 10^1$  and not  $7.46 \times 10^1$ .

**Any number raised to the power zero is equal to one.**

### Addition and Subtraction

To add or subtract using scientific notation, we first write each quantity—say  $N_1$  and  $N_2$ —with the same exponent  $n$ . Then we combine  $N_1$  and  $N_2$ ; the exponents remain the same. Consider the following examples:

$$\begin{aligned}(7.4 \times 10^3) + (2.1 \times 10^3) &= 9.5 \times 10^3 \\(4.31 \times 10^4) + (3.9 \times 10^3) &= (4.31 \times 10^4) + (0.39 \times 10^4) \\&= 4.70 \times 10^4 \\(2.22 \times 10^{-2}) - (4.10 \times 10^{-3}) &= (2.22 \times 10^{-2}) - (0.41 \times 10^{-2}) \\&= 1.81 \times 10^{-2}\end{aligned}$$

### Multiplication and Division

To multiply numbers expressed in scientific notation, we multiply  $N_1$  and  $N_2$  in the usual way, but *add* the exponents together. To divide using scientific notation, we divide  $N_1$  and  $N_2$  as usual and subtract the exponents. The following examples show how these operations are performed:

$$\begin{aligned}(8.0 \times 10^4) \times (5.0 \times 10^2) &= (8.0 \times 5.0)(10^{4+2}) \\&= 40 \times 10^6 \\&= 4.0 \times 10^7 \\(4.0 \times 10^{-5}) \times (7.0 \times 10^3) &= (4.0 \times 7.0)(10^{-5+3}) \\&= 28 \times 10^{-2} \\&= 2.8 \times 10^{-1} \\ \frac{6.9 \times 10^7}{3.0 \times 10^{-5}} &= \frac{6.9}{3.0} \times 10^{7-(-5)} \\&= 2.3 \times 10^{12} \\ \frac{8.5 \times 10^4}{5.0 \times 10^9} &= \frac{8.5}{5.0} \times 10^{4-9} \\&= 1.7 \times 10^{-5}\end{aligned}$$

### Significant Figures

Except when all the numbers involved are integers (for example, in counting the number of students in a class), obtaining the exact value of the quantity under investigation is often impossible. For this reason, it is important to indicate the margin of error in a measurement by clearly indicating the number of *significant figures*, which are the *meaningful digits in a measured or calculated quantity*. When significant figures are used, the last digit is understood to be uncertain. For example, we might measure the volume of a given amount of liquid using a graduated cylinder with a scale that gives an uncertainty of 1 mL in the measurement. If the volume is found to be 6 mL, then the actual volume is in the range of 5 mL to 7 mL. We represent the volume of the liquid as  $(6 \pm 1)$  mL. In this case, there is only one significant figure (the digit 6) that is uncertain by either plus or minus 1 mL. For greater accuracy, we might use a graduated cylinder that has finer divisions, so that the volume we measure is now uncertain by only 0.1 mL. If the volume of the liquid is now found to be 6.0 mL, we may express the quantity as  $(6.0 \pm 0.1)$  mL, and the actual value is somewhere between 5.9 mL and 6.1 mL. We can further improve the measuring device and obtain more significant figures, but in every case, the last digit is always uncertain; the amount of this uncertainty depends on the particular measuring device we use.

Figure 1.9 shows a modern balance. Balances such as this one are available in many general chemistry laboratories; they readily measure the mass of objects to four decimal places. Therefore, the measured mass typically will have four significant figures (for example, 0.8642 g) or more (for example, 3.9745 g). Keeping track of the number of significant figures in a measurement such as mass ensures that calculations involving the data will reflect the precision of the measurement.

### **Guidelines for Using Significant Figures**

We must always be careful in scientific work to write the proper number of significant figures. In general, it is fairly easy to determine how many significant figures a number has by following these rules:

1. Any digit that is not zero is significant. Thus, 845 cm has three significant figures, 1.234 kg has four significant figures, and so on.
2. Zeros between nonzero digits are significant. Thus, 606 m contains three significant figures, 40,501 kg contains five significant figures, and so on.
3. Zeros to the left of the first nonzero digit are not significant. Their purpose is to indicate the placement of the decimal point. For example, 0.08 L contains one significant figure, 0.0000349 g contains three significant figures, and so on.
4. If a number is greater than 1, then all the zeros written to the right of the decimal point count as significant figures. Thus, 2.0 mg has two significant figures, 40.062 mL has five significant figures, and 3.040 dm has four significant figures. If a number is less than 1, then only the zeros that are at the end of the number and the zeros that are between nonzero digits are significant. This means that 0.090 kg has two significant figures, 0.3005 L has four significant figures, 0.00420 min has three significant figures, and so on.
5. For numbers that do not contain decimal points, the trailing zeros (that is, zeros after the last nonzero digit) may or may not be significant. Thus, 400 cm may have one significant figure (the digit 4), two significant figures (40), or three significant figures (400). We cannot know which is correct without more information. By using scientific notation, however, we avoid this ambiguity. In this particular case, we can express the number 400 as  $4 \times 10^2$  for one significant figure,  $4.0 \times 10^2$  for two significant figures, or  $4.00 \times 10^2$  for three significant figures.



**Figure 1.9**  
A single-pan balance.

### **Example 1.3**

Determine the number of significant figures in the following measurements: (a) 478 cm, (b) 6.01 g, (c) 0.825 m, (d) 0.043 kg, (e)  $1.310 \times 10^{22}$  atoms, (f) 7000 mL.

**Solution** (a) Three, because each digit is a nonzero digit. (b) Three, because zeros between nonzero digits are significant. (c) Three, because zeros to the left of the first nonzero digit do not count as significant figures. (d) Two. Same reason as in (c). (e) Four, because the number is greater than one, all the zeros written to the right of the decimal point count as significant figures. (f) This is an ambiguous case. The number of significant figures may be four ( $7.000 \times 10^3$ ), three ( $7.00 \times 10^3$ ), two ( $7.0 \times 10^3$ ), or one ( $7 \times 10^3$ ). This example illustrates why scientific notation must be used to show the proper number of significant figures.

**Practice Exercise** Determine the number of significant figures in each of the following measurements: (a) 24 mL, (b) 3001 g, (c)  $0.0320 \text{ m}^3$ , (d)  $6.4 \times 10^4$  molecules, (e) 560 kg.

Similar problems: 1.27, 1.28.

A second set of rules specifies how to handle significant figures in calculations.

- In addition and subtraction, the answer cannot have more digits to the right of the decimal point than either of the original numbers. Consider these examples:

$$\begin{array}{r}
 89.332 \\
 + 1.1 \\
 \hline
 90.432 \leftarrow \text{one digit after the decimal point} \\
 \end{array}$$

$$\begin{array}{r}
 2.097 \\
 - 0.12 \\
 \hline
 1.977 \leftarrow \text{two digits after the decimal point} \\
 \end{array}$$

$$\begin{array}{r}
 1.98 \\
 \end{array}$$

The rounding-off procedure is as follows. To round off a number at a certain point we simply drop the digits that follow if the first of them is less than 5. Thus, 8.724 rounds off to 8.72 if we want only two digits after the decimal point. If the first digit following the point of rounding off is equal to or greater than 5, we add 1 to the preceding digit. Thus, 8.727 rounds off to 8.73, and 0.425 rounds off to 0.43.

- In multiplication and division, the number of significant figures in the final product or quotient is determined by the original number that has the *smallest* number of significant figures. The following examples illustrate this rule:

$$2.8 \times 4.5039 = 12.61092 \leftarrow \text{round off to 13}$$

$$\begin{array}{r}
 6.85 \\
 \hline
 112.04 \\
 \end{array}$$

$$= 0.0611388789 \leftarrow \text{round off to 0.0611}$$

- Keep in mind that *exact numbers* obtained from definitions (such as 1 ft = 12 in, where 12 is an exact number) or by counting numbers of objects can be considered to have an infinite number of significant figures.

### Example 1.4

Carry out the following arithmetic operations to the correct number of significant figures: (a) 11,254.1 g + 0.1983 g, (b) 66.59 L – 3.113 L, (c) 8.16 m × 5.1355, (d) 0.0154 kg ÷ 88.3 mL, (e)  $2.64 \times 10^3$  cm +  $3.27 \times 10^2$  cm.

**Solution** In addition and subtraction, the number of decimal places in the answer is determined by the number having the lowest number of decimal places. In multiplication and division, the significant number of the answer is determined by the number having the smallest number of significant figures.

- $$\begin{array}{r}
 11,254.1 \text{ g} \\
 + 0.1983 \text{ g} \\
 \hline
 11,254.2983 \text{ g} \leftarrow \text{round off to } 11,254.3 \text{ g}
 \end{array}$$
- $$\begin{array}{r}
 66.59 \text{ L} \\
 - 3.113 \text{ L} \\
 \hline
 63.477 \text{ L} \leftarrow \text{round off to } 63.48 \text{ L}
 \end{array}$$
- $$8.16 \text{ m} \times 5.1355 = 41.90568 \text{ m} \leftarrow \text{round off to } 41.9 \text{ m}$$
- $$\begin{array}{r}
 0.0154 \text{ kg} \\
 \hline
 88.3 \text{ mL} \\
 \end{array}$$

$$= 0.000174405436 \text{ kg/mL} \leftarrow \text{round off to } 0.000174 \text{ kg/mL}$$

$$\text{or } 1.74 \times 10^{-4} \text{ kg/mL}$$

(Continued)

- (e) First we change  $3.27 \times 10^2$  cm to  $0.327 \times 10^3$  cm and then carry out the addition  $(2.64 \text{ cm} + 0.327 \text{ cm}) \times 10^3$ . Following the procedure in (a), we find the answer is  $2.97 \times 10^3$  cm.

**Similar problems:** 1.29, 1.30.

**Practice Exercise** Carry out the following arithmetic operations and round off the answers to the appropriate number of significant figures: (a)  $26.5862 \text{ L} + 0.17 \text{ L}$ , (b)  $9.1 \text{ g} - 4.682 \text{ g}$ , (c)  $7.1 \times 10^4 \text{ dm} \times 2.2654 \times 10^2 \text{ dm}$ , (d)  $6.54 \text{ g} \div 86.5542 \text{ mL}$ , (e)  $(7.55 \times 10^4 \text{ m}) - (8.62 \times 10^3 \text{ m})$ .

The preceding rounding-off procedure applies to one-step calculations. In *chain calculations*, that is, calculations involving more than one step, we can get a different answer depending on how we round off. Consider the following two-step calculations:

$$\begin{array}{ll} \text{First step:} & A \times B = C \\ \text{Second step:} & C \times D = E \end{array}$$

Let's suppose that  $A = 3.66$ ,  $B = 8.45$ , and  $D = 2.11$ . Depending on whether we round off  $C$  to three (Method 1) or four (Method 2) significant figures, we obtain a different number for  $E$ :

Method 1	Method 2
$3.66 \times 8.45 = 30.9$	$3.66 \times 8.45 = 30.93$
$30.9 \times 2.11 = 65.2$	$30.93 \times 2.11 = 65.3$

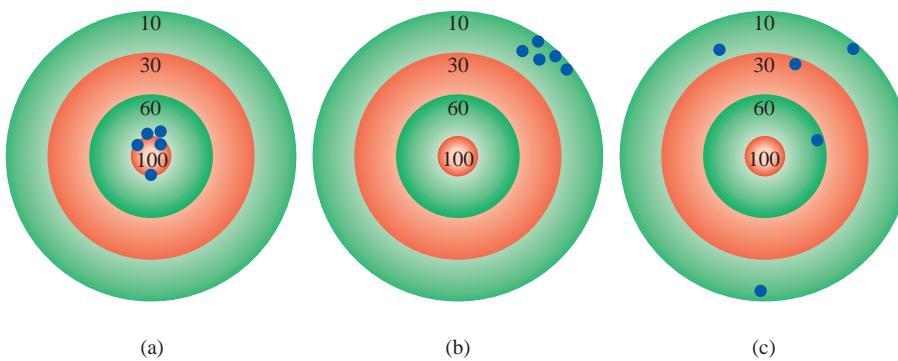
However, if we had carried out the calculation as  $3.66 \times 8.45 \times 2.11$  on a calculator without rounding off the intermediate answer, we would have obtained 65.3 as the answer for  $E$ . Although retaining an additional digit past the number of significant figures for intermediate steps helps to eliminate errors from rounding, this procedure is not necessary for most calculations because the difference between the answers is usually quite small. Therefore, for most examples and end-of-chapter problems where intermediate answers are reported, all answers, intermediate and final, will be rounded.

## Accuracy and Precision

In discussing measurements and significant figures it is useful to distinguish between *accuracy* and *precision*. **Accuracy** tells us *how close a measurement is to the true value of the quantity that was measured*. To a scientist there is a distinction between accuracy and precision. **Precision** refers to *how closely two or more measurements of the same quantity agree with one another* (Figure 1.10).



**Interactivity:**  
Accuracy and Precision  
ARIS, Interactives



**Figure 1.10**

The distribution of darts on a dart board shows the difference between precise and accurate. (a) Good accuracy and good precision. (b) Poor accuracy and good precision. (c) Poor accuracy and poor precision. The blue dots show the positions of the darts.

The difference between accuracy and precision is a subtle but important one. Suppose, for example, that three students are asked to determine the mass of a piece of copper wire. The results of two successive weighings by each student are

	Student A	Student B	Student C
	1.964 g	1.972 g	2.000 g
	1.978 g	1.968 g	2.002 g
Average value	1.971 g	1.970 g	2.001 g

The true mass of the wire is 2.000 g. Therefore, Student B's results are more *precise* than those of Student A (1.972 g and 1.968 g deviate less from 1.970 g than 1.964 g and 1.978 g from 1.971 g), but neither set of results is very *accurate*. Student C's results are not only the most *precise*, but also the most *accurate*, because the average value is closest to the true value. Highly accurate measurements are usually precise too. On the other hand, highly precise measurements do not necessarily guarantee accurate results. For example, an improperly calibrated meterstick or a faulty balance may give precise readings that are in error.



Dimensional analysis might also have led Einstein to his famous mass-energy equation ( $E = mc^2$ ).  
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## 1.7 Dimensional Analysis in Solving Problems

Careful measurements and the proper use of significant figures, along with correct calculations, will yield accurate numerical results. But to be meaningful, the answers also must be expressed in the desired units. The procedure we use to convert between units in solving chemistry problems is called *dimensional analysis* (also called the *factor-label method*). A simple technique requiring little memorization, dimensional analysis is based on the relationship between different units that express the same physical quantity. For example, we know that the monetary unit "dollar" is different from the unit "penny." However, 1 dollar is *equivalent* to 100 pennies because they both represent the same amount of money; that is,

$$1 \text{ dollar} = 100 \text{ pennies}$$

This equivalence enables us to write a conversion factor

$$\frac{1 \text{ dollar}}{100 \text{ pennies}}$$

if we want to convert pennies to dollars. Conversely, the conversion factor

$$\frac{100 \text{ pennies}}{1 \text{ dollar}}$$

enables us to convert dollars to pennies. A conversion factor, then, is a fraction whose numerator and denominator are the same quantity expressed in different units.

Now consider the problem

$$? \text{ pennies} = 2.46 \text{ dollars}$$

Because this is a dollar-to-penny conversion, we choose the conversion factor that has the unit "dollar" in the denominator (to cancel the "dollars" in 2.46 dollars) and write

$$2.46 \cancel{\text{ dollars}} \times \frac{100 \text{ pennies}}{1 \cancel{\text{ dollar}}} = 246 \text{ pennies}$$



**Interactivity:**  
Dimensional Analysis  
ARIS, Interactives

Note that the conversion factor 100 pennies/1 dollar contains exact numbers, so it does not affect the number of significant figures in the final answer.

Next, let us consider the conversion of 57.8 meters to centimeters. This problem can be expressed as

$$\text{? cm} = 57.8 \text{ m}$$

By definition,

$$1 \text{ cm} = 1 \times 10^{-2} \text{ m}$$

Because we are converting “m” to “cm,” we choose the conversion factor that has meters in the denominator:

$$\frac{1 \text{ cm}}{1 \times 10^{-2} \text{ m}}$$

and write the conversion as

$$\begin{aligned}\text{? cm} &= 57.8 \cancel{\text{m}} \times \frac{1 \text{ cm}}{1 \times 10^{-2} \cancel{\text{m}}} \\ &= 5780 \text{ cm} \\ &= 5.78 \times 10^3 \text{ cm}\end{aligned}$$

Note that scientific notation is used to indicate that the answer has three significant figures. Again, the conversion factor  $1 \text{ cm}/1 \times 10^{-2} \text{ m}$  contains exact numbers; therefore, it does not affect the number of significant figures.

In general, to apply dimensional analysis we use the relationship

$$\text{given quantity} \times \text{conversion factor} = \text{desired quantity}$$

and the units cancel as follows:

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

In dimensional analysis the units are carried through the entire sequence of calculations. Therefore, if the equation is set up correctly, then all the units will cancel except the desired one. If this is not the case, then an error must have been made somewhere, and it can usually be spotted by reviewing the solution.

## A Note on Problem Solving

At this point you have been introduced to scientific notation, significant figures, and dimensional analysis, which will help you in solving numerical problems. Chemistry is an experimental science and many of the problems are quantitative in nature. The key to success in problem solving is practice. Just as a marathon runner cannot prepare for a race by simply reading books on running and a violinist cannot give a successful concert by only memorizing the musical score, you cannot be sure of your understanding of chemistry without solving problems. The following steps will help to improve your skill at solving numerical problems:

1. Read the question carefully. Understand the information that is given and what you are asked to solve. Frequently it is helpful to make a sketch that will help you to visualize the situation.

2. Find the appropriate equation that relates the given information and the unknown quantity. Sometimes solving a problem will involve more than one step, and you may be expected to look up quantities in tables that are not provided in the problem. Dimensional analysis is often needed to carry out conversions.
3. Check your answer for the correct sign, units, and significant figures.
4. A very important part of problem solving is being able to judge whether the answer is reasonable. It is relatively easy to spot a wrong sign or incorrect units. But if a number (say 8) is incorrectly placed in the denominator instead of in the numerator, the answer would be too small even if the sign and units of the calculated quantity were correct.
5. One way to quickly check the answer is to make a “ball-park” estimate. The idea here is to round off the numbers in the calculation in such a way that we simplify the arithmetic. This approach is sometimes called the “back-of-the-envelope calculation” because it can be done easily without using a calculator. The answer you get will not be exact, but it will be close to the correct one.

### Example 1.5

**Conversion factors for some of the English system units commonly used in the United States for nonscientific measurements (for example, pounds and inches) are provided inside the back cover of this book.**

A person’s average daily intake of glucose (a form of sugar) is 0.0833 pound (lb). What is this mass in milligrams (mg)? (1 lb = 453.6 g.)

**Strategy** The problem can be stated as

$$\text{? mg} = 0.0833 \text{ lb}$$

The relationship between pounds and grams is given in the problem. This relationship will enable conversion from pounds to grams. A metric conversion is then needed to convert grams to milligrams ( $1 \text{ mg} = 1 \times 10^{-3} \text{ g}$ ). Arrange the appropriate conversion factors so that pounds and grams cancel and the unit milligrams is obtained in your answer.

**Solution** The sequence of conversions is

$$\text{pounds} \longrightarrow \text{grams} \longrightarrow \text{milligrams}$$

Using the following conversion factors:

$$\frac{453.6 \text{ g}}{1 \text{ lb}} \quad \text{and} \quad \frac{1 \text{ mg}}{1 \times 10^{-3} \text{ g}}$$

we obtain the answer in one step:

$$\text{? mg} = 0.0833 \cancel{\text{lb}} \times \frac{453.6 \cancel{\text{g}}}{1 \cancel{\text{lb}}} \times \frac{1 \text{ mg}}{1 \times 10^{-3} \cancel{\text{g}}} = 3.78 \times 10^4 \text{ mg}$$

**Check** As an estimate, we note that 1 lb is roughly 500 g and that 1 g = 1000 mg. Therefore, 1 lb is roughly  $5 \times 10^5$  mg. Rounding off 0.0833 lb to 0.1 lb, we get  $5 \times 10^4$  mg, which is close to the preceding quantity.

**Similar problem:** 1.37(a).

**Practice Exercise** A roll of aluminum foil has a mass of 1.07 kg. What is its mass in pounds?

As Examples 1.6 and 1.7 illustrate, conversion factors can be squared or cubed in dimensional analysis.

### Example 1.6

An average adult has 5.2 L of blood. What is the volume of blood in  $\text{m}^3$ ?

**Strategy** The problem can be stated as

$$\text{? m}^3 = 5.2 \text{ L}$$

How many conversion factors are needed for this problem? Recall that  $1 \text{ L} = 1000 \text{ cm}^3$  and  $1 \text{ cm} = 1 \times 10^{-2} \text{ m}$ .

**Solution** We need two conversion factors here: one to convert liters to  $\text{cm}^3$  and one to convert centimeters to meters:

$$\frac{1000 \text{ cm}^3}{1 \text{ L}} \quad \text{and} \quad \frac{1 \times 10^{-2} \text{ m}}{1 \text{ cm}}$$

Because the second conversion factor deals with length (cm and m) and we want volume here, it must therefore be cubed to give

$$\frac{1 \times 10^{-2} \text{ m}}{1 \text{ cm}} \times \frac{1 \times 10^{-2} \text{ m}}{1 \text{ cm}} \times \frac{1 \times 10^{-2} \text{ m}}{1 \text{ cm}} = \left( \frac{1 \times 10^{-2} \text{ m}}{1 \text{ cm}} \right)^3$$

This means that  $1 \text{ cm}^3 = 1 \times 10^{-6} \text{ m}^3$ . Now we can write

$$\text{? m}^3 = 5.2 \cancel{\text{L}} \times \frac{1000 \text{ cm}^3}{1 \cancel{\text{L}}} \times \left( \frac{1 \times 10^{-2} \text{ m}}{1 \text{ cm}} \right)^3 = 5.2 \times 10^{-3} \text{ m}^3$$

**Check** From the preceding conversion factors you can show that  $1 \text{ L} = 1 \times 10^{-3} \text{ m}^3$ . Therefore, 5 L of blood would be equal to  $5 \times 10^{-3} \text{ m}^3$ , which is close to the answer.

**Similar problem:** 1.38(g).

**Practice Exercise** The volume of a room is  $1.08 \times 10^8 \text{ dm}^3$ . What is the volume in  $\text{m}^3$ ?

### Example 1.7

Liquid nitrogen is obtained from liquefied air and is used to prepare frozen goods and in low-temperature research. The density of the liquid at its boiling point ( $-196^\circ\text{C}$  or  $77 \text{ K}$ ) is  $0.808 \text{ g/cm}^3$ . Convert the density to units of  $\text{kg/m}^3$ .

**Strategy** The Problem can be stated as

$$\text{? kg/m}^3 = 0.808 \text{ g/cm}^3$$

Two separate conversions are required for this problem:  $\text{g} \longrightarrow \text{kg}$  and  $\text{cm}^3 \longrightarrow \text{m}^3$ . Recall that  $1 \text{ kg} = 1000 \text{ g}$  and  $1 \text{ cm} = 1 \times 10^{-2} \text{ m}$ .

**Solution** In Example 1.6 we saw that  $1 \text{ cm}^3 = 1 \times 10^{-6} \text{ m}^3$ . The conversion factors are

$$\frac{1 \text{ kg}}{1000 \text{ g}} \quad \text{and} \quad \frac{1 \text{ cm}^3}{1 \times 10^{-6} \text{ m}^3}$$

Finally,

$$\text{? kg/m}^3 = \frac{0.808 \cancel{\text{g}}}{1 \cancel{\text{cm}}^3} \times \frac{1 \text{ kg}}{1000 \cancel{\text{g}}} \times \frac{1 \text{ cm}^3}{1 \times 10^{-6} \text{ m}^3} = 808 \text{ kg/m}^3$$



Liquid nitrogen.

**Similar problem:** 1.39.

**Check** Because  $1 \text{ m}^3 = 1 \times 10^6 \text{ cm}^3$ , we would expect much more mass in  $1 \text{ m}^3$  than in  $1 \text{ cm}^3$ . Therefore, the answer is reasonable.

**Practice Exercise** The density of the lightest metal, lithium (Li), is  $5.34 \times 10^2 \text{ kg/m}^3$ . Convert the density to  $\text{g/cm}^3$ .

## KEY EQUATIONS

$$d = \frac{m}{V} \quad (1.1)$$

Equation for density

$$\text{? } ^\circ\text{C} = (\text{? } ^\circ\text{F} - 32^\circ\text{F}) \times \frac{5^\circ\text{C}}{9^\circ\text{F}} \quad (1.2)$$

Converting  $^\circ\text{F}$  to  $^\circ\text{C}$

$$\text{? } ^\circ\text{F} = \frac{9^\circ\text{F}}{5^\circ\text{C}} \times (\text{? } ^\circ\text{C}) + 32^\circ\text{F} \quad (1.3)$$

Converting  $^\circ\text{C}$  to  $^\circ\text{F}$

$$\text{? } ^\circ\text{K} = (\text{? } ^\circ\text{C} + 273.15^\circ\text{C}) \frac{1 \text{ K}}{1^\circ\text{C}} \quad (1.4)$$

Converting  $^\circ\text{C}$  to K

## SUMMARY OF FACTS AND CONCEPTS

- The scientific method is a systematic approach to research that begins with the gathering of information through observation and measurements. In the process, hypotheses, laws, and theories are devised and tested.
- Chemists study matter and the substances of which it is composed. All substances, in principle, can exist in three states: solid, liquid, and gas. The interconversion between these states can be effected by a change in temperature.
- The simplest substances in chemistry are elements. Compounds are formed by the combination of atoms of different elements. Substances have both unique physical properties that can be observed without changing the identity of the substances and unique chemical properties that, when they are demonstrated, do change the identity of the substances.
- SI units are used to express physical quantities in all sciences, including chemistry. Numbers expressed in scientific notation have the form  $N \times 10^n$ , where  $N$  is between 1 and 10 and  $n$  is a positive or negative integer. Scientific notation helps us handle very large and very small quantities. Most measured quantities are inexact to some extent. The number of significant figures indicates the exactness of the measurement.
- In the dimensional analysis method of solving problems the units are multiplied together, divided into each other, or canceled like algebraic quantities. Obtaining the correct units for the final answer ensures that the calculation has been carried out properly.

## KEY WORDS

Accuracy, p. 17	Homogeneous mixture, p. 5	Macroscopic property, p. 8	Quantitative, p. 3
Chemical property, p. 7	Hypothesis, p. 3	Mass, p. 9	Scientific method, p. 2
Chemistry, p. 4	Intensive property, p. 8	Matter, p. 4	Significant figures, p. 14
Compound, p. 6	International System of Units, p. 9	Microscopic property, p. 8	Substance, p. 5
Density, p. 10	Kelvin, p. 11	Mixture, p. 5	Theory, p. 3
Element, p. 5	Law, p. 3	Physical property, p. 7	Volume, p. 10
Extensive property, p. 7	Liter, p. 10	Precision, p. 17	Weight, p. 9
Heterogeneous mixture, p. 5		Qualitative, p. 3	

## QUESTIONS AND PROBLEMS

### Basic Definitions

#### Review Questions

- 1.1 Define these terms: (a) matter, (b) mass, (c) weight, (d) substance, (e) mixture.
- 1.2 Which of these statements is scientifically correct?  
“The mass of the student is 56 kg.”  
“The weight of the student is 56 kg.”
- 1.3 Give an example of a homogeneous mixture and an example of a heterogeneous mixture.
- 1.4 What is the difference between a physical property and a chemical property?
- 1.5 Give an example of an intensive property and an example of an extensive property.
- 1.6 Define these terms: (a) element, (b) compound.

#### Problems

- 1.7 Do these statements describe chemical or physical properties? (a) Oxygen gas supports combustion. (b) Fertilizers help to increase agricultural production. (c) Water boils below 100°C on top of a mountain. (d) Lead is denser than aluminum. (e) Uranium is a radioactive element.
- 1.8 Does each of these describe a physical change or a chemical change? (a) The helium gas inside a balloon tends to leak out after a few hours. (b) A flashlight beam slowly gets dimmer and finally goes out. (c) Frozen orange juice is reconstituted by adding water to it. (d) The growth of plants depends on the sun’s energy in a process called photosynthesis. (e) A spoonful of table salt dissolves in a bowl of soup.
- 1.9 Which of these properties are intensive and which are extensive? (a) length, (b) volume, (c) temperature, (d) mass.
- 1.10 Which of these properties are intensive and which are extensive? (a) area, (b) color, (c) density.
- 1.11 Classify each of these substances as an element or a compound: (a) hydrogen, (b) water, (c) gold, (d) sugar.
- 1.12 Classify each of these as an element or a compound: (a) sodium chloride (table salt), (b) helium, (c) alcohol, (d) platinum.

### Units

#### Review Questions

- 1.13 Give the SI units for expressing these: (a) length, (b) area, (c) volume, (d) mass, (e) time, (f) force, (g) energy, (h) temperature.

- 1.14 Write the numbers for these prefixes: (a) mega-, (b) kilo-, (c) deci-, (d) centi-, (e) milli-, (f) micro-, (g) nano-, (h) pico-.
- 1.15 Define density. What units do chemists normally use for density? Is density an intensive or extensive property?
- 1.16 Write the equations for converting degrees Celsius to degrees Fahrenheit and degrees Fahrenheit to degrees Celsius.

#### Problems

- 1.17 A lead sphere has a mass of  $1.20 \times 10^4$  g, and its volume is  $1.05 \times 10^3$  cm<sup>3</sup>. Calculate the density of lead.
- 1.18 Mercury is the only metal that is a liquid at room temperature. Its density is 13.6 g/mL. How many grams of mercury will occupy a volume of 95.8 mL?
- 1.19 (a) Normally the human body can endure a temperature of 105°F for only short periods of time without permanent damage to the brain and other vital organs. What is this temperature in degrees Celsius? (b) Ethylene glycol is a liquid organic compound that is used as an antifreeze in car radiators. It freezes at -11.5°C. Calculate its freezing temperature in degrees Fahrenheit. (c) The temperature on the surface of the sun is about 6300°C. What is this temperature in degrees Fahrenheit? (d) The ignition temperature of paper is 451°F. What is the temperature in degrees Celsius?
- 1.20 (a) Convert the following temperatures to kelvin: (i) 113°C, the melting point of sulfur, (ii) 37°C, the normal body temperature, (iii) 357°C, the boiling point of mercury. (b) Convert the following temperatures to degrees Celsius: (i) 77 K, the boiling point of liquid nitrogen, (ii) 4.2 K, the boiling point of liquid helium, (iii) 601 K, the melting point of lead.

### Scientific Notation

#### Problems

- 1.21 Express these numbers in scientific notation: (a) 0.000000027, (b) 356, (c) 0.096.
- 1.22 Express these numbers in scientific notation: (a) 0.749, (b) 802.6, (c) 0.000000621.
- 1.23 Convert these to nonscientific notation: (a)  $1.52 \times 10^4$ , (b)  $7.78 \times 10^{-8}$ .
- 1.24 Convert these to nonscientific notation: (a)  $3.256 \times 10^{-5}$ , (b)  $6.03 \times 10^6$ .

- 1.25 Express the answers to these in scientific notation:  
 (a)  $145.75 + (2.3 \times 10^{-1})$   
 (b)  $79,500 \div (2.5 \times 10^2)$   
 (c)  $(7.0 \times 10^{-3}) - (8.0 \times 10^{-4})$   
 (d)  $(1.0 \times 10^4) \times (9.9 \times 10^6)$
- 1.26 Express the answers to these in scientific notation:  
 (a)  $0.0095 + (8.5 \times 10^{-3})$   
 (b)  $653 \div (5.75 \times 10^{-8})$   
 (c)  $850,000 - (9.0 \times 10^5)$   
 (d)  $(3.6 \times 10^{-4}) \times (3.6 \times 10^6)$

## Significant Figures

### Problems

- 1.27 What is the number of significant figures in each of these measured quantities? (a) 4867 miles, (b) 56 mL, (c) 60,104 tons, (d) 2900 g.
- 1.28 What is the number of significant figures in each of these measured quantities? (a)  $40.2 \text{ g/cm}^3$ , (b) 0.000003 cm, (c) 70 min, (d)  $4.6 \times 10^{19}$  atoms.
- 1.29 Carry out these operations as if they were calculations of experimental results, and express each answer in the correct units and with the correct number of significant figures:  
 (a)  $5.6792 \text{ m} + 0.6 \text{ m} + 4.33 \text{ m}$   
 (b)  $3.70 \text{ g} - 2.9133 \text{ g}$   
 (c)  $4.51 \text{ cm} \times 3.6666 \text{ cm}$   
 (d)  $(3 \times 10^4 \text{ g} + 6.827 \text{ g}) / (0.043 \text{ cm}^3 - 0.021 \text{ cm}^3)$
- 1.30 Carry out these operations as if they were calculations of experimental results, and express each answer in the correct units and with the correct number of significant figures:  
 (a)  $7.310 \text{ km} \div 5.70 \text{ km}$   
 (b)  $(3.26 \times 10^{-3} \text{ mg}) - (7.88 \times 10^{-5} \text{ mg})$   
 (c)  $(4.02 \times 10^6 \text{ dm}) + (7.74 \times 10^7 \text{ dm})$   
 (d)  $(7.8 \text{ m} - 0.34 \text{ m}) / (1.15 \text{ s} + 0.82 \text{ s})$

## Dimensional Analysis

### Problems

- 1.31 Carry out these conversions: (a) 22.6 m to decimeters, (b) 25.4 mg to kilograms.
- 1.32 Carry out these conversions: (a) 242 lb to milligrams, (b)  $68.3 \text{ cm}^3$  to cubic meters.
- 1.33 The price of gold on a certain day in 2004 was \$315 per troy ounce. How much did 1.00 g of gold cost that day? (1 troy ounce = 31.03 g.)
- 1.34 How many seconds are in a solar year (365.24 days)?
- 1.35 How many minutes does it take light from the sun to reach Earth? (The distance from the sun to Earth is 93 million mi; the speed of light =  $3.00 \times 10^8 \text{ m/s}$ .)

- 1.36 A slow jogger runs a mile in 13 min. Calculate the speed in (a) in/s, (b) m/min, (c) km/h. (1 mi = 1609 m; 1 in = 2.54 cm.)
- 1.37 Carry out these conversions: (a) A 6.0-ft person weighs 168 lb. Express this person's height in meters and weight in kilograms. (1 lb = 453.6 g; 1 m = 3.28 ft.) (b) The current speed limit in some states in the United States is 55 miles per hour. What is the speed limit in kilometers per hour? (c) The speed of light is  $3.0 \times 10^{10} \text{ cm/s}$ . How many miles does light travel in 1 hour? (d) Lead is a toxic substance. The "normal" lead content in human blood is about 0.40 part per million (that is, 0.40 g of lead per million grams of blood). A value of 0.80 part per million (ppm) is considered to be dangerous. How many grams of lead are contained in  $6.0 \times 10^3 \text{ g}$  of blood (the amount in an average adult) if the lead content is 0.62 ppm?
- 1.38 Carry out these conversions: (a) 1.42 light-years to miles (a light-year is an astronomical measure of distance—the distance traveled by light in a year, or 365 days), (b) 32.4 yd to centimeters, (c)  $3.0 \times 10^{10} \text{ cm/s}$  to ft/s, (d)  $47.4^\circ\text{F}$  to degrees Celsius, (e)  $-273.15^\circ\text{C}$  (the lowest temperature) to degrees Fahrenheit, (f)  $71.2 \text{ cm}^3$  to  $\text{m}^3$ , (g)  $7.2 \text{ m}^3$  to liters.
- 1.39 Aluminum is a lightweight metal (density =  $2.70 \text{ g/cm}^3$ ) used in aircraft construction, high-voltage transmission lines, and foils. What is its density in  $\text{kg/m}^3$ ?
- 1.40 The density of ammonia gas under certain conditions is  $0.625 \text{ g/L}$ . Calculate its density in  $\text{g/cm}^3$ .
- Additional Problems**
- 1.41 Which of these describe physical and which describe chemical properties? (a) Iron has a tendency to rust. (b) Rainwater in industrialized regions tends to be acidic. (c) Hemoglobin molecules have a red color. (d) When a glass of water is left out in the sun, the water gradually disappears. (e) Carbon dioxide in air is converted to more complex molecules by plants during photosynthesis.
- 1.42 In 2004 about 87.0 billion pounds of sulfuric acid were produced in the United States. Convert this quantity to tons.
- 1.43 Suppose that a new temperature scale has been devised on which the melting point of ethanol ( $-117.3^\circ\text{C}$ ) and the boiling point of ethanol ( $78.3^\circ\text{C}$ ) are taken as  $0^\circ\text{S}$  and  $100^\circ\text{S}$ , respectively, where S is the symbol for the new temperature scale. Derive an equation relating a reading on this scale to a reading on the Celsius scale. What would this thermometer read at  $25^\circ\text{C}$ ?
- 1.44 In the determination of the density of a rectangular metal bar, a student made the following measurements:

- length, 8.53 cm; width, 2.4 cm; height, 1.0 cm; mass, 52.7064 g. Calculate the density of the metal to the correct number of significant figures.
- 1.45** Calculate the mass of each of these: (a) a sphere of gold of radius 10.0 cm [the volume of a sphere of radius  $r$  is  $V = \left(\frac{4}{3}\right)\pi r^3$ ; the density of gold = 19.3 g/cm<sup>3</sup>], (b) a cube of platinum of edge length 0.040 mm (the density of platinum = 21.4 g/cm<sup>3</sup>), (c) 50.0 mL of ethanol (the density of ethanol = 0.798 g/mL).
- 1.46** A cylindrical glass tube 12.7 cm in length is filled with mercury. The mass of mercury needed to fill the tube is found to be 105.5 g. Calculate the inner diameter of the tube. (The density of mercury = 13.6 g/mL.)
- 1.47** This procedure was carried out to determine the volume of a flask. The flask was weighed dry and then filled with water. If the masses of the empty flask and the filled flask were 56.12 g and 87.39 g, respectively, and the density of water is 0.9976 g/cm<sup>3</sup>, calculate the volume of the flask in cubic centimeters.
- 1.48** A silver (Ag) object weighing 194.3 g is placed in a graduated cylinder containing 242.0 mL of water. The volume of water now reads 260.5 mL. From these data calculate the density of silver.
- 1.49** The experiment described in Problem 1.48 is a crude but convenient way to determine the density of some solids. Describe a similar experiment that would enable you to measure the density of ice. Specifically, what would be the requirements for the liquid used in your experiment?
- 1.50** The speed of sound in air at room temperature is about 343 m/s. Calculate this speed in miles per hour (mph).
- 1.51** The medicinal thermometer commonly used in homes can be read to  $\pm 0.1^\circ\text{F}$ , whereas those in the doctor's office may be accurate to  $\pm 0.1^\circ\text{C}$ . In degrees Celsius, express the percent error expected from each of these thermometers in measuring a person's body temperature of 38.9°C.
- 1.52** A thermometer gives a reading of  $24.2^\circ\text{C} \pm 0.1^\circ\text{C}$ . Calculate the temperature in degrees Fahrenheit. What is the uncertainty?
- 1.53** Vanillin (used to flavor vanilla ice cream and other foods) is the substance whose aroma the human nose detects in the smallest amount. The threshold limit is  $2.0 \times 10^{-11}$  g per liter of air. If the current price of 50 g of vanillin is \$112, determine the cost to supply enough vanillin so that the aroma could be detectable in a large aircraft hangar of volume  $5.0 \times 10^7$  ft<sup>3</sup>.
- 1.54** A resting adult requires about 240 mL of pure oxygen/min and breathes about 12 times every minute. If inhaled air contains 20 percent oxygen by volume and exhaled air 16 percent, what is the volume of air per breath? (Assume that the volume of inhaled air is equal to that of exhaled air.)
- 1.55** The total volume of seawater is  $1.5 \times 10^{21}$  L. Assume that seawater contains 3.1 percent sodium chloride by mass and that its density is 1.03 g/mL. Calculate the total mass of sodium chloride in kilograms and in tons. (1 ton = 2000 lb; 1 lb = 453.6 g.)
- 1.56** Magnesium (Mg) is a valuable metal used in alloys, in batteries, and in chemical synthesis. It is obtained mostly from seawater, which contains about 1.3 g of Mg for every kilogram of seawater. Calculate the volume of seawater (in liters) needed to extract  $8.0 \times 10^4$  tons of Mg, which is roughly the annual production in the United States. (Density of seawater = 1.03 g/mL.)
- 1.57** A student is given a crucible and asked to prove whether it is made of pure platinum. She first weighs the crucible in air and then weighs it suspended in water (density = 0.9986 g/cm<sup>3</sup>). The readings are 860.2 g and 820.2 g, respectively. Given that the density of platinum is 21.45 g/cm<sup>3</sup>, what should her conclusion be based on these measurements? (*Hint:* An object suspended in a fluid is buoyed up by the mass of the fluid displaced by the object. Neglect the buoyancy of air.)
- 1.58** At what temperature does the numerical reading on a Celsius thermometer equal that on a Fahrenheit thermometer?
- 1.59** The surface area and average depth of the Pacific Ocean are  $1.8 \times 10^8$  km<sup>2</sup> and  $3.9 \times 10^3$  m, respectively. Calculate the volume of water in the ocean in liters.
- 1.60** Percent error is often expressed as the absolute value of the difference between the true value and the experimental value, divided by the true value:
- $$\text{Percent error} = \frac{|\text{true value} - \text{experimental value}|}{|\text{true value}|} \times 100\%$$
- where the vertical lines indicate absolute value. Calculate the percent error for these measurements: (a) The density of alcohol (ethanol) is found to be 0.802 g/mL. (True value: 0.798 g/mL.) (b) The mass of gold in an earring is analyzed to be 0.837 g. (True value: 0.864 g.)
- 1.61** Osmium (Os) is the densest element known (density = 22.57 g/cm<sup>3</sup>). Calculate the mass in pounds and kilograms of an Os sphere 15 cm in diameter (about the size of a grapefruit). See Problem 1.45 for volume of a sphere.
- 1.62** A 1.0-mL volume of seawater contains about  $4.0 \times 10^{-12}$  g of gold. The total volume of ocean water is

$1.5 \times 10^{21}$  L. Calculate the total amount of gold in grams that is present in seawater and its worth in dollars, assuming that the price of gold is \$350 an ounce. With so much gold out there, why hasn't someone become rich by mining gold from the ocean?

- 1.63 The thin outer layer of Earth, called the crust, contains only 0.50 percent of Earth's total mass and yet is the source of almost all the elements (the atmosphere provides elements such as oxygen, nitrogen, and a few other gases). Silicon (Si) is the second most abundant element in Earth's crust (27.2 percent by mass). Calculate the mass of silicon in kilograms in Earth's crust. (The mass of Earth is  $5.9 \times 10^{21}$  tons. 1 ton = 2000 lb; 1 lb = 453.6 g.)

- 1.64 The diameter of a copper (Cu) atom is roughly  $1.3 \times 10^{-10}$  m. How many times can you divide evenly a piece of 10-cm copper wire until it is reduced to two separate copper atoms? (Assume there are appropriate tools for this procedure and that copper atoms are lined up in a straight line, in contact with each other.) Round off your answer to an integer.

- 1.65 One gallon of gasoline burned in an automobile's engine produces on the average 9.5 kg of carbon dioxide, which is a greenhouse gas, that is, it promotes the warming of Earth's atmosphere. Calculate the annual production of carbon dioxide in kilograms if there are 40 million cars in the United States, and each car covers a distance of 5000 mi at a consumption rate of 20 mi per gallon.

- 1.66 A sheet of aluminum (Al) foil has a total area of  $1.000 \text{ ft}^2$  and a mass of 3.636 g. What is the thickness of the foil in millimeters? (Density of Al =  $2.699 \text{ g/cm}^3$ .)

- 1.67 Chlorine is used to disinfect swimming pools. The accepted concentration for this purpose is 1 ppm chlorine or 1 g of chlorine per million g of water. Calculate the volume of a chlorine solution (in milliliters) a homeowner should add to her swimming pool if the solution contains 6.0 percent chlorine by mass

and there are  $2 \times 10^4$  gallons of water in the pool. (1 gallon = 3.79 L; density of liquids =  $1.0 \text{ g/mL}$ .)

- 1.68 Fluoridation is the process of adding fluorine compounds to drinking water to help fight tooth decay. A concentration of 1 ppm of fluorine is sufficient for the purpose. (1 ppm means 1 g of fluorine per 1 million g of water.) The compound normally chosen for fluoridation is sodium fluoride, which is also added to some toothpastes. Calculate the quantity of sodium fluoride in kilograms needed per year for a city of 50,000 people if the daily consumption of water per person is 150 gallons. What percent of the sodium fluoride is "wasted" if each person uses only 6.0 L of water a day for drinking and cooking? (Sodium fluoride is 45.0 percent fluorine by mass. 1 gallon = 3.79 L; 1 year = 365 days; density of water =  $1.0 \text{ g/mL}$ .)

- 1.69 In water conservation, chemists spread a thin film of certain inert material over the surface of water to cut down the rate of evaporation of water in reservoirs. This technique was pioneered by Benjamin Franklin three centuries ago. Franklin found that 0.10 mL of oil could spread over the surface of water of about  $40 \text{ m}^2$  in area. Assuming that the oil forms a *monolayer*, that is, a layer that is only one molecule thick, estimate the length of each oil molecule in nanometers. (1 nm =  $1 \times 10^{-9}$  m.)

- 1.70 Pheromones are compounds secreted by females of many insect species to attract mates. Typically,  $1.0 \times 10^{-8}$  g of a pheromone is sufficient to reach all targeted males within a radius of 0.50 mi. Calculate the density of the pheromone (in grams per liter) in a cylindrical air space having a radius of 0.50 mi and a height of 40 ft.

- 1.71 A gas company in Massachusetts charges \$1.30 for  $15.0 \text{ ft}^3$  of natural gas. (a) Convert this rate to dollars per liter of gas. (b) If it takes  $0.304 \text{ ft}^3$  of gas to boil a liter of water, starting at room temperature ( $25^\circ\text{C}$ ), how much would it cost to boil a 2.1-L kettle of water?

## SPECIAL PROBLEMS

- 1.72 Dinosaurs dominated life on Earth for millions of years and then disappeared very suddenly. In the experimentation and data-collecting stage, paleontologists studied fossils and skeletons found in rocks in various layers of Earth's crust. Their findings enabled them to map out which species existed on Earth during specific geologic periods. They also revealed no dinosaur skeletons in rocks formed immediately after the Cretaceous period, which dates back some 65 million years. It is therefore assumed that the dinosaurs became extinct about 65 million years ago.

Among the many hypotheses put forward to account for their disappearance were disruptions of the food chain and a dramatic change in climate caused by violent volcanic eruptions. However, there was no convincing evidence for any one hypothesis until 1977. It was then that a group of paleontologists working in Italy obtained some very puzzling data at a site near Gubbio. The chemical analysis of a layer of clay deposited above sediments formed during the Cretaceous period (and therefore a layer that records events occurring *after* the Cretaceous period)

showed a surprisingly high content of the element iridium. Iridium is very rare in Earth's crust but is comparatively abundant in asteroids.

This investigation led to the hypothesis that the extinction of dinosaurs occurred as follows. To account for the quantity of iridium found, scientists suggested that a large asteroid several miles in diameter hit Earth about the time the dinosaurs disappeared. The impact of the asteroid on Earth's surface must have been so tremendous that it literally vaporized a large quantity of surrounding rocks, soils, and other objects. The resulting dust and debris floated through the air and blocked the sunlight for months or perhaps years. Without ample sunlight most plants could not grow, and the fossil record confirms that many types of plants did indeed die out at this time. Consequently, of course, many plant-eating animals gradually perished, and then, in turn, meat-eating animals began to starve. Limitation of food sources obviously affects large animals needing great amounts of food more quickly and more severely than small animals. Therefore, the huge dinosaurs vanished because of lack of food.

- (a) How does the study of dinosaur extinction illustrate the scientific method?
- (b) Suggest two ways to test the hypothesis.
- (c) In your opinion, is it justifiable to refer to the asteroid explanation as the theory of dinosaur extinction?
- (d) Available evidence suggests that about 20 percent of the asteroid's mass turned to dust and spread uniformly over Earth after eventually settling out of the upper atmosphere. This dust amounted to about  $0.02 \text{ g/cm}^2$  of Earth's surface. The asteroid very likely had a density of about  $2 \text{ g/cm}^3$ . Calculate the mass (in kilograms and tons) of the asteroid and its radius in meters, assuming that it was a sphere. (The area of Earth is  $5.1 \times 10^{14} \text{ m}^2$ ; 1 lb = 453.6 g.)  
(Source: *Consider a Spherical Cow—A Course in Environmental Problem Solving* by J. Harte, University Science Books, Mill Valley, CA, 1988. Used with permission.)

- 1.73 You are given a liquid. Briefly describe steps you would take to show whether it is a pure substance or a homogeneous mixture.

**1.74** A bank teller is asked to assemble "one-dollar" sets of coins for his clients. Each set is made of three quarters, one nickel, and two dimes. The masses of the coins are: quarter: 5.645 g; nickel: 4.967 g; dime: 2.316 g. What is the maximum number of sets that can be assembled from 33.871 kg of quarters, 10.432 kg of nickels, and 7.990 kg of dimes? What is the total mass (in g) of this collection of coins?

**1.75** A graduated cylinder is filled to the 40.00-mL mark with a mineral oil. The masses of the cylinder before and after the addition of the mineral oil are 124.966 g and 159.446 g, respectively. In a separate experiment, a metal ball bearing of mass 18.713 g is placed in the cylinder and the cylinder is again filled to the 40.00-mL mark with the mineral oil. The combined mass of the ball bearing and mineral oil is 50.952 g. Calculate the density and radius of the ball bearing. [The volume of a sphere of radius  $r$  is  $(4/3)\pi r^3$ .]

**1.76** Bronze is an alloy made of copper (Cu) and tin (Sn). Calculate the mass of a bronze cylinder of radius 6.44 cm and length 44.37 cm. The composition of the bronze is 79.42 percent Cu and 20.58 percent Sn and the densities of Cu and Sn are  $8.94 \text{ g/cm}^3$  and  $7.31 \text{ g/cm}^3$ , respectively. What assumption should you make in this calculation?

**1.77** A chemist in the nineteenth century prepared an unknown substance. In general, do you think it would be more difficult to prove that it is an element or a compound? Explain.

**1.78** Tums is a popular remedy for acid indigestion. A typical Tums tablet contains calcium carbonate plus some inert substances. When ingested, it reacts with the gastric juice (hydrochloric acid) in the stomach to give off carbon dioxide gas. When a 1.328-g tablet reacted with 40.00 mL of hydrochloric acid (density: 1.140 g/mL), carbon dioxide gas was given off and the resulting solution weighed 46.699 g. Calculate the number of liters of carbon dioxide gas released if its density is 1.81 g/L.

**1.79** A 250-mL glass bottle was filled with 242 mL of water at  $20^\circ\text{C}$  and tightly capped. It was then left outdoors overnight, where the average temperature was  $-5^\circ\text{C}$ . Predict what would happen. The density of water at  $20^\circ\text{C}$  is  $0.998 \text{ g/cm}^3$  and that of ice at  $-5^\circ\text{C}$  is  $0.916 \text{ g/cm}^3$ .

## ANSWERS TO PRACTICE EXERCISES

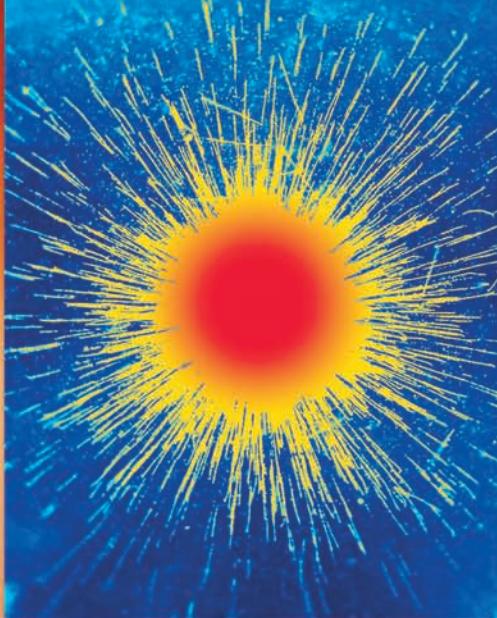
**1.1** 96.5 g. **1.2** (a) 621.5°F, (b) 78.3°C, (c)  $-196^\circ\text{C}$ .

**1.3** (a) Two, (b) four, (c) three, (d) two, (e) three or two.

**1.4** (a) 26.76 L, (b) 4.4 g, (c)  $1.6 \times 10^7 \text{ dm}^2$ , (d) 0.0756 g/mL,

(e)  $6.69 \times 10^4 \text{ m}$ . **1.5** 2.36 lb. **1.6**  $1.08 \times 10^5 \text{ m}^3$ .

**1.7**  $0.534 \text{ g/cm}^3$ .



Colored images of the radioactive emission of radium (Ra). Study of radioactivity helped to advance scientists' knowledge about atomic structure.

## Atoms, Molecules, and Ions

### CHAPTER OUTLINE

- 2.1** The Atomic Theory 29
- 2.2** The Structure of the Atom 30
  - The Electron • Radioactivity • The Proton and the Nucleus •
  - The Neutron
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  - Ionic Compounds • Molecular Compounds • Acids and Bases •
  - Hydrates
- 2.8** Introduction to Organic Compounds 51

### ESSENTIAL CONCEPTS

**Development of the Atomic Theory** The search for the fundamental units of matter began in ancient times. The modern version of atomic theory was laid out by John Dalton, who postulated that elements are composed of extremely small particles, called atoms, and that all atoms of a given element are identical, but they are different from atoms of all other elements.



### Interactive

#### Activity Summary

1. Animation: Cathode Ray Tube (2.2)
2. Animation: Millikan Oil Drop (2.2)
3. Animation: Alpha, Beta, and Gamma Rays (2.2)
4. Animation:  $\alpha$ -Particle Scattering (2.2)
5. Interactivity: Build an Ionic Compound (2.6)
6. Interactivity: Build a Covalent Compound (2.7)

**The Structure of the Atom** Through experimentation in the nineteenth and early twentieth centuries, scientists have learned that an atom is composed of three elementary particles: proton, electron, and neutron. The proton has a positive charge, the electron has a negative charge, and the neutron has no charge. Protons and neutrons are located in a small region at the center of the atom, called the nucleus, and electrons are spread out about the nucleus at some distance from it.

**Ways to Identify Atoms** Atomic number is the number of protons in a nucleus; atoms of different elements have different atomic numbers. Isotopes are atoms of the same element having different numbers of neutrons. Mass number is the sum of the number of protons and neutrons in an atom. Because an atom is electrically neutral, the number of its protons is equal to the number of its electrons.

**The Periodic Table** Elements can be grouped together according to their chemical and physical properties in a chart called the periodic table. The periodic table enables us to classify elements (as metals, metalloids, and nonmetals) and correlate their properties in a systematic way. It is the most useful source of chemical information.

**From Atoms to Molecules and Ions** Atoms of most elements interact to form compounds, which are classified as molecules or ionic compounds made of positive (cations) and negative (anions) ions. Chemical formulas tell us the type and number of atoms present in a molecule or compound.

**Naming Compounds** The names of many inorganic compounds can be deduced from a set of simple rules.

**Organic Compounds** The simplest type of organic compounds is the hydrocarbons.

## 2.1 The Atomic Theory

In the fifth century B.C. the Greek philosopher Democritus expressed the belief that all matter consists of very small, indivisible particles, which he named *atomos* (meaning uncuttable or indivisible). Although Democritus' idea was not accepted by many of his contemporaries (notably Plato and Aristotle), somehow it endured. Experimental evidence from early scientific investigations provided support for the notion of "atomism" and gradually gave rise to the modern definitions of elements and compounds. It was in 1808 that an English scientist and schoolteacher, John Dalton, formulated a precise definition of the indivisible building blocks of matter that we call atoms.

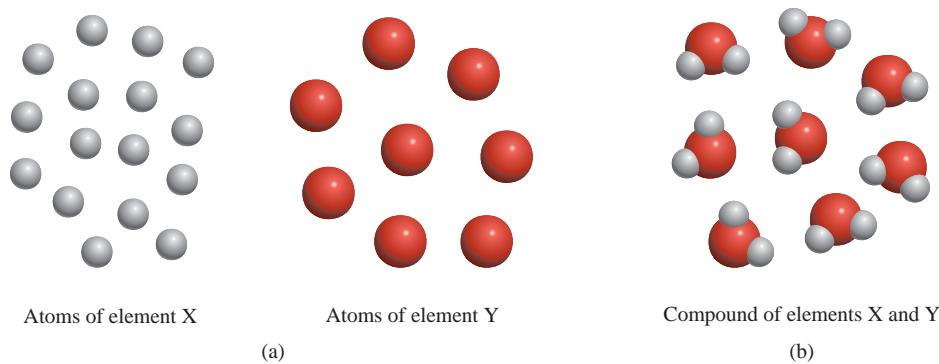
Dalton's work marked the beginning of the modern era of chemistry. The hypotheses about the nature of matter on which Dalton's atomic theory is based can be summarized as

1. Elements are composed of extremely small particles, called atoms.
  2. All atoms of a given element are identical, having the same size, mass, and chemical properties. The atoms of one element are different from the atoms of all other elements.
  3. Compounds are composed of atoms of more than one element. In any compound, the ratio of the numbers of atoms of any two of the elements present is either an integer or a simple fraction.
  4. A chemical reaction involves only the separation, combination, or rearrangement of atoms; it does not result in their creation or destruction.

Figure 2.1 is a schematic representation of hypotheses 2 and 3.

Dalton's concept of an atom was far more detailed and specific than Democritus'. The second hypothesis states that atoms of one element are different from atoms of all other elements. Dalton made no attempt to describe the structure or composition of atoms—he had no idea what an atom is really like. But he did realize that the different properties shown by elements such as hydrogen and oxygen can be explained by assuming that hydrogen atoms are not the same as oxygen atoms.

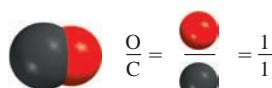
The third hypothesis suggests that, to form a certain compound, we need not only atoms of the right kinds of elements, but the specific numbers of these atoms as well. This idea is an extension of a law published in 1799 by Joseph Proust, a French chemist. Proust's ***law of definite proportions*** states that *different samples of the same compound always contain its constituent elements in the same proportion by mass*. Thus, if we were to analyze samples of carbon dioxide gas obtained from different



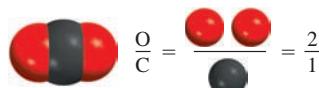
**Figure 2.1**

(a) According to Dalton's atomic theory, atoms of the same element are identical, but atoms of one element are different from atoms of other elements. (b) Compound formed from atoms of elements X and Y. In this case, the ratio of the atoms of element X to the atoms of element Y is 2:1

Carbon monoxide



Carbon dioxide



Ratio of oxygen in carbon monoxide to oxygen in carbon dioxide: 1:2

**Figure 2.2**  
An illustration of the law of multiple proportions.

sources, we would find in each sample the same ratio by mass of carbon to oxygen. It stands to reason, then, that if the ratio of the masses of different elements in a given compound is fixed, the ratio of the atoms of these elements in the compound also must be constant.

Dalton's third hypothesis also supports another important law, the *law of multiple proportions*. According to this law, *if two elements can combine to form more than one compound, the masses of one element that combine with a fixed mass of the other element are in ratios of small whole numbers*. Dalton's theory explains the law of multiple proportions quite simply: The compounds differ in the number of atoms of each kind that combine. For example, carbon forms two stable compounds with oxygen, namely, carbon monoxide and carbon dioxide. Modern measurement techniques indicate that one atom of carbon combines with one atom of oxygen in carbon monoxide and that one atom of carbon combines with two oxygen atoms in carbon dioxide. Thus, the ratio of oxygen in carbon monoxide to oxygen in carbon dioxide is 1:2. This result is consistent with the law of multiple proportions because the mass of an element in a compound is proportional to the number of atoms of the element present (Figure 2.2).

Dalton's fourth hypothesis is another way of stating the *law of conservation of mass*, which is that *matter can be neither created nor destroyed*.<sup>†</sup> Because matter is made of atoms that are unchanged in a chemical reaction, it follows that mass must be conserved as well. Dalton's brilliant insight into the nature of matter was the main stimulus for the rapid progress of chemistry during the nineteenth century.

## 2.2 The Structure of the Atom

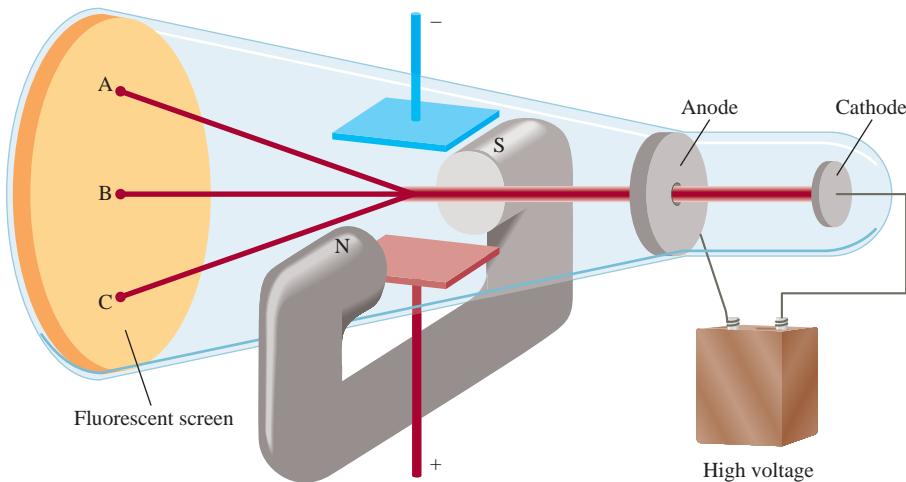
On the basis of Dalton's atomic theory, we can define an **atom** as *the basic unit of an element that can enter into chemical combination*. Dalton imagined an atom that was both extremely small and indivisible. However, a series of investigations that began in the 1850s and extended into the twentieth century clearly demonstrated that atoms actually possess internal structure; that is, they are made up of even smaller particles, which are called *subatomic particles*. This research led to the discovery of three such particles—electrons, protons, and neutrons.

### The Electron



In the 1890s many scientists became caught up in the study of *radiation, the emission and transmission of energy through space in the form of waves*. Information gained from this research contributed greatly to our understanding of atomic structure. One device used to investigate this phenomenon was a cathode ray tube, the fore-runner of the television tube (Figure 2.3). It is a glass tube from which most of the air has been evacuated. When the two metal plates are connected to a high-voltage source, the negatively charged plate, called the *cathode*, emits an invisible ray. The cathode ray is drawn to the positively charged plate, called the *anode*, where it passes through a hole and continues traveling to the other end of the tube. When the ray strikes the specially coated surface, it produces a strong fluorescence, or bright light.

<sup>†</sup>According to Albert Einstein, mass and energy are alternate aspects of a single entity called *mass-energy*. Chemical reactions usually involve a gain or loss of heat and other forms of energy. Thus, when energy is lost in a reaction, for example, mass is also lost. Except for nuclear reactions (see Chapter 21), however, changes of mass in chemical reactions are too small to detect. Therefore, for all practical purposes mass is conserved.

**Figure 2.3**

A cathode ray tube with an electric field perpendicular to the direction of the cathode rays and an external magnetic field. The symbols N and S denote the north and south poles of the magnet. The cathode rays will strike the end of the tube at A in the presence of a magnetic field, at C in the presence of an electric field, and at B when there are no external fields present or when the effects of the electric field and magnetic field cancel each other.

In some experiments, two electrically charged plates and a magnet were added to the *outside* of the cathode ray tube (see Figure 2.3). When the magnetic field is on and the electric field is off, the cathode ray strikes point A. When only the electric field is on, the ray strikes point C. When both the magnetic and the electric fields are off or when they are both on but balanced so that they cancel each other's influence, the ray strikes point B. According to electromagnetic theory, a moving charged body behaves like a magnet and can interact with electric and magnetic fields through which it passes. Because the cathode ray is attracted by the plate bearing positive charges and repelled by the plate bearing negative charges, it must consist of negatively charged particles. We know these *negatively charged particles* as **electrons**. Figure 2.4 shows the effect of a bar magnet on the cathode ray.

An English physicist, J. J. Thomson, used a cathode ray tube and his knowledge of electromagnetic theory to determine the ratio of electric charge to the mass of an individual electron. The number he came up with is  $-1.76 \times 10^8 \text{ C/g}$ , where C stands for *coulomb*, which is the unit of electric charge. Thereafter, in a series of experiments carried out between 1908 and 1917, R. A. Millikan, an American physicist, found the charge of an electron to be  $-1.6022 \times 10^{-19} \text{ C}$ . From these data he calculated the mass of an electron:

$$\begin{aligned}\text{mass of an electron} &= \frac{\text{charge}}{\text{charge/mass}} \\ &= \frac{-1.6022 \times 10^{-19} \text{ C}}{-1.76 \times 10^8 \text{ C/g}} \\ &= 9.10 \times 10^{-28} \text{ g}\end{aligned}$$

which is an exceedingly small mass.

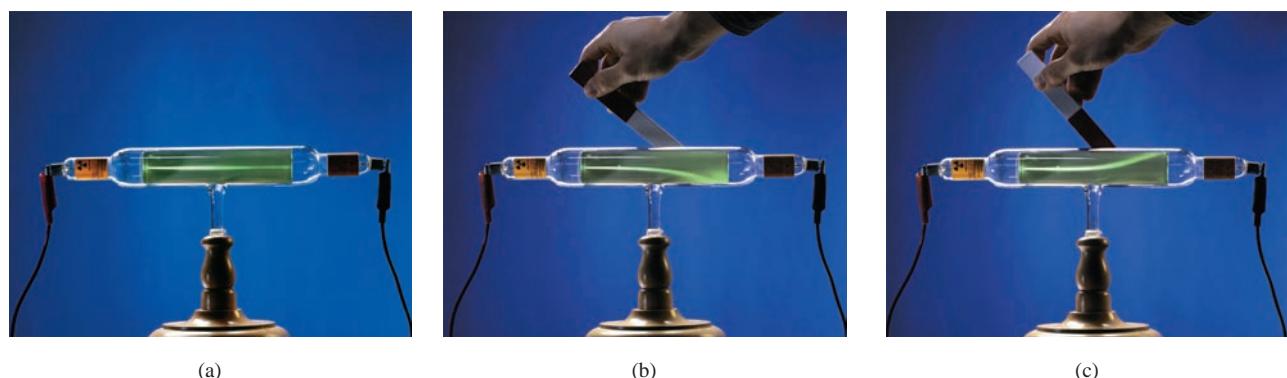
Electrons are normally associated with atoms. However, they can also be studied individually.



**Animation:**  
Millikan Oil Drop  
ARIS, Animations

## Radioactivity

In 1895, the German physicist Wilhelm Röntgen noticed that cathode rays caused glass and metals to emit very unusual rays. This highly energetic radiation penetrated matter, darkened covered photographic plates, and caused a variety of substances to

**Figure 2.4**

(a) A cathode ray produced in a discharge tube traveling from the cathode (left) to the anode (right). The ray itself is invisible, but the fluorescence of a zinc sulfide coating on the glass causes it to appear green. (b) The cathode ray is bent downward when the north pole of the bar magnet is brought toward it. (c) When the polarity of the magnet is reversed, the ray bends in the opposite direction.

fluoresce. Because these rays could not be deflected by a magnet, they could not contain charged particles as cathode rays do. Röntgen called them X rays.

Not long after Röntgen's discovery, Antoine Becquerel, a professor of physics in Paris, began to study fluorescent properties of substances. Purely by accident, he found that exposing thickly wrapped photographic plates to a certain uranium compound caused them to darken, even without the stimulation of cathode rays. Like X rays, the rays from the uranium compound were highly energetic and could not be deflected by a magnet, but they differed from X rays because they were generated spontaneously. One of Becquerel's students, Marie Curie, suggested the name **radioactivity** to describe this *spontaneous emission of particles and/or radiation*. Consequently, any element that spontaneously emits radiation is said to be *radioactive*.

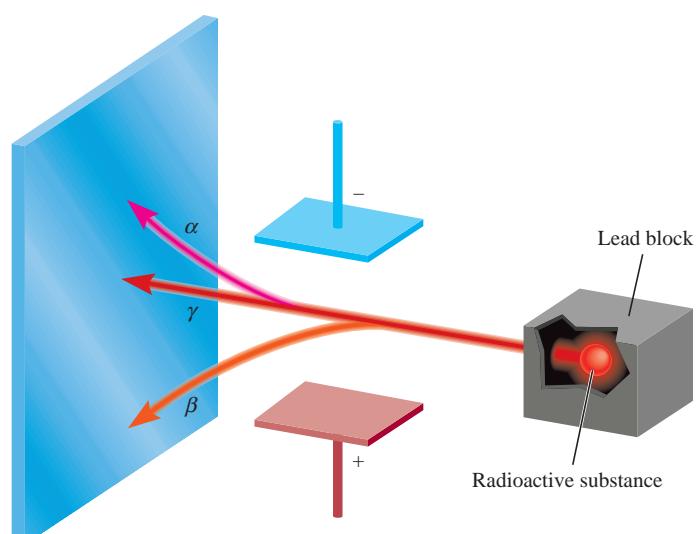
Further investigation revealed that three types of rays are produced by the *decay*, or breakdown, of radioactive substances such as uranium. Two of the three kinds are deflected by oppositely charged metal plates (Figure 2.5). **Alpha ( $\alpha$ ) rays** consist of



**Animation:**  
Alpha, Beta, and Gamma Rays  
ARIS, Animations

**Figure 2.5**

Three types of rays emitted by radioactive elements.  $\beta$  rays consist of negatively charged particles (electrons) and are therefore attracted by the positively charged plate. The opposite holds true for  $\alpha$  rays—they are positively charged and are drawn to the negatively charged plate. Because  $\gamma$  rays have no charges, their path is unaffected by an external electric field.



positively charged particles, called  **$\alpha$  particles**, and therefore are deflected by the positively charged plate. **Beta ( $\beta$ ) rays**, or  **$\beta$  particles**, are electrons and are deflected by the negatively charged plate. The third type of radioactive radiation consists of **high-energy rays** called **gamma ( $\gamma$ ) rays**. Like X rays,  $\gamma$  rays have no charge and are not affected by an external electric or magnetic field.

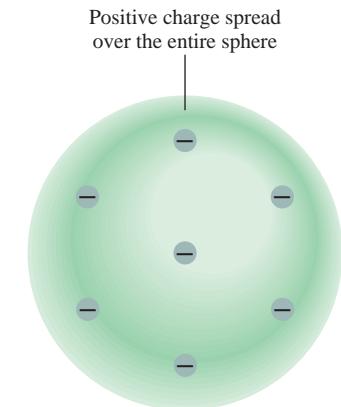
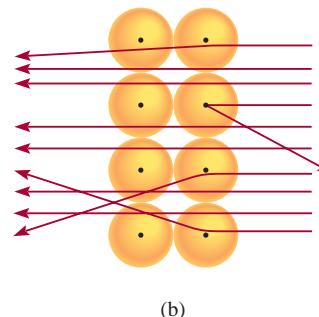
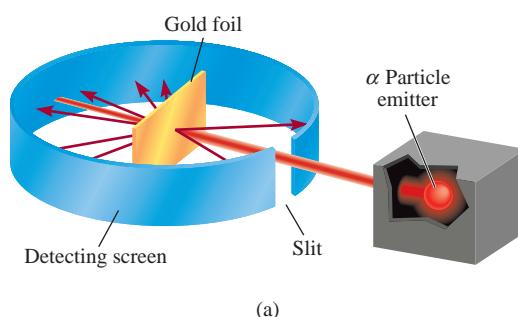
## The Proton and the Nucleus

By the early 1900s, two features of atoms had become clear: They contain electrons, and they are electrically neutral. To maintain electrical neutrality, an atom must contain an equal number of positive and negative charges. On the basis of this information, Thomson proposed that an atom could be thought of as a uniform, positive sphere of matter in which electrons are embedded (Figure 2.6). Thomson's so-called "plum-pudding" model was the accepted theory for a number of years.

In 1910 the New Zealand physicist Ernest Rutherford, who had earlier studied with Thomson at Cambridge University, decided to use  $\alpha$  particles to probe the structure of atoms. Together with his associate Hans Geiger and an undergraduate named Ernest Marsden, Rutherford carried out a series of experiments using very thin foils of gold and other metals as targets for  $\alpha$  particles from a radioactive source (Figure 2.7). They observed that the majority of particles penetrated the foil either undeflected or with only a slight deflection. They also noticed that every now and then an  $\alpha$  particle was scattered (or deflected) at a large angle. In some instances, an  $\alpha$  particle actually bounced back in the direction from which it had come! This was a most surprising finding, for in Thomson's model the positive charge of the atom was so diffuse (spread out) that the positive  $\alpha$  particles were expected to pass through with very little deflection. To quote Rutherford's initial reaction when told of this discovery: "It was as incredible as if you had fired a 15-inch shell at a piece of tissue paper and it came back and hit you."

To explain the results of the  $\alpha$ -scattering experiment, Rutherford devised a new model of atomic structure, suggesting that most of the atom must be empty space. This structure would allow most of the  $\alpha$  particles to pass through the gold foil with little or no deflection. The atom's positive charges, Rutherford proposed, are all concentrated in the **nucleus**, a dense central core within the atom. Whenever an  $\alpha$  particle came close to a nucleus in the scattering experiment, it experienced a large repulsive force and therefore a large deflection. Moreover, an  $\alpha$  particle traveling directly toward a nucleus would experience an enormous repulsion that could completely reverse the direction of the moving particle.

The positively charged particles in the nucleus are called **protons**. In separate experiments, it was found that the charge of each proton has the same magnitude as that of an electron and that the mass of the proton is  $1.67262 \times 10^{-24}$  g—about 1840 times the mass of the oppositely charged electron.



**Figure 2.6**

*Thomson's model of the atom, sometimes described as the "plum-pudding" model, after a traditional English dessert containing raisins. The electrons are embedded in a uniform, positively charged sphere.*



**Animation:**  
 $\alpha$ -Particle Scattering  
ARIS, Animations

**Figure 2.7**

(a) Rutherford's experimental design for measuring the scattering of  $\alpha$  particles by a piece of gold foil. Most of the  $\alpha$  particles passed through the gold foil with little or no deflection. A few were deflected at wide angles. Occasionally an  $\alpha$  particle was turned back. (b) Magnified view of  $\alpha$  particles passing through and being deflected by nuclei.

A common non-SI unit for atomic length is the angstrom ( $\text{\AA}$ ;  $1 \text{\AA} = 100 \text{ pm}$ ).

At this stage of investigation, scientists perceived the atom as follows. The mass of a nucleus constitutes most of the mass of the entire atom, but the nucleus occupies only about  $1/10^{13}$  of the volume of the atom. We express atomic (and molecular) dimensions in terms of the SI unit called the *picometer* ( $\text{pm}$ ), and

$$1 \text{ pm} = 1 \times 10^{-12} \text{ m}$$



If the size of an atom were expanded to that of this sports stadium, the size of the nucleus would be that of a marble.

A typical atomic radius is about 100 pm, whereas the radius of an atomic nucleus is only about  $5 \times 10^{-3}$  pm. You can appreciate the relative sizes of an atom and its nucleus by imagining that if an atom were the size of a sports stadium, the volume of its nucleus would be comparable to that of a small marble. Although the protons are confined to the nucleus of the atom, the electrons are conceived of as being spread out about the nucleus at some distance from it.

## The Neutron

Rutherford's model of atomic structure left one major problem unsolved. It was known that hydrogen, the simplest atom, contains only one proton and that the helium atom contains two protons. Therefore, the ratio of the mass of a helium atom to that of a hydrogen atom should be 2:1. (Because electrons are much lighter than protons, their contribution can be ignored.) In reality, however, the ratio is 4:1.

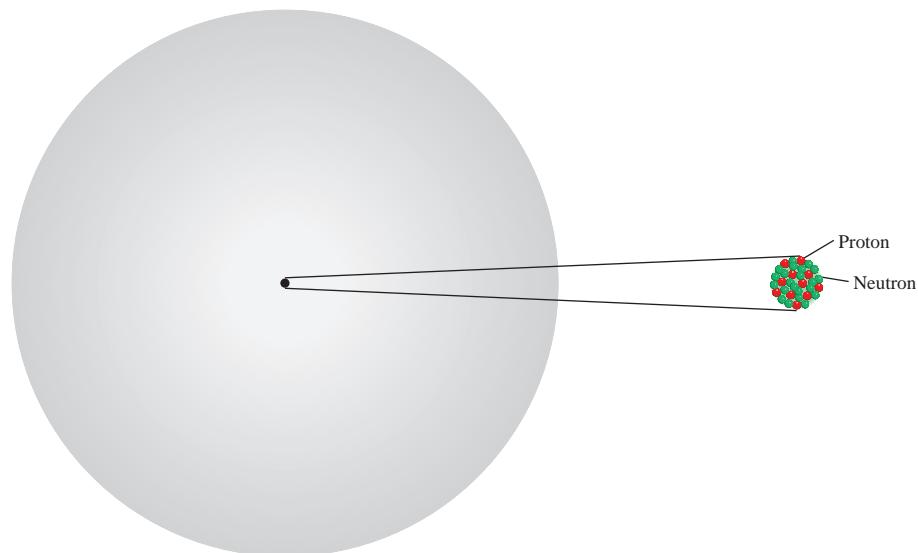
Rutherford and others postulated that there must be another type of subatomic particle in the atomic nucleus; the proof was provided by another English physicist, James Chadwick, in 1932. When Chadwick bombarded a thin sheet of beryllium with  $\alpha$  particles, a very high energy radiation similar to  $\gamma$  rays was emitted by the metal. Later experiments showed that the rays actually consisted of *electrically neutral particles having a mass slightly greater than that of protons*. Chadwick named these particles **neutrons**.

The mystery of the mass ratio could now be explained. In the helium nucleus there are two protons and two neutrons, but in the hydrogen nucleus there is only one proton and no neutrons; therefore, the ratio is 4:1.

Figure 2.8 shows the location of the elementary particles (protons, neutrons, and electrons) in an atom. There are other subatomic particles, but the electron, the

**Figure 2.8**

The protons and neutrons of an atom are packed in an extremely small nucleus. Electrons are shown as “clouds” around the nucleus.



**TABLE 2.1** Mass and Charge of Subatomic Particles

Particle	Mass (g)	Charge	
		Coulomb	Charge Unit
Electron*	$9.10938 \times 10^{-28}$	$-1.6022 \times 10^{-19}$	-1
Proton	$1.67262 \times 10^{-24}$	$+1.6022 \times 10^{-19}$	+1
Neutron	$1.67493 \times 10^{-24}$	0	0

\*More refined experiments have given us a more accurate value of an electron's mass than Millikan's.

proton, and the neutron are the three fundamental components of the atom that are important in chemistry. Table 2.1 shows the masses and charges of these three elementary particles.

## 2.3 Atomic Number, Mass Number, and Isotopes

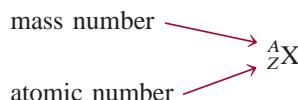
All atoms can be identified by the number of protons and neutrons they contain. *The number of protons in the nucleus of each atom of an element* is called the **atomic number (Z)**. In a neutral atom the number of protons is equal to the number of electrons, so the atomic number also indicates the number of electrons present in the atom. The chemical identity of an atom can be determined solely by its atomic number. For example, the atomic number of nitrogen is 7; this means that each neutral nitrogen atom has 7 protons and 7 electrons. Or viewed another way, every atom in the universe that contains 7 protons is correctly named “nitrogen.”

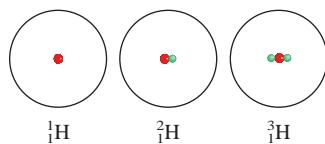
The **mass number (A)** is *the total number of neutrons and protons present in the nucleus of an atom of an element*. Except for the most common form of hydrogen, which has one proton and no neutrons, all atomic nuclei contain both protons and neutrons. In general, the mass number is given by

$$\begin{aligned}\text{mass number} &= \text{number of protons} + \text{number of neutrons} \\ &= \text{atomic number} + \text{number of neutrons}\end{aligned}$$

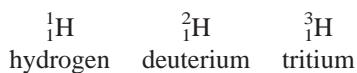
The number of neutrons in an atom is equal to the difference between the mass number and the atomic number, or  $(A - Z)$ . For example, if the mass number of a particular boron atom is 12 and the atomic number is 5 (indicating 5 protons in the nucleus), then the number of neutrons is  $12 - 5 = 7$ . Note that all three quantities (atomic number, number of neutrons, and mass number) must be positive integers, or whole numbers.

In most cases atoms of a given element do not all have the same mass. *Atoms that have the same atomic number but different mass numbers* are called **isotopes**. For example, there are three isotopes of hydrogen. One, simply known as hydrogen, has one proton and no neutrons. The deuterium isotope has one proton and one neutron, and tritium has one proton and two neutrons. The accepted way to denote the atomic number and mass number of an atom of element X is as follows:





Thus, for the isotopes of hydrogen, we write



As another example, consider two common isotopes of uranium with mass numbers of 235 and 238, respectively:



The first isotope is used in nuclear reactors and atomic bombs, whereas the second isotope lacks the properties necessary for these applications. With the exception of hydrogen, isotopes of elements are identified by their mass numbers. Thus these two isotopes are called uranium-235 (pronounced “uranium two thirty-five”) and uranium-238 (pronounced “uranium two thirty-eight”).

The chemical properties of an element are determined primarily by the protons and electrons in its atoms; neutrons do not take part in chemical changes under normal conditions. Therefore, isotopes of the same element have similar chemistries, forming the same types of compounds and displaying similar reactivities.

### Example 2.1

Give the number of protons, neutrons, and electrons in each of the following species:  
 (a)  ${}_{8}^{17}\text{O}$ , (b)  ${}_{80}^{199}\text{Hg}$ , and (c)  ${}_{80}^{200}\text{Hg}$ .

**Strategy** Recall that the superscript denotes mass number and the subscript denotes atomic number. Mass number is always greater than atomic number. (The only exception is  ${}_1^1\text{H}$ , where the mass number is equal to the atomic number.)

#### Solution

- The atomic number is 8, so there are 8 protons. The mass number is 17, so the number of neutrons is  $17 - 8 = 9$ . The number of electrons is the same as the number of protons, that is, 8.
- The atomic number is 80, so there are 80 protons. The mass number is 199, so the number of neutrons is  $199 - 80 = 119$ . The number of electrons is 80.
- Here the number of protons is the same as in (b), or 80. The number of neutrons is  $200 - 80 = 120$ . The number of electrons is also the same as in (b), 80. The species in (b) and (c) are chemically similar isotopes of mercury.

Similar problems: 2.14, 2.16.

**Practice Exercise** How many protons, neutrons, and electrons are in the following isotope of copper:  ${}_{29}^{63}\text{Cu}$ ?

## 2.4 The Periodic Table

More than half of the elements known today were discovered between 1800 and 1900. During this period, chemists noted that many elements show very strong similarities to one another. Recognition of periodic regularities in physical and chemical behavior and the need to organize the large volume of available information about the structure and properties of elemental substances led to the development of the *periodic table*—a chart in which elements having similar chemical and physical properties are grouped together. Figure 2.9 shows the modern periodic table, in which the elements are arranged by atomic number (shown above the element symbol) in horizontal rows called **periods** and in vertical columns known as **groups**

1 1A	2 2A													18 8A			
1 H	2 Be													2 He			
3 Li	4 Be													10 Ne			
11 Na	12 Mg	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9	10	11 1B	12 2B	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112	(113)	114	(115)	116	(117)	(118)
	Metals	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu		
		90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr		

**Figure 2.9**

The modern periodic table. The elements are arranged according to the atomic numbers above their symbols. With the exception of hydrogen (H), nonmetals appear at the far right of the table. The two rows of metals beneath the main body of the table are conventionally set apart to keep the table from being too wide. Actually, cerium (Ce) should follow lanthanum (La), and thorium (Th) should come right after actinium (Ac). The 1–18 group designation has been recommended by the International Union of Pure and Applied Chemistry (IUPAC), but is not yet in wide use. In this text, we use the standard U.S. notation for group numbers (1A–8A and 1B–8B). No names have been assigned to elements 112, 114, and 116. Elements 113, 115, 117, and 118 have not yet been synthesized.

or **families**, according to similarities in their chemical properties. Note that elements 112, 114, and 116 have recently been synthesized, although they have not yet been named.

The elements can be divided into three categories—metals, nonmetals, and metalloids. A **metal** is a good conductor of heat and electricity, whereas a **nonmetal** is usually a poor conductor of heat and electricity. A **metalloid** has properties that are intermediate between those of metals and nonmetals. Figure 2.9 shows that the majority of known elements are metals; only seventeen elements are nonmetals, and eight elements are metalloids. From left to right across any period, the physical and chemical properties of the elements change gradually from metallic to nonmetallic. The periodic table is a handy tool that correlates the properties of the elements in a systematic way and helps us to make predictions about chemical behavior. We will take a closer look at this keystone of chemistry in Chapter 8.

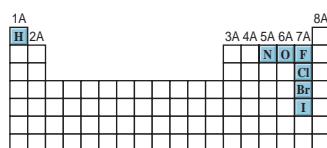
Elements are often referred to collectively by their periodic table group number (Group 1A, Group 2A, and so on). However, for convenience, some element groups have special names. *The Group 1A elements (Li, Na, K, Rb, Cs, and Fr)* are called **alkali metals**, and *the Group 2A elements (Be, Mg, Ca, Sr, Ba, and Ra)* are called **alkaline earth metals**. Elements in Group 7A (*F, Cl, Br, I, and At*) are known as **halogens**, and those in Group 8A (*He, Ne, Ar, Kr, Xe, and Rn*) are called **noble gases** (or **rare gases**). The names of other groups or families will be introduced later.

## 2.5 Molecules and Ions

Of all the elements, only the six noble gases in Group 8A of the periodic table (He, Ne, Ar, Kr, Xe, and Rn) exist in nature as single atoms. For this reason, they are called *monatomic* (meaning a single atom) gases. Most matter is composed of molecules or ions formed by atoms.

### Molecules

We will discuss the nature of chemical bonds in Chapters 9 and 10.



Elements that exist as diatomic molecules.

A **molecule** is an aggregate of at least two atoms in a definite arrangement held together by chemical forces (also called *chemical bonds*). A molecule may contain atoms of the same element or atoms of two or more elements joined in a fixed ratio, in accordance with the law of definite proportions stated in Section 2.1. Thus, a molecule is not necessarily a compound, which, by definition, is made up of two or more elements. Hydrogen gas, for example, is a pure element, but it consists of molecules made up of two H atoms each. Water, on the other hand, is a molecular compound that contains hydrogen and oxygen in a ratio of two H atoms and one O atom. Like atoms, molecules are electrically neutral.

The hydrogen molecule, symbolized as  $H_2$ , is called a **diatomic molecule** because it contains only two atoms. Other elements that normally exist as diatomic molecules are nitrogen ( $N_2$ ) and oxygen ( $O_2$ ), as well as the Group 7A elements—fluorine ( $F_2$ ), chlorine ( $Cl_2$ ), bromine ( $Br_2$ ), and iodine ( $I_2$ ). Of course, a diatomic molecule can contain atoms of different elements. Examples are hydrogen chloride ( $HCl$ ) and carbon monoxide ( $CO$ ).

The vast majority of molecules contain more than two atoms. They can be atoms of the same element, as in ozone ( $O_3$ ), which is made up of three atoms of oxygen, or they can be combinations of two or more different elements. *Molecules containing more than two atoms* are called **polyatomic molecules**. Like ozone, water ( $H_2O$ ) and ammonia ( $NH_3$ ) are polyatomic molecules.

### Ions

In Chapter 8 we will see why atoms of different elements gain (or lose) a specific number of electrons.

An **ion** is an atom or a group of atoms that has a net positive or negative charge. The number of positively charged protons in the nucleus of an atom remains the same during ordinary chemical changes (called chemical reactions), but negatively charged electrons may be lost or gained. The loss of one or more electrons from a neutral atom results in a **cation**, an ion with a net positive charge. For example, a sodium atom ( $Na$ ) can readily lose an electron to become a sodium cation, which is represented by  $Na^+$ :

Na Atom	$Na^+$ Ion
11 protons	11 protons
11 electrons	10 electrons

1 1A	2 2A																18 8A
$\text{Li}^+$																	
$\text{Na}^+$	$\text{Mg}^{2+}$	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10	11 1B	12 2B	$\text{Al}^{3+}$		$\text{P}^{3-}$	$\text{S}^{2-}$	$\text{Cl}^-$	
$\text{K}^+$	$\text{Ca}^{2+}$				$\text{Cr}^{2+}$ $\text{Cr}^{3+}$	$\text{Mn}^{2+}$ $\text{Mn}^{3+}$	$\text{Fe}^{2+}$ $\text{Fe}^{3+}$	$\text{Co}^{2+}$ $\text{Co}^{3+}$	$\text{Ni}^{2+}$ $\text{Ni}^{3+}$	$\text{Cu}^+$ $\text{Cu}^{2+}$	$\text{Zn}^{2+}$				$\text{Se}^{2-}$	$\text{Br}^-$	
$\text{Rb}^+$	$\text{Sr}^{2+}$									$\text{Ag}^+$	$\text{Cd}^{2+}$		$\text{Sn}^{2+}$ $\text{Sn}^{4+}$		$\text{Te}^{2-}$	$\text{I}^-$	
$\text{Cs}^+$	$\text{Ba}^{2+}$									$\text{Au}^+$ $\text{Au}^{3+}$	$\text{Hg}_2^{2+}$ $\text{Hg}^{2+}$		$\text{Pb}^{2+}$ $\text{Pb}^{4+}$				

**Figure 2.10**

Common monatomic ions arranged according to their positions in the periodic table. Note that the  $\text{Hg}_2^{2+}$  ion contains two atoms.

On the other hand, an **anion** is an ion whose net charge is negative due to an increase in the number of electrons. A chlorine atom ( $\text{Cl}$ ), for instance, can gain an electron to become the chloride ion  $\text{Cl}^-$ :

Cl Atom	$\text{Cl}^-$ Ion
17 protons	17 protons
17 electrons	18 electrons

Sodium chloride ( $\text{NaCl}$ ), ordinary table salt, is called an **ionic compound** because it is formed from cations and anions.

An atom can lose or gain more than one electron. Examples of ions formed by the loss or gain of more than one electron are  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{S}^{2-}$ , and  $\text{N}^{3-}$ . These ions, as well as  $\text{Na}^+$  and  $\text{Cl}^-$ , are called **monatomic ions** because they contain only one atom. Figure 2.10 shows the charges of a number of monatomic ions. With very few exceptions, metals tend to form cations and nonmetals form anions.

In addition, two or more atoms can combine to form an ion that has a net positive or net negative charge. **Polyatomic ions** such as  $\text{OH}^-$  (hydroxide ion),  $\text{CN}^-$  (cyanide ion), and  $\text{NH}_4^+$  (ammonium ion) are ions containing more than one atom.

## 2.6 Chemical Formulas

Chemists use **chemical formulas** to express the composition of molecules and ionic compounds in terms of chemical symbols. By composition we mean not only the elements present but also the ratios in which the atoms are combined. Here we are mainly concerned with two types of formulas: molecular formulas and empirical formulas.

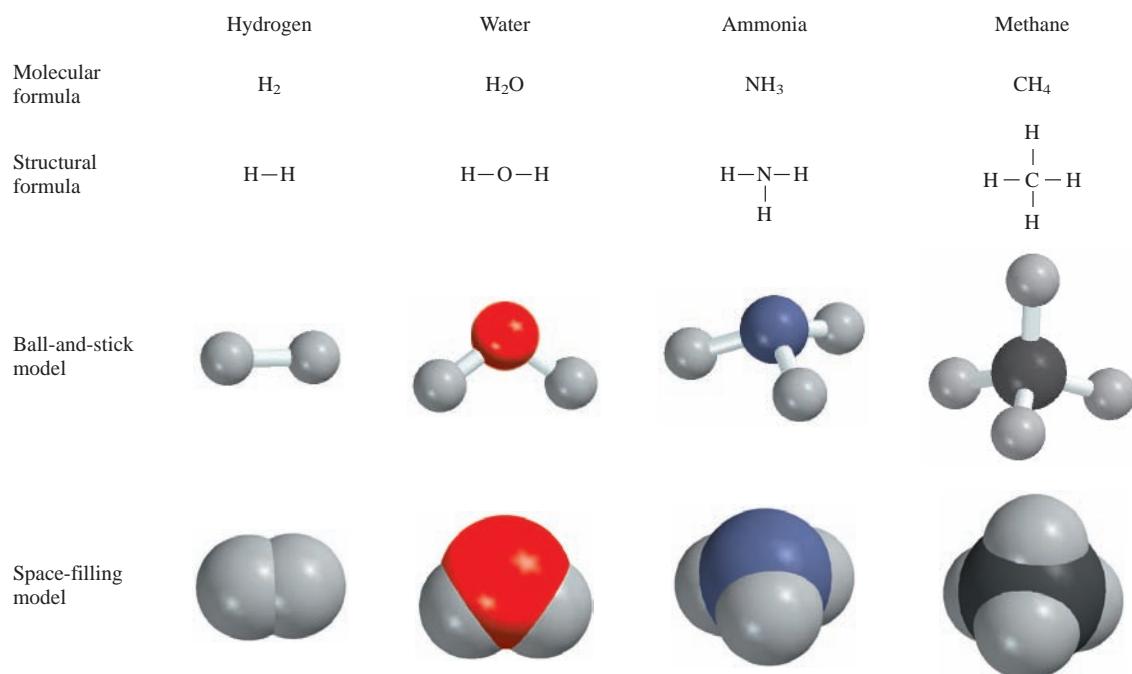
## Molecular Formulas

A **molecular formula** shows the exact number of atoms of each element in the smallest unit of a substance. In our discussion of molecules, each example was given with its molecular formula in parentheses. Thus, H<sub>2</sub> is the molecular formula for hydrogen, O<sub>2</sub> is oxygen, O<sub>3</sub> is ozone, and H<sub>2</sub>O is water. The subscript numeral indicates the number of atoms of an element present. There is no subscript for O in H<sub>2</sub>O because there is only one atom of oxygen in a molecule of water, and so the number “one” is omitted from the formula. Note that oxygen (O<sub>2</sub>) and ozone (O<sub>3</sub>) are allotropes of oxygen. An **allotrope** is *one of two or more distinct forms of an element*. Two allotropic forms of the element carbon—diamond and graphite—are dramatically different not only in properties but also in their relative cost.

### Molecular Models

Molecules are too small for us to observe directly. An effective means of visualizing them is by the use of molecular models. Two standard types of molecular models are currently in use: *ball-and-stick* models and *space-filling* models (Figure 2.11). In ball-and-stick model kits, the atoms are wooden or plastic balls with holes in them. Sticks or springs are used to represent chemical bonds. The angles they form between atoms approximate the bond angles in actual molecules. With the exception of the H atom, the balls are all the same size and each type of atom is represented by a specific color. In space-filling models, atoms are represented by truncated balls held together by snap fasteners, so that the bonds are not visible. The balls are proportional in size to atoms. The first step toward building a molecular model is writing the **structural formula**, which shows how atoms are bonded

See back end paper for color codes for atoms.



**Figure 2.11**  
Molecular and structural formulas and molecular models of four common molecules.

to one another in a molecule. For example, it is known that each of the two H atoms is bonded to an O atom in the water molecule. Therefore, the structural formula of water is H—O—H. A line connecting the two atomic symbols represents a chemical bond.

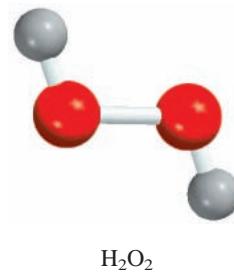
Ball-and-stick models show the three-dimensional arrangement of atoms clearly, and they are fairly easy to construct. However, the balls are not proportional to the size of atoms. Furthermore, the sticks greatly exaggerate the space between atoms in a molecule. Space-filling models are more accurate because they show the variation in atomic size. Their drawbacks are that they are time-consuming to put together and they do not show the three-dimensional positions of atoms very well. We will use both models extensively in this text.

## Empirical Formulas

The molecular formula of hydrogen peroxide, a substance used as an antiseptic and as a bleaching agent for textiles and hair, is  $\text{H}_2\text{O}_2$ . This formula indicates that each hydrogen peroxide molecule consists of two hydrogen atoms and two oxygen atoms. The ratio of hydrogen to oxygen atoms in this molecule is 2:2 or 1:1. The empirical formula of hydrogen peroxide is HO. Thus, the *empirical formula tells us which elements are present and the simplest whole-number ratio of their atoms*, but not necessarily the actual number of atoms in a given molecule. As another example, consider the compound hydrazine ( $\text{N}_2\text{H}_4$ ), which is used as a rocket fuel. The empirical formula of hydrazine is  $\text{NH}_2$ . Although the ratio of nitrogen to hydrogen is 1:2 in both the molecular formula ( $\text{N}_2\text{H}_4$ ) and the empirical formula ( $\text{NH}_2$ ), only the molecular formula tells us the actual number of N atoms (two) and H atoms (four) present in a hydrazine molecule.

Empirical formulas are the *simplest* chemical formulas; they are written by reducing the subscripts in the molecular formulas to the smallest possible whole numbers. Molecular formulas are the *true* formulas of molecules. If we know the molecular formula, we also know the empirical formula, but the reverse is not true. Why, then, do chemists bother with empirical formulas? As we will see in Chapter 3, when chemists analyze an unknown compound, the first step is usually the determination of the compound's empirical formula. With additional information, it is possible to deduce the molecular formula.

For many molecules, the molecular formula and empirical formula are one and the same. Some examples are water ( $\text{H}_2\text{O}$ ), ammonia ( $\text{NH}_3$ ), carbon dioxide ( $\text{CO}_2$ ), and methane ( $\text{CH}_4$ ).



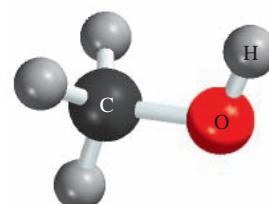
The word “empirical” means “derived from experiment.” As we will see in Chapter 3, empirical formulas are determined experimentally.

### Example 2.2

Write the molecular formula of methanol, an organic solvent and antifreeze, from its ball-and-stick model, shown in the margin.

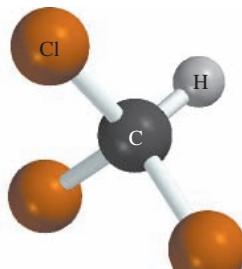
**Solution** Refer to the labels (also see back endpapers). There are four H atoms, one C atom, and one O atom. Therefore, the molecular formula is  $\text{CH}_4\text{O}$ . However, the standard way of writing the molecular formula for methanol is  $\text{CH}_3\text{OH}$  because it shows how the atoms are joined in the molecule.

**Practice Exercise** Write the molecular formula of chloroform, which is used as a solvent and a cleansing agent. The ball-and-stick model of chloroform is shown in the margin on p. 42.



Methanol

Similar problems: 2.43, 2.44.



Chloroform

**Similar problems:** 2.41, 2.42.



Sodium metal reacting with chlorine gas to form sodium chloride.

 **Interactivity:**  
Build an Ionic Compound  
ARIS, Interactives

### Example 2.3

Write the empirical formulas for the following molecules: (a) acetylene ( $C_2H_2$ ), which is used in welding torches; (b) glucose ( $C_6H_{12}O_6$ ), a substance known as blood sugar; and (c) nitrous oxide ( $N_2O$ ), a gas that is used as an anesthetic gas (“laughing gas”) and as an aerosol propellant for whipped creams.

**Strategy** Recall that to write the empirical formula, the subscripts in the molecular formula must be converted to the smallest possible whole numbers.

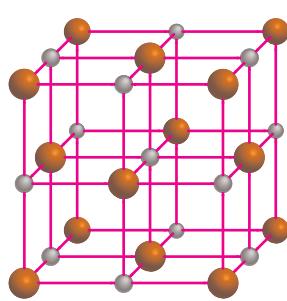
#### Solution

- There are two carbon atoms and two hydrogen atoms in acetylene. Dividing the subscripts by 2, we obtain the empirical formula  $CH$ .
- In glucose there are 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. Dividing the subscripts by 6, we obtain the empirical formula  $CH_2O$ . Note that if we had divided the subscripts by 3, we would have obtained the formula  $C_2H_4O_2$ . Although the ratio of carbon to hydrogen to oxygen atoms in  $C_2H_4O_2$  is the same as that in  $C_6H_{12}O_6$  (1:2:1),  $C_2H_4O_2$  is not the simplest formula because its subscripts are not in the smallest whole-number ratio.
- Because the subscripts in  $N_2O$  are already the smallest possible whole numbers, the empirical formula for nitrous oxide is the same as its molecular formula.

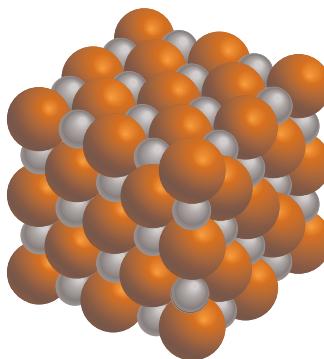
**Practice Exercise** Write the empirical formula for caffeine ( $C_8H_{10}N_4O_2$ ), a stimulant found in tea and coffee.

### Formula of Ionic Compounds

The formulas of ionic compounds are usually the same as their empirical formulas because ionic compounds do not consist of discrete molecular units. For example, a solid sample of sodium chloride ( $NaCl$ ) consists of equal numbers of  $Na^+$  and  $Cl^-$  ions arranged in a three-dimensional network (Figure 2.12). In such a compound, there is a 1:1 ratio of cations to anions so that the compound is electrically neutral. As you can see in Figure 2.12, no  $Na^+$  ion in  $NaCl$  is associated with just one particular  $Cl^-$  ion. In fact, each  $Na^+$  ion is equally held by six surrounding  $Cl^-$  ions and vice versa. Thus,  $NaCl$  is the empirical formula for sodium chloride. In other ionic compounds,



(a)



(b)



(c)

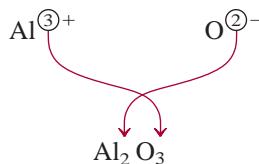
**Figure 2.12**

(a) Structure of solid  $NaCl$ . (b) In reality, the cations are in contact with the anions. In both (a) and (b), the smaller spheres represent  $Na^+$  ions and the larger spheres,  $Cl^-$  ions. (c) Crystals of  $NaCl$ .

the actual structure may be different, but the arrangement of cations and anions is such that the compounds are all electrically neutral. Note that the charges on the cation and anion are not shown in the formula for an ionic compound.

In order for ionic compounds to be electrically neutral, the sum of the charges on the cation and anion in each formula unit must be zero. If the charges on the cation and anion are numerically different, we apply the following rule to make the formula electrically neutral: *The subscript of the cation is numerically equal to the charge on the anion, and the subscript of the anion is numerically equal to the charge on the cation.* If the charges are numerically equal, then no subscripts are necessary. This rule follows from the fact that because the formulas of most ionic compounds are empirical formulas, the subscripts must always be reduced to the smallest ratios. Let us consider some examples.

- **Potassium Bromide.** The potassium cation  $K^+$  and the bromine anion  $Br^-$  combine to form the ionic compound potassium bromide. The sum of the charges is  $+1 + (-1) = 0$ , so no subscripts are necessary. The formula is  $KBr$ .
- **Zinc Iodide.** The zinc cation  $Zn^{2+}$  and the iodine anion  $I^-$  combine to form zinc iodide. The sum of the charges of one  $Zn^{2+}$  ion and one  $I^-$  ion is  $+2 + (-1) = +1$ . To make the charges add up to zero we multiply the  $-1$  charge of the anion by 2 and add the subscript “2” to the symbol for iodine. Therefore, the formula for zinc iodide is  $ZnI_2$ .
- **Aluminum Oxide.** The cation is  $Al^{3+}$  and the oxygen anion is  $O^{2-}$ . The following diagram helps us determine the subscripts for the compound formed by the cation and the anion:



The sum of the charges is  $2(+3) + 3(-2) = 0$ . Thus, the formula for aluminum oxide is  $Al_2O_3$ .

Refer to Figure 2.10 for charges of cations and anions.

## 2.7 Naming Compounds

In addition to using formulas to show the composition of molecules and compounds, chemists have developed a system for naming substances on the basis of their composition. First, we divide them into three categories: ionic compounds, molecular compounds, and acids and bases. Then we apply certain rules to derive the scientific name for a given substance.

### Ionic Compounds

In Section 2.5 we learned that ionic compounds are made up of cations (positive ions) and anions (negative ions). With the important exception of the ammonium ion,  $NH_4^+$ , all cations of interest to us are derived from metal atoms. Metal cations take their names from the elements. For example,

Element	Name of Cation	
Na	sodium	$Na^+$ sodium ion (or sodium cation)
K	potassium	$K^+$ potassium ion (or potassium cation)
Mg	magnesium	$Mg^{2+}$ magnesium ion (or magnesium cation)
Al	aluminum	$Al^{3+}$ aluminum ion (or aluminum cation)

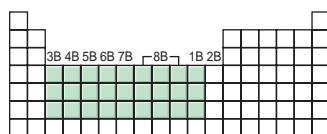
The most reactive metals (green) and the most reactive nonmetals (blue) combine to form ionic compounds.

TABLE 2.2

**The “-ide” Nomenclature of Some Common Monatomic Anions According to Their Positions in the Periodic Table**

Group 4A	Group 5A	Group 6A	Group 7A
C Carbide ( $\text{C}^{4-}$ )*	N Nitride ( $\text{N}^{3-}$ )	O Oxide ( $\text{O}^{2-}$ )	F Fluoride ( $\text{F}^-$ )
Si Silicide ( $\text{Si}^{4-}$ )	P Phosphide ( $\text{P}^{3-}$ )	S Sulfide ( $\text{S}^{2-}$ )	Cl Chloride ( $\text{Cl}^-$ )
		Se Selenide ( $\text{Se}^{2-}$ )	Br Bromide ( $\text{Br}^-$ )
		Te Telluride ( $\text{Te}^{2-}$ )	I Iodide ( $\text{I}^-$ )

\*The word “carbide” is also used for the anion  $\text{C}_2^{2-}$ .



The transition metals are the elements in Groups 1B and 3B–8B (see Figure 2.9).



$\text{FeCl}_2$  (left) and  $\text{FeCl}_3$  (right).

Many ionic compounds are ***binary compounds***, or *compounds formed from just two elements*. For binary ionic compounds the first element named is the metal cation, followed by the nonmetallic anion. Thus,  $\text{NaCl}$  is sodium chloride. The anion is named by taking the first part of the element name (chlorine) and adding “-ide.” Potassium bromide ( $\text{KBr}$ ), zinc iodide ( $\text{ZnI}_2$ ), and aluminum oxide ( $\text{Al}_2\text{O}_3$ ) are also binary compounds. Table 2.2 shows the “-ide” nomenclature of some common monatomic anions according to their positions in the periodic table.

The “-ide” ending is also used for certain anion groups containing different elements, such as hydroxide ( $\text{OH}^-$ ) and cyanide ( $\text{CN}^-$ ). Thus, the compounds  $\text{LiOH}$  and  $\text{KCN}$  are named lithium hydroxide and potassium cyanide. These and a number of other such ionic substances are called ***ternary compounds***, meaning *compounds consisting of three elements*. Table 2.3 lists alphabetically the names of a number of common cations and anions.

Certain metals, especially the ***transition metals***, can form more than one type of cation. Take iron as an example. Iron can form two cations:  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . The accepted procedure for designating different cations of the *same element* is to use Roman numerals. The Roman numeral I is used for one positive charge, II for two positive charges, and so on. This is called the *Stock system*. In this system, the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions are called iron(II) and iron(III), and the compounds  $\text{FeCl}_2$  (containing the  $\text{Fe}^{2+}$  ion) and  $\text{FeCl}_3$  (containing the  $\text{Fe}^{3+}$  ion) are called iron-two chloride and iron-three chloride, respectively. As another example, manganese (Mn) atoms can assume several different positive charges:

$\text{Mn}^{2+}$ :	$\text{MnO}$	manganese(II) oxide
$\text{Mn}^{3+}$ :	$\text{Mn}_2\text{O}_3$	manganese(III) oxide
$\text{Mn}^{4+}$ :	$\text{MnO}_2$	manganese(IV) oxide

These compound names are pronounced manganese-two oxide, manganese-three oxide, and manganese-four oxide.

### Example 2.4

Name the following compounds: (a)  $\text{Cu}(\text{NO}_3)_2$ , (b)  $\text{KH}_2\text{PO}_4$ , and (c)  $\text{NH}_4\text{ClO}_3$ .

**Strategy** Our reference for the names of cations and anions is Table 2.3. Keep in mind that if a metal can form cations of different charges (see Figure 2.10), we need to use the Stock system.

(Continued)

**TABLE 2.3****Names and Formulas of Some Common Inorganic Cations and Anions**

Cation	Anion
aluminum ( $\text{Al}^{3+}$ )	bromide ( $\text{Br}^-$ )
ammonium ( $\text{NH}_4^+$ )	carbonate ( $\text{CO}_3^{2-}$ )
barium ( $\text{Ba}^{2+}$ )	chlorate ( $\text{ClO}_3^-$ )
cadmium ( $\text{Cd}^{2+}$ )	chloride ( $\text{Cl}^-$ )
calcium ( $\text{Ca}^{2+}$ )	chromate ( $\text{CrO}_4^{2-}$ )
cesium ( $\text{Cs}^+$ )	cyanide ( $\text{CN}^-$ )
chromium(III) or chromic ( $\text{Cr}^{3+}$ )	dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ )
cobalt(II) or cobaltous ( $\text{Co}^{2+}$ )	dihydrogen phosphate ( $\text{H}_2\text{PO}_4^-$ )
copper(I) or cuprous ( $\text{Cu}^+$ )	fluoride ( $\text{F}^-$ )
copper(II) or cupric ( $\text{Cu}^{2+}$ )	hydride ( $\text{H}^-$ )
hydrogen ( $\text{H}^+$ )	hydrogen carbonate or bicarbonate ( $\text{HCO}_3^-$ )
iron(II) or ferrous ( $\text{Fe}^{2+}$ )	hydrogen phosphate ( $\text{HPO}_4^{2-}$ )
iron(III) or ferric ( $\text{Fe}^{3+}$ )	hydrogen sulfate or bisulfate ( $\text{HSO}_4^-$ )
lead(II) or plumbous ( $\text{Pb}^{2+}$ )	hydroxide ( $\text{OH}^-$ )
lithium ( $\text{Li}^+$ )	iodide ( $\text{I}^-$ )
magnesium ( $\text{Mg}^{2+}$ )	nitrate ( $\text{NO}_3^-$ )
manganese(II) or manganous ( $\text{Mn}^{2+}$ )	nitride ( $\text{N}^{3-}$ )
mercury(I) or mercurous ( $\text{Hg}_2^{2+}$ )*	nitrite ( $\text{NO}_2^-$ )
mercury(II) or mercuric ( $\text{Hg}^{2+}$ )	oxide ( $\text{O}^{2-}$ )
potassium ( $\text{K}^+$ )	permanganate ( $\text{MnO}_4^-$ )
rubidium ( $\text{Rb}^+$ )	peroxide ( $\text{O}_2^{2-}$ )
silver ( $\text{Ag}^+$ )	phosphate ( $\text{PO}_4^{3-}$ )
sodium ( $\text{Na}^+$ )	sulfate ( $\text{SO}_4^{2-}$ )
strontium ( $\text{Sr}^{2+}$ )	sulfide ( $\text{S}^{2-}$ )
tin(II) or stannous ( $\text{Sn}^{2+}$ )	sulfite ( $\text{SO}_3^{2-}$ )
zinc ( $\text{Zn}^{2+}$ )	thiocyanate ( $\text{SCN}^-$ )

\*Mercury(I) exists as a pair as shown.

**Solution**

- The nitrate ion ( $\text{NO}_3^-$ ) bears one negative charge, so the copper ion must have two positive charges. Because copper forms both  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  ions, we need to use the Stock system and call the compound copper(II) nitrate.
- The cation is  $\text{K}^+$  and the anion is  $\text{H}_2\text{PO}_4^-$  (dihydrogen phosphate). Because potassium only forms one type of ion ( $\text{K}^+$ ), there is no need to use potassium(I) in the name. The compound is potassium dihydrogen phosphate.
- The cation is  $\text{NH}_4^+$  (ammonium ion) and the anion is  $\text{ClO}_3^-$ . The compound is ammonium chlorate.

Similar problems: 2.47(a), (b), (e).

**Practice Exercise** Name the following compounds: (a)  $\text{PbO}$  and (b)  $\text{Li}_2\text{SO}_3$ .

### Example 2.5

Write chemical formulas for the following compounds: (a) mercury(I) nitrite, (b) cesium sulfide, and (c) calcium phosphate.

**Strategy** We refer to Table 2.3 for the formulas of cations and anions. Recall that the Roman numerals in the Stock system provide useful information about the charges of the cation.

#### Solution

Note that the subscripts of this ionic compound are not reduced to the smallest ratio because the Hg(I) ion exists as a pair or dimer.

- The Roman numeral shows that the mercury ion bears a +1 charge. According to Table 2.3, however, the mercury(I) ion is diatomic (that is,  $\text{Hg}_2^{2+}$ ) and the nitrite ion is  $\text{NO}_2^-$ . Therefore, the formula is  $\text{Hg}_2(\text{NO}_2)_2$ .
- Each sulfide ion bears two negative charges, and each cesium ion bears one positive charge (cesium is in Group 1A, as is sodium). Therefore, the formula is  $\text{Cs}_2\text{S}$ .
- Each calcium ion ( $\text{Ca}^{2+}$ ) bears two positive charges, and each phosphate ion ( $\text{PO}_4^{3-}$ ) bears three negative charges. To make the sum of the charges equal zero, we must adjust the numbers of cations and anions:

$$3(+2) + 2(-3) = 0$$

Similar problems: 2.49(a), (b), (h).

**Practice Exercise** Write formulas for the following ionic compounds: (a) rubidium sulfate and (b) barium hydride.

## Molecular Compounds



**Interactivity:**  
Build a Covalent Compound  
ARIS, Interactives

**TABLE 2.4**

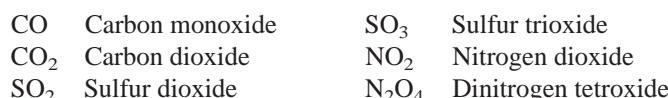
### Greek Prefixes Used in Naming Molecular Compounds

Prefix	Meaning
mono-	1
di-	2
tri-	3
tetra-	4
penta-	5
hexa-	6
hepta-	7
octa-	8
nona-	9
deca-	10

Unlike ionic compounds, molecular compounds contain discrete molecular units. They are usually composed of nonmetallic elements (see Figure 2.9). Many molecular compounds are binary compounds. Naming binary molecular compounds is similar to naming binary ionic compounds. We place the name of the first element in the formula first, and the second element is named by adding “-ide” to the root of the element name. Some examples are



It is quite common for one pair of elements to form several different compounds. In these cases, confusion in naming the compounds is avoided by the use of Greek prefixes to denote the number of atoms of each element present (Table 2.4). Consider these examples:



These guidelines are helpful when you are naming compounds with prefixes:

- The prefix “mono-” may be omitted for the first element. For example,  $\text{PCl}_3$  is named phosphorus trichloride, not monophosphorus trichloride. Thus, the absence of a prefix for the first element usually means that only one atom of that element is present in the molecule.
- For oxides, the ending “a” in the prefix is sometimes omitted. For example,  $\text{N}_2\text{O}_4$  may be called dinitrogen tetroxide rather than dinitrogen tetraoxide.

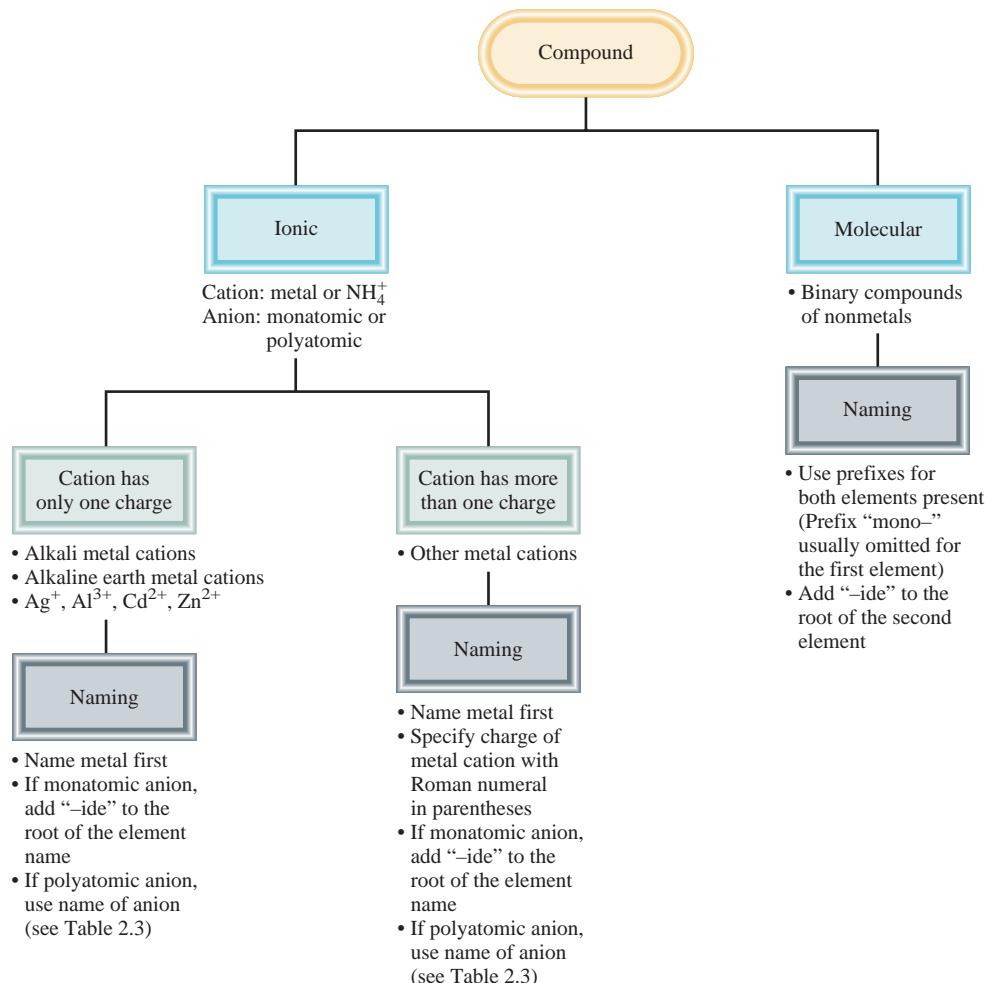
Exceptions to the use of Greek prefixes are molecular compounds containing hydrogen. Traditionally, many of these compounds are called either by their common, nonsystematic names or by names that do not specifically indicate the number of H atoms present:

$\text{B}_2\text{H}_6$	Diborane	$\text{PH}_3$	Phosphine
$\text{CH}_4$	Methane	$\text{H}_2\text{O}$	Water
$\text{SiH}_4$	Silane	$\text{H}_2\text{S}$	Hydrogen sulfide
$\text{NH}_3$	Ammonia		

Note that even the order of writing the elements in the formulas is irregular. These examples show that H is written first in water and hydrogen sulfide, whereas H is written last in the other compounds.

Writing formulas for molecular compounds is usually straightforward. Thus, the name arsenic trifluoride means that there are one As atom and three F atoms in each molecule and the molecular formula is  $\text{AsF}_3$ . Note that the order of elements in the formula is the same as that in its name.

Figure 2.13 summarizes the steps for naming ionic and molecular compounds.



**Figure 2.13**  
Steps for naming ionic and molecular compounds.

### Example 2.6

Name the following molecular compounds: (a)  $\text{SiCl}_4$  and (b)  $\text{P}_4\text{O}_{10}$ .

**Solution** We refer to Table 2.4 for prefixes.

- Because there are four chlorine atoms present, the compound is silicon tetrachloride.
- There are four phosphorus atoms and ten oxygen atoms present, so the compound is tetraphosphorus decoxide. Note that the “a” is omitted in “deca.”

**Practice Exercise** Name the following molecular compounds: (a)  $\text{NF}_3$  and (b)  $\text{Cl}_2\text{O}_7$ .

Similar problems: 2.47(c), (h), (j).

### Example 2.7

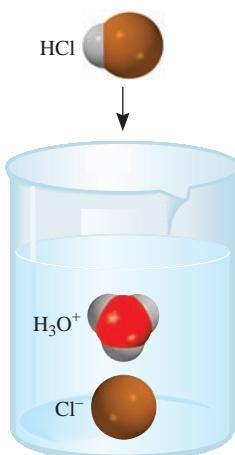
Write chemical formulas for the following molecular compounds: (a) carbon disulfide and (b) disilicon hexabromide.

**Solution** We refer to Table 2.4 for prefixes.

- Because there are two sulfur atoms and one carbon atom present, the formula is  $\text{CS}_2$ .
- There are two silicon atoms and six bromine atoms present, so the formula is  $\text{Si}_2\text{Br}_6$ .

Similar problems: 2.49(f), (g).

**Practice Exercise** Write chemical formulas for the following molecular compounds: (a) sulfur tetrafluoride and (b) dinitrogen pentoxide.



When dissolved in water, the  $\text{HCl}$  molecule is converted to the  $\text{H}^+$  and  $\text{Cl}^-$  ions. The  $\text{H}^+$  ion is associated with one or more water molecules, and is usually represented as  $\text{H}_3\text{O}^+$ .

Note that these acids all exist as molecular compounds in the gas phase.

## Acids and Bases

### Naming Acids

An **acid** can be described as *a substance that yields hydrogen ions ( $\text{H}^+$ ) when dissolved in water.* ( $\text{H}^+$  is equivalent to one proton, and is often referred to that way.) Formulas for acids contain one or more hydrogen atoms as well as an anionic group. Anions whose names end in “-ide” have associated acids with a “hydro-” prefix and an “-ic” ending, as shown in Table 2.5. In some cases two different names are assigned to the same chemical formula. For instance,  $\text{HCl}$  is known as both hydrogen chloride and hydrochloric acid. The name used for this compound

**TABLE 2.5** Some Simple Acids

Anion	Corresponding Acid
$\text{F}^-$ (fluoride)	$\text{HF}$ (hydrofluoric acid)
$\text{Cl}^-$ (chloride)	$\text{HCl}$ (hydrochloric acid)
$\text{Br}^-$ (bromide)	$\text{HBr}$ (hydrobromic acid)
$\text{I}^-$ (iodide)	$\text{HI}$ (hydroiodic acid)
$\text{CN}^-$ (cyanide)	$\text{HCN}$ (hydrocyanic acid)
$\text{S}^{2-}$ (sulfide)	$\text{H}_2\text{S}$ (hydrosulfuric acid)

depends on its physical state. In the gaseous or pure liquid state, HCl is a molecular compound called hydrogen chloride. When it is dissolved in water, the molecules break up into  $\text{H}^+$  and  $\text{Cl}^-$  ions; in this condition, the substance is called hydrochloric acid.

*Acids that contain hydrogen, oxygen, and another element (the central element)* are called **oxoacids**. The formulas of oxoacids are usually written with the H first, followed by the central element and then O, as illustrated by this series of common oxoacids:

$\text{H}_2\text{CO}_3$	carbonic acid
$\text{HClO}_3$	chloric acid
$\text{HNO}_3$	nitric acid
$\text{H}_3\text{NO}_4$	phosphoric acid
$\text{H}_2\text{SO}_4$	sulfuric acid

Often two or more oxoacids have the same central atom but a different number of O atoms. Starting with the oxoacids whose names end with “-ic,” we use these rules to name these compounds.

1. Addition of one O atom to the “-ic” acid: The acid is called “per . . . -ic” acid. Thus, adding an O atom to  $\text{HClO}_3$  changes chloric acid to perchloric acid,  $\text{HClO}_4$ .
2. Removal of one O atom from the “-ic” acid: The acid is called “-ous” acid. Thus, nitric acid,  $\text{HNO}_3$ , becomes nitrous acid,  $\text{HNO}_2$ .
3. Removal of two O atoms from the “-ic” acid: The acid is called “hypo . . . -ous” acid. Thus, when  $\text{HBrO}_3$  is converted to  $\text{HBrO}$ , the acid is called hypobromous acid.

The rules for naming *anions of oxoacids*, called **oxoanions**, are

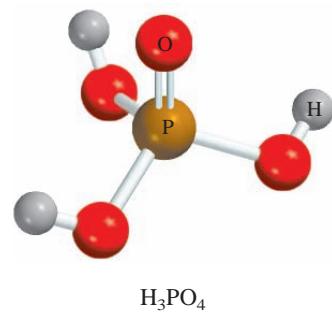
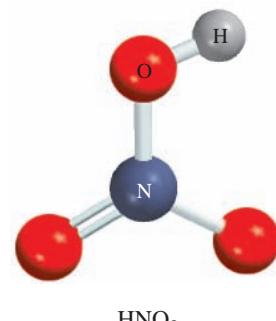
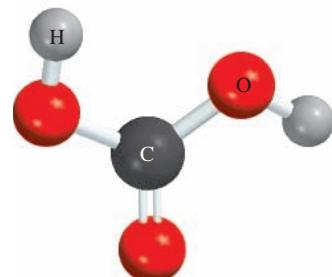
1. When all the H ions are removed from the “-ic” acid, the anion’s name ends with “-ate.” For example, the anion  $\text{CO}_3^{2-}$  derived from  $\text{H}_2\text{CO}_3$  is called carbonate.
2. When all the H ions are removed from the “-ous” acid, the anion’s name ends with “-ite.” Thus, the anion  $\text{ClO}_2^-$  derived from  $\text{HClO}_2$  is called chlorite.
3. The names of anions in which one or more but not all of the hydrogen ions have been removed must indicate the number of H ions present. For example, consider the anions derived from phosphoric acid:



Note that we usually omit the prefix “mono-” when there is only one H in the anion. Table 2.6 gives the names of the oxoacids and oxoanions that contain

**TABLE 2.6 Names of Oxoacids and Oxoanions That Contain Chlorine**

Acid	Anion
$\text{HClO}_4$ (perchloric acid)	$\text{ClO}_4^-$ (perchlorate)
$\text{HClO}_3$ (chloric acid)	$\text{ClO}_3^-$ (chlorate)
$\text{HClO}_2$ (chlorous acid)	$\text{ClO}_2^-$ (chlorite)
$\text{HClO}$ (hypochlorous acid)	$\text{ClO}^-$ (hypochlorite)



chlorine, and Figure 2.14 summarizes the nomenclature for the oxoacids and oxoanions.

### Example 2.8

Name the following oxoacid and oxoanion: (a)  $\text{H}_3\text{PO}_3$  and (b)  $\text{IO}_4^-$ .

**Solution** We refer to Figure 2.14 and Table 2.6.

- We start with our reference acid, phosphoric acid ( $\text{H}_3\text{PO}_4$ ). Because  $\text{H}_3\text{PO}_3$  has one fewer O atom, it is called phosphorous acid.
- The parent acid is  $\text{HIO}_4$ . Because the acid has one more O atom than our reference iodic acid ( $\text{HIO}_3$ ), it is called periodic acid. Therefore, the anion derived from  $\text{HIO}_4$  is called periodate.

**Similar problems:** 2.48(f), 2.49(c).

**Practice Exercise** Name the following oxoacid and oxoanion: (a)  $\text{HBrO}$  and (b)  $\text{HSO}_4^-$ .

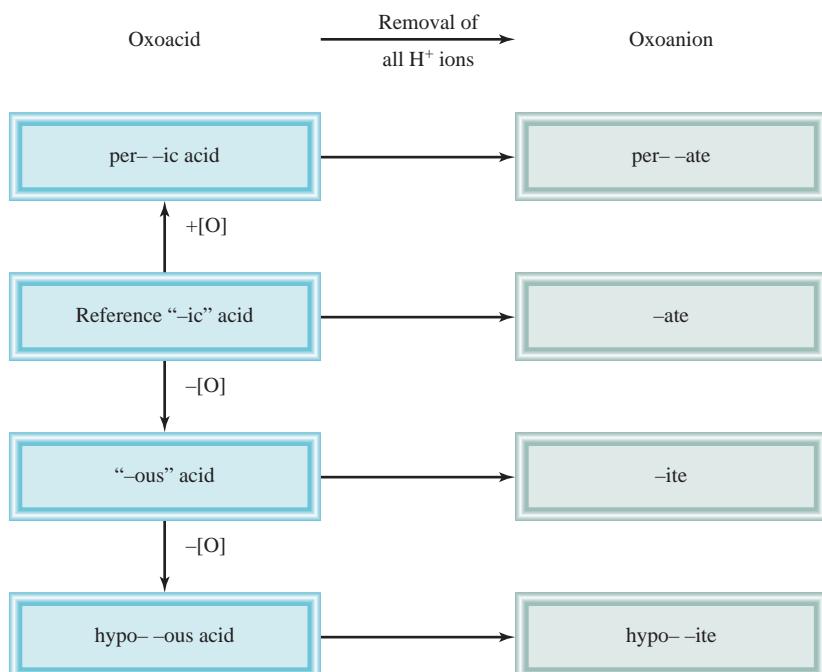
### Naming Bases

A **base** can be described as *a substance that yields hydroxide ions ( $\text{OH}^-$ ) when dissolved in water*. Some examples are



Ammonia ( $\text{NH}_3$ ), a molecular compound in the gaseous or pure liquid state, is also classified as a common base. At first glance this may seem to be an exception to the definition of a base. But note that as long as a substance *yields* hydroxide

**Figure 2.14**  
Naming oxoacids and oxoanions.



ions when dissolved in water, it need not contain hydroxide ions in its structure to be considered a base. In fact, when ammonia dissolves in water,  $\text{NH}_3$  reacts partially with water to yield  $\text{NH}_4^+$  and  $\text{OH}^-$  ions. Thus, it is properly classified as a base.

## Hydrates

**Hydrates** are compounds that have a specific number of water molecules attached to them. For example, in its normal state, each unit of copper(II) sulfate has five water molecules associated with it. The systematic name for this compound is copper(II) sulfate pentahydrate, and its formula is written as  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . The water molecules can be driven off by heating. When this occurs, the resulting compound is  $\text{CuSO}_4$ , which is sometimes called *anhydrous* copper(II) sulfate; “anhydrous” means that the compound no longer has water molecules associated with it (see the photo in the margin). Some other hydrates are

$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	barium chloride dihydrate
$\text{LiCl} \cdot \text{H}_2\text{O}$	lithium chloride monohydrate
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	magnesium sulfate heptahydrate

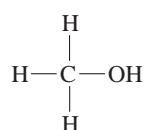


$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (left) is blue;  
 $\text{CuSO}_4$  (right) is white.

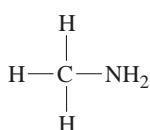
## 2.8 Introduction to Organic Compounds

The simplest type of organic compounds is the *hydrocarbons*, which contain only carbon and hydrogen atoms. The hydrocarbons are used as fuels for domestic and industrial heating, for generating electricity and powering internal combustion engines, and as starting materials for the chemical industry. One class of hydrocarbons is called the *alkanes*. Table 2.7 shows the names, formulas, and molecular models of the first ten straight-chain alkanes, in which the carbon chains have no branches. Note that all the names end with *-ane*. Starting with  $\text{C}_5\text{H}_{12}$ , we use the Greek prefixes in Table 2.4 to indicate the number of carbon atoms present.

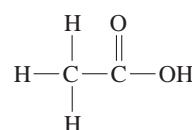
The chemistry of organic compounds is largely determined by the *functional groups*, which consist of one or a few atoms bonded in a specific way. For example, when an H atom in methane is replaced by a hydroxyl group ( $-\text{OH}$ ), an amino group ( $-\text{NH}_2$ ), and a carboxyl group ( $-\text{COOH}$ ), the following molecules are generated:



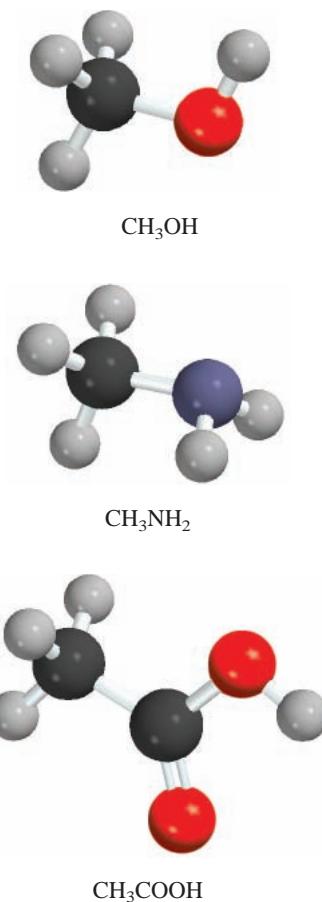
Methanol



Methylamine



Acetic acid



The chemical properties of these molecules can be predicted based on the reactivity of the functional groups. We will frequently use organic compounds as examples to illustrate chemical bonding, acid-base reactions, and other properties throughout the book.

**TABLE 2.7** The First Ten Straight-Chain Alkanes

Name	Formula	Molecular Model
Methane	$\text{CH}_4$	
Ethane	$\text{C}_2\text{H}_6$	
Propane	$\text{C}_3\text{H}_8$	
Butane	$\text{C}_4\text{H}_{10}$	
Pentane	$\text{C}_5\text{H}_{12}$	
Hexane	$\text{C}_6\text{H}_{14}$	
Heptane	$\text{C}_7\text{H}_{16}$	
Octane	$\text{C}_8\text{H}_{18}$	
Nonane	$\text{C}_9\text{H}_{20}$	
Decane	$\text{C}_{10}\text{H}_{22}$	

## SUMMARY OF FACTS AND CONCEPTS

- Modern chemistry began with Dalton's atomic theory, which states that all matter is composed of tiny, indivisible particles called atoms; that all atoms of the same element are identical; that compounds contain atoms of different elements combined in whole-number ratios; and that atoms are neither created nor destroyed in chemical reactions (the law of conservation of mass).
- Atoms of constituent elements in a particular compound are always combined in the same proportions by

mass (law of definite proportions). When two elements can combine to form more than one type of compound, the masses of one element that combine with a fixed mass of the other element are in a ratio of small whole numbers (law of multiple proportions).

- An atom consists of a very dense central nucleus made up of protons and neutrons, plus electrons that move about the nucleus at a relatively large distance from it. Protons are positively charged, neutrons have no charge, and electrons are negatively charged. Protons and

- neutrons have roughly the same mass, which is about 1840 times greater than the mass of an electron.
- The atomic number of an element is the number of protons in the nucleus of an atom of the element; it determines the identity of an element. The mass number is the sum of the number of protons and the number of neutrons in the nucleus. Isotopes are atoms of the same element that have the same number of protons but different numbers of neutrons.
  - Chemical formulas combine the symbols for the constituent elements with whole-number subscripts to show the type and number of atoms contained in the smallest unit of a compound. The molecular formula conveys the specific number and types of atoms combined in each molecule of a compound. The empirical formula shows the simplest ratios of the atoms in a molecule.
  - Chemical compounds are either molecular compounds (in which the smallest units are discrete, individual molecules) or ionic compounds (in which positive and negative ions are held together by mutual attraction). Ionic compounds are made up of cations and anions, formed when atoms lose electrons and gain electrons, respectively.
  - The names of many inorganic compounds can be deduced from a set of simple rules. The formulas can be written from the names of the compounds.
  - The simplest type of organic compounds is the hydrocarbons.

## KEY WORDS

Acid, p. 48	Chemical formula, p. 39	Law of definite proportions, p. 29	Oxoacid, p. 49
Alkali metals, p. 38	Diatomeric molecule, p. 38	Law of multiple proportions, p. 30	Oxoanion, p. 49
Alkaline earth metals, p. 38	Electron, p. 31	Mass number ( <i>A</i> ), p. 35	Periodic table, p. 36
Allotrope, p. 40	Empirical formula, p. 41	Metal, p. 37	Periods, p. 36
Alpha ( $\alpha$ ) particles, p. 33	Families, p. 37	Metalloid, p. 37	Polyatomic ion, p. 39
Alpha ( $\alpha$ ) rays, p. 32	Gamma ( $\gamma$ ) rays, p. 33	Molecular formula, p. 40	Polyatomic molecule, p. 38
Anion, p. 39	Groups, p. 36	Molecule, p. 38	Proton, p. 33
Atom, p. 30	Halogens, p. 38	Monatomic ion, p. 39	Radiation, p. 30
Atomic number ( <i>Z</i> ), p. 35	Hydrate, p. 51	Neutron, p. 34	Radioactivity, p. 32
Base, p. 50	Ion, p. 38	Noble gases, p. 38	Rare gases, p. 38
Beta ( $\beta$ ) particles, p. 33	Ionic compound, p. 39	Nonmetal, p. 37	Structural formula, p. 40
Beta ( $\beta$ ) rays, p. 33	Isotope, p. 35	Nucleus, p. 33	Ternary compound, p. 44
Binary compound, p. 44	Law of conservation of mass, p. 30		
Cation, p. 38			

## QUESTIONS AND PROBLEMS

### Structure of the Atom

#### Review Questions

- Define these terms: (a)  $\alpha$  particle, (b)  $\beta$  particle, (c)  $\gamma$  ray, (d) X ray.
- List the types of radiation that are known to be emitted by radioactive elements.
- Compare the properties of:  $\alpha$  particles, cathode rays, protons, neutrons, and electrons. What is meant by the term “fundamental particle”?
- Describe the contributions of these scientists to our knowledge of atomic structure: J. J. Thomson, R. A. Millikan, Ernest Rutherford, James Chadwick.
- A sample of a radioactive element is found to be losing mass gradually. Explain what is happening to the sample.

- Describe the experimental basis for believing that the nucleus occupies a very small fraction of the volume of the atom.

#### Problems

- The diameter of a neutral helium atom is about  $1 \times 10^2$  pm. Suppose that we could line up helium atoms side by side in contact with one another. Approximately how many atoms would it take to make the distance from end to end 1 cm?
- Roughly speaking, the radius of an atom is about 10,000 times greater than that of its nucleus. If an atom were magnified so that the radius of its nucleus became 10 cm, what would be the radius of the atom in miles? (1 mi = 1609 m.)

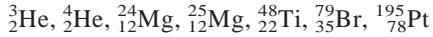
## Atomic Number, Mass Number, and Isotopes

### Review Questions

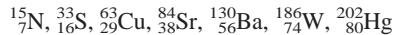
- 2.9 Define these terms: (a) atomic number, (b) mass number. Why does a knowledge of atomic number enable us to deduce the number of electrons present in an atom?
- 2.10 Why do all atoms of an element have the same atomic number, although they may have different mass numbers? What do we call atoms of the same element with different mass numbers? Explain the meaning of each term in the symbol  ${}_{Z}^{A}X$ .

### Problems

- 2.11 What is the mass number of an iron atom that has 28 neutrons?
- 2.12** Calculate the number of neutrons of  ${}^{239}\text{Pu}$ .
- 2.13 For each of these species, determine the number of protons and the number of neutrons in the nucleus:



- 2.14** Indicate the number of protons, neutrons, and electrons in each of these species:



- 2.15 Write the appropriate symbol for each of these isotopes: (a)  $Z = 11, A = 23$ ; (b)  $Z = 28, A = 64$ .
- 2.16** Write the appropriate symbol for each of these isotopes: (a)  $Z = 74, A = 186$ ; (b)  $Z = 80, A = 201$ .

## The Periodic Table

### Review Questions

- 2.17 What is the periodic table, and what is its significance in the study of chemistry? What are groups and periods in the periodic table?
- 2.18 Give two differences between a metal and a nonmetal.
- 2.19 Write the names and symbols for four elements in each of these categories: (a) nonmetal, (b) metal, (c) metalloid.
- 2.20 Define, with two examples, these terms: (a) alkali metals, (b) alkaline earth metals, (c) halogens, (d) noble gases.

### Problems

- 2.21 Elements whose names end with “-ium” are usually metals; sodium is one example. Identify a nonmetal whose name also ends with “-ium.”
- 2.22** Describe the changes in properties (from metals to nonmetals or from nonmetals to metals) as we move (a) down a periodic group and (b) across the periodic table.
- 2.23 Consult a handbook of chemical and physical data (ask your instructor where you can locate a copy of

the handbook) to find (a) two metals less dense than water, (b) two metals more dense than mercury, (c) the densest known solid metallic element, (d) the densest known solid nonmetallic element.

- 2.24** Group these elements in pairs that you would expect to show similar chemical properties: K, F, P, Na, Cl, and N.

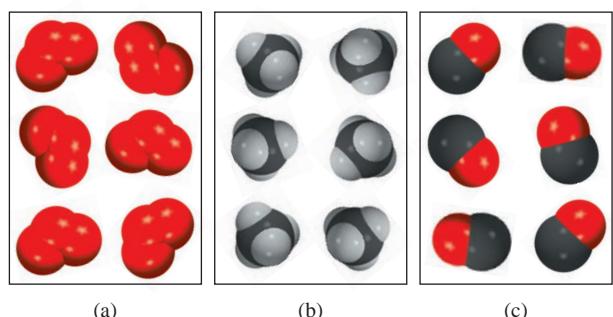
## Molecules and Ions

### Review Questions

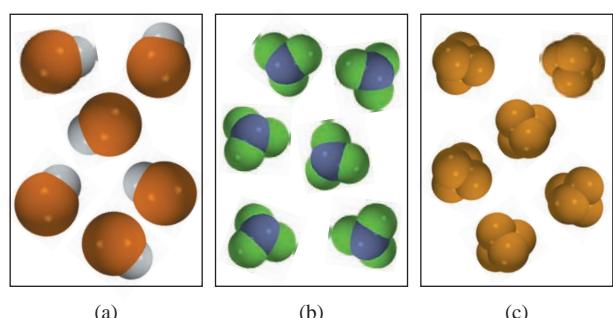
- 2.25 What is the difference between an atom and a molecule?
- 2.26 What are allotropes? Give an example. How are allotropes different from isotopes?
- 2.27 Describe the two commonly used molecular models.
- 2.28 Give an example of each of the following: (a) a monatomic cation, (b) a monatomic anion, (c) a polyatomic cation, (d) a polyatomic anion.

### Problems

- 2.29 Which of the following diagrams represent diatomic molecules, polyatomic molecules, molecules that are not compounds, molecules that are compounds, or an elemental form of the substance?



- 2.30** Which of the following diagrams represent diatomic molecules, polyatomic molecules, molecules that are not compounds, molecules that are compounds, or an elemental form of the substance?



- 2.31 Identify the following as elements or compounds:  $\text{NH}_3$ ,  $\text{N}_2$ ,  $\text{S}_8$ ,  $\text{NO}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{SO}_2$ .

- 2.32** Give two examples of each of the following: (a) a diatomic molecule containing atoms of the same element, (b) a diatomic molecule containing atoms of different elements, (c) a polyatomic molecule containing atoms of the same element, (d) a polyatomic molecule containing atoms of different elements.
- 2.33 Give the number of protons and electrons in each of the following common ions:  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{I}^-$ ,  $\text{F}^-$ ,  $\text{S}^{2-}$ ,  $\text{O}^{2-}$ ,  $\text{N}^{3-}$ .
- 2.34** Give the number of protons and electrons in each of the following common ions:  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Br}^-$ ,  $\text{Mn}^{2+}$ ,  $\text{C}^{4-}$ ,  $\text{Cu}^{2+}$ .

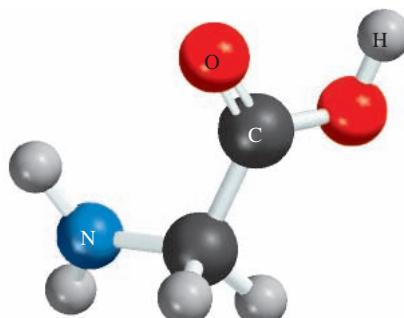
## Chemical Formulas

### Review Questions

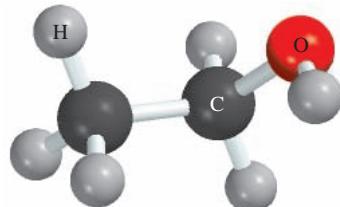
- 2.35 What does a chemical formula represent? What is the ratio of the atoms in the following molecular formulas? (a)  $\text{NO}$ , (b)  $\text{NCl}_3$ , (c)  $\text{N}_2\text{O}_4$ , (d)  $\text{P}_4\text{O}_6$
- 2.36 Define molecular formula and empirical formula. What are the similarities and differences between the empirical formula and molecular formula of a compound?
- 2.37 Give an example of a case in which two molecules have different molecular formulas but the same empirical formula.
- 2.38 What does  $\text{P}_4$  signify? How does it differ from  $4\text{P}$ ?
- 2.39 What is an ionic compound? How is electrical neutrality maintained in an ionic compound?
- 2.40 Explain why the chemical formulas of ionic compounds are usually the same as their empirical formulas.

### Problems

- 2.41 What are the empirical formulas of the following compounds? (a)  $\text{C}_2\text{N}_2$ , (b)  $\text{C}_6\text{H}_6$ , (c)  $\text{C}_9\text{H}_{20}$ , (d)  $\text{P}_4\text{O}_{10}$ , (e)  $\text{B}_2\text{H}_6$
- 2.42** What are the empirical formulas of the following compounds? (a)  $\text{Al}_2\text{Br}_6$ , (b)  $\text{Na}_2\text{S}_2\text{O}_4$ , (c)  $\text{N}_2\text{O}_5$ , (d)  $\text{K}_2\text{Cr}_2\text{O}_7$
- 2.43 Write the molecular formula of glycine, an amino acid present in proteins. The color codes are: black (carbon), blue (nitrogen), red (oxygen), and gray (hydrogen).



- 2.44** Write the molecular formula of ethanol. The color codes are: black (carbon), red (oxygen), and gray (hydrogen).



- 2.45 Which of the following compounds are likely to be ionic? Which are likely to be molecular?  $\text{SiCl}_4$ ,  $\text{LiF}$ ,  $\text{BaCl}_2$ ,  $\text{B}_2\text{H}_6$ ,  $\text{KCl}$ ,  $\text{C}_2\text{H}_4$
- 2.46** Which of the following compounds are likely to be ionic? Which are likely to be molecular?  $\text{CH}_4$ ,  $\text{NaBr}$ ,  $\text{BaF}_2$ ,  $\text{CCl}_4$ ,  $\text{ICl}$ ,  $\text{CsCl}$ ,  $\text{NF}_3$

## Naming Compounds

### Problems

- 2.47 Name these compounds: (a)  $\text{Na}_2\text{CrO}_4$ , (b)  $\text{K}_2\text{HPO}_4$ , (c)  $\text{HBr}$  (gas), (d)  $\text{HBr}$  (in water), (e)  $\text{Li}_2\text{CO}_3$ , (f)  $\text{K}_2\text{Cr}_2\text{O}_7$ , (g)  $\text{NH}_4\text{NO}_2$ , (h)  $\text{PF}_3$ , (i)  $\text{PF}_5$ , (j)  $\text{P}_4\text{O}_6$ , (k)  $\text{CdI}_2$ , (l)  $\text{SrSO}_4$ , (m)  $\text{Al}(\text{OH})_3$ , (n)  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ .
- 2.48** Name these compounds: (a)  $\text{KClO}$ , (b)  $\text{Ag}_2\text{CO}_3$ , (c)  $\text{FeCl}_2$ , (d)  $\text{KMnO}_4$ , (e)  $\text{CsClO}_3$ , (f)  $\text{HIO}$ , (g)  $\text{FeO}$ , (h)  $\text{Fe}_2\text{O}_3$ , (i)  $\text{TiCl}_4$ , (j)  $\text{NaH}$ , (k)  $\text{Li}_3\text{N}$ , (l)  $\text{Na}_2\text{O}$ , (m)  $\text{Na}_2\text{O}_2$ , (n)  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ .
- 2.49 Write the formulas for these compounds: (a) rubidium nitrite, (b) potassium sulfide, (c) perbromic acid, (d) magnesium phosphate, (e) calcium hydrogen phosphate, (f) boron trichloride, (g) iodine heptafluoride, (h) ammonium sulfate, (i) silver perchlorate, (j) iron(III) chromate, (k) calcium sulfate dihydrate.
- 2.50** Write the formulas for these compounds: (a) copper(I) cyanide, (b) strontium chlorite, (c) perchloric acid, (d) hydroiodic acid, (e) disodium ammonium phosphate, (f) lead(II) carbonate, (g) tin(II) fluoride, (h) tetraphosphorus decasulfide, (i) mercury(II) oxide, (j) mercury(I) iodide, (k) cobalt(II) chloride hexahydrate.

## Additional Problems

- 2.51 One isotope of a metallic element has a mass number of 65 and has 35 neutrons in the nucleus. The cation derived from the isotope has 28 electrons. Write the symbol for this cation.
- 2.52** In which one of these pairs do the two species resemble each other most closely in chemical properties? (a)  ${}^1\text{H}$  and  ${}^1\text{H}^+$ , (b)  ${}^{14}\text{N}$  and  ${}^{14}\text{N}^{3-}$ , (c)  ${}^{12}\text{C}$  and  ${}^{13}\text{C}$ .
- 2.53 This table gives numbers of electrons, protons, and neutrons in atoms or ions of a number of elements.

(a) Which of the species are neutral? (b) Which are negatively charged? (c) Which are positively charged? (d) What are the conventional symbols for all the species?

Atom or Ion of Element	A	B	C	D	E	F	G
Number of electrons	5	10	18	28	36	5	9
Number of protons	5	7	19	30	35	5	9
Number of neutrons	5	7	20	36	46	6	10

**2.54** What is wrong or ambiguous about these descriptions?  
(a) 1 g of hydrogen, (b) four molecules of NaCl.

**2.55** These phosphorus sulfides are known:  $P_4S_3$ ,  $P_4S_7$ , and  $P_4S_{10}$ . Do these compounds obey the law of multiple proportions?

**2.56** Which of these are elements, which are molecules but not compounds, which are compounds but not molecules, and which are both compounds and molecules? (a)  $SO_2$ , (b)  $S_8$ , (c) Cs, (d)  $N_2O_5$ , (e) O, (f)  $O_2$ , (g)  $O_3$ , (h)  $CH_4$ , (i) KBr, (j) S, (k)  $P_4$ , (l) LiF.

**2.57** Why is magnesium chloride ( $MgCl_2$ ) not called magnesium(II) chloride?

**2.58** Some compounds are better known by their common names than by their systematic chemical names. Consult a handbook, a dictionary, or your instructor for the chemical formulas of these substances: (a) dry ice, (b) table salt, (c) laughing gas, (d) marble (chalk, limestone), (e) quicklime, (f) slaked lime, (g) baking soda, (h) milk of magnesia.

**2.59** Fill in the blanks in this table:

Symbol		$^{54}_{26}Fe^{2+}$			
Protons	5			79	86
Neutrons	6		16	117	136
Electrons	5		18	79	
Net charge			-3		0

**2.60** (a) Which elements are most likely to form ionic compounds? (b) Which metallic elements are most likely to form cations with different charges?

**2.61** Many ionic compounds contain either aluminum (a Group 3A metal) or a metal from Group 1A or Group 2A and a nonmetal—oxygen, nitrogen, or a halogen (Group 7A). Write the chemical formulas and names of all the binary compounds that can result from such combinations.

**2.62** Which of these symbols provides more information about the atom:  $^{23}Na$  or  $_{11}Na$ ? Explain.

**2.63** Write the chemical formulas and names of acids that contain Group 7A elements. Do the same for elements in Groups 3A, 4A, 5A, and 6A.

**2.64** Of the 114-elements known, only two are liquids at room temperature (25°C). What are they? (Hint: One element is a familiar metal and the other element is in Group 7A.)

**2.65** Group the following elements in pairs that you would expect to show similar chemical properties: K, F, P, Na, Cl, and N.

**2.66** List the elements that exist as gases at room temperature. (Hint: All except one element can be found in Groups 5A, 6A, 7A, and 8A.)

**2.67** The Group 1B metals, Cu, Ag, and Au, are called coinage metals. What chemical properties make them specially suitable for making coins and jewels?

**2.68** The elements in Group 8A of the periodic table are called noble gases. Can you guess the meaning of “noble” in this context?

**2.69** The formula for calcium oxide is CaO. What are the formulas for magnesium oxide and strontium oxide?

**2.70** A common mineral of barium is barytes, or barium sulfate ( $BaSO_4$ ). Because elements in the same periodic group have similar chemical properties, we might expect to find some radium sulfate ( $RaSO_4$ ) mixed with barytes because radium is the last member of Group 2A. However, the only source of radium compounds in nature is in uranium minerals. Why?

**2.71** Fluorine reacts with hydrogen (H) and with deuterium (D) to form hydrogen fluoride (HF) and deuterium fluoride (DF) [deuterium ( $^2H$ ) is an isotope of hydrogen]. Would a given amount of fluorine react with different masses of the two hydrogen isotopes? Does this violate the law of definite proportions? Explain.

**2.72** Predict the formula and name of a binary compound formed from these elements: (a) Na and H, (b) B and O, (c) Na and S, (d) Al and F, (e) F and O, (f) Sr and Cl.

**2.73** Fill the blanks in the following table.

Cation	Anion	Formula	Name
			Magnesium bicarbonate
		$SrCl_2$	
$Fe^{3+}$	$NO_2^-$		
			Manganese(II) chlorate
		$SnBr_4$	
$Co^{2+}$	$PO_4^{3-}$		
$Hg_2^{2+}$	$I^-$		
		$Cu_2CO_3$	
			Lithium nitride
$Al^{3+}$	$S^{2-}$		

**2.74** Identify each of the following elements: (a) a halogen whose anion contains 36 electrons, (b) a radioactive noble gas with 86 protons, (c) a Group 6A

element whose anion contains 36 electrons, (d) an alkali metal cation that contains 36 electrons, (e) a Group 4A cation that contains 80 electrons.

## SPECIAL PROBLEM

**2.75** (a) Describe Rutherford's experiment and how it led to the structure of the atom. How was he able to estimate the number of protons in a nucleus from the scattering of the  $\alpha$  particles? (b) Consider the  $^{23}\text{Na}$  atom. Given that the radius and mass of the nucleus are  $3.04 \times 10^{-15}$  m and  $3.82 \times 10^{-23}$  g, respectively, calculate the density of the nucleus in g/cm<sup>3</sup>. The radius of a  $^{23}\text{Na}$  atom is 186 pm. Calculate the density of the space occupied by the electrons in the sodium atom. Do your results support Rutherford's model of an atom? [The volume of a sphere is  $(4/3)\pi r^3$ , where  $r$  is the radius.]

**2.76** On p. 30 it was pointed out that mass and energy are alternate aspects of a single entity called *mass-energy*. The relationship between these two physical quantities is Einstein's famous equation,  $E = mc^2$ , where  $E$  is energy,  $m$  is mass, and  $c$  is the speed of light. In a combustion experiment, it was found that 12.096 g of hydrogen molecules combined with 96.000 g of oxygen molecules to form water and released  $1.715 \times 10^3$  kJ of heat. Calculate the corresponding mass change in this process and comment on whether the law of conservation of mass holds for ordinary chemical processes. (*Hint:* The Einstein equation can be used to calculate the change in mass

as a result of the change in energy.  $1\text{ J} = 1\text{ kg m}^2/\text{s}^2$  and  $c = 3.00 \times 10^8\text{ m/s.}$ )

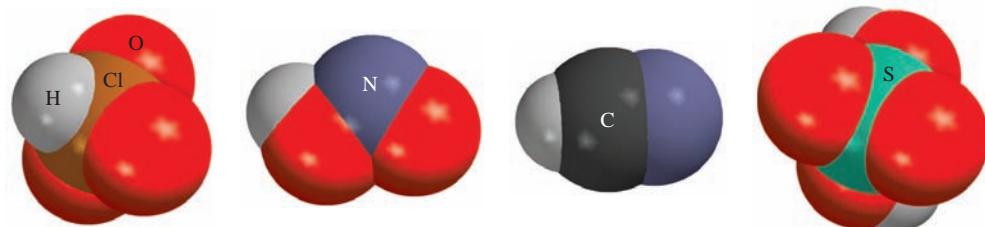
**2.77** Draw all possible structural formulas of the following hydrocarbons:  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$ , and  $\text{C}_5\text{H}_{12}$ .

**2.78** Ethane and acetylene are two gaseous hydrocarbons. Chemical analyses show that in one sample of ethane, 2.65 g of carbon are combined with 0.665 g of hydrogen, and in one sample of acetylene, 4.56 g of carbon are combined with 0.383 g of hydrogen. (a) Are these results consistent with the law of multiple proportions? (b) Write reasonable molecular formulas for these compounds.

**2.79** Draw two different structural formulas based on the molecular formula  $\text{C}_2\text{H}_6\text{O}$ . Is the fact that you can have more than one compound with the same molecular formula consistent with Dalton's atomic theory?

**2.80** A monatomic ion has a charge of +2. The nucleus of the parent atom has a mass number of 55. If the number of neutrons in the nucleus is 1.2 times that of the number of protons, what is the name and symbol of the element?

**2.81** Name the following acids:



## ANSWERS TO PRACTICE EXERCISES

**2.1** 29 protons, 34 neutrons, and 29 electrons. **2.2**  $\text{CHCl}_3$ .

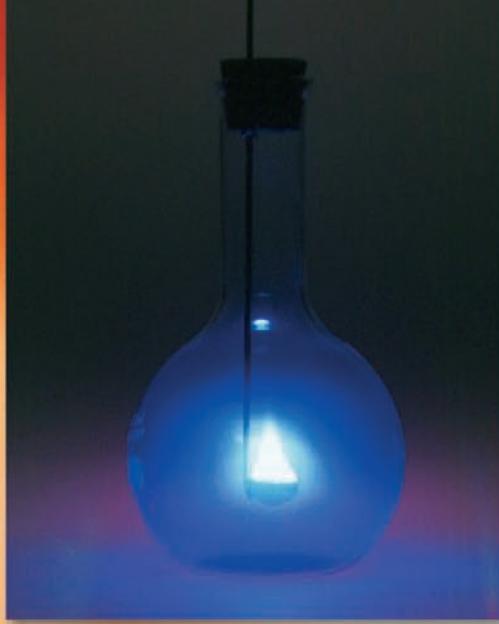
**2.3**  $\text{C}_4\text{H}_5\text{N}_2\text{O}$ . **2.4** (a) Lead(II) oxide, (b) lithium sulfite.

**2.5** (a)  $\text{Rb}_2\text{SO}_4$ , (b)  $\text{BaH}_2$ . **2.6** (a) Nitrogen trifluoride,

(b) dichlorine heptoxide. **2.7** (a)  $\text{SF}_4$ , (b)  $\text{N}_2\text{O}_5$ .

**2.8** (a) Hypobromous acid, (b) hydrogen sulfate ion.

# 3



Sulfur burning in oxygen to form sulfur dioxide. About 50 million tons of SO<sub>2</sub> are released to the atmosphere every year.

## Stoichiometry

### CHAPTER OUTLINE

- 3.1** Atomic Mass 59  
Average Atomic Mass
- 3.2** Avogadro's Number and the Molar Mass of an Element 60
- 3.3** Molecular Mass 64
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Determination of Molecular Formulas
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Writing Chemical Equations • Balancing Chemical Equations
- 3.8** Amounts of Reactants and Products 77
- 3.9** Limiting Reagents 81
- 3.10** Reaction Yield 83

### Interactive



### Activity Summary

- |  |   |
|--|---|
| 1. Interactivity: Molecular Mass (3.3)<br>2. Interactivity: Balance the Equation (3.7)<br>3. Interactivity: Balancing Chemical Equations (3.7) | 4. Interactivity: The Mole Method (3.8)<br>5. Animation: Limiting Reagent (3.9)<br>6. Interactivity: Limiting Reactant Game (3.9) |
|--|---|

### ESSENTIAL CONCEPTS

**Atomic Mass and Molar Mass** The mass of an atom, which is extremely small, is based on the carbon-12 isotope scale. An atom of the carbon-12 isotope is assigned a mass of exactly 12 atomic mass units (amu). To work with the more convenient scale of grams, chemists use the molar mass. The molar mass of carbon-12 is exactly 12 g and contains an Avogadro's number ( $6.022 \times 10^{23}$ ) of atoms. The molar masses of other elements are also expressed in grams and contain the same number of atoms. The molar mass of a molecule is the sum of the molar masses of its constituent atoms.

**Percent Composition of a Compound** The makeup of a compound is most conveniently expressed in terms of its percent composition, which is the percent by mass of each element the compound contains. A knowledge of its chemical formula enables us to calculate the percent composition. Experimental determination of percent composition and the molar mass of a compound enables us to determine its chemical formula.

**Writing Chemical Equations** An effective way to represent the outcome of a chemical reaction is to write a chemical equation, which uses chemical formulas to describe what happens. A chemical equation must be balanced so that we have the same number and type of atoms for the reactants, the starting materials, and the products, the substances formed at the end of the reaction.

**Mass Relationships of a Chemical Reaction** A chemical equation enables us to predict the amount of product(s) formed, called the yield, knowing how much reactant(s) was (were) used. This information is of great importance for reactions run on the laboratory or industrial scale. In practice, the actual yield is almost always less than that predicted from the equation because of various complications.

## 3.1 Atomic Mass

In this chapter we will use what we have learned about chemical structure and formulas in studying the mass relationships of atoms and molecules. These relationships in turn will help us to explain the composition of compounds and the ways in which composition changes.

The mass of an atom depends on the number of electrons, protons, and neutrons it contains. Knowledge of an atom's mass is important in laboratory work. But atoms are extremely small particles—even the smallest speck of dust that our unaided eyes can detect contains as many as  $1 \times 10^{16}$  atoms! Clearly we cannot weigh a single atom, but it is possible to determine the mass of one atom *relative* to another experimentally. The first step is to assign a value to the mass of one atom of a given element so that it can be used as a standard.

By international agreement, **atomic mass** (sometimes called *atomic weight*) is *the mass of the atom in atomic mass units (amu)*. One **atomic mass unit** is defined as *a mass exactly equal to one-twelfth the mass of one carbon-12 atom*. Carbon-12 is the carbon isotope that has six protons and six neutrons. Setting the atomic mass of carbon-12 at 12 amu provides the standard for measuring the atomic mass of the other elements. For example, experiments have shown that, on average, a hydrogen atom is only 8.400 percent as massive as the carbon-12 atom. Thus, if the mass of one carbon-12 atom is exactly 12 amu, the atomic mass of hydrogen must be  $0.084 \times 12.00$  amu or 1.008 amu. Similar calculations show that the atomic mass of oxygen is 16.00 amu and that of iron is 55.85 amu. Thus, although we do not know just how much an average iron atom's mass is, we know that it is approximately 56 times as massive as a hydrogen atom.

**Section 3.4 describes a method for determining atomic mass.**

**One atomic mass unit is also called one dalton.**

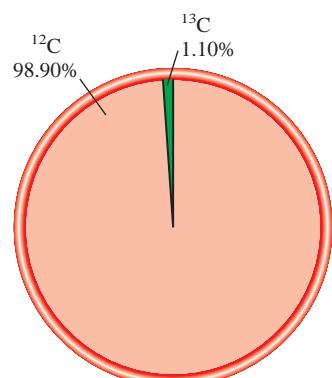
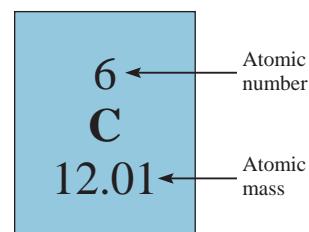
### Average Atomic Mass

When you look up the atomic mass of carbon in a table such as the one on the inside front cover of this book, you will find that its value is not 12.00 amu but 12.01 amu. The reason for the difference is that most naturally occurring elements (including carbon) have more than one isotope. This means that when we measure the atomic mass of an element, we must generally settle for the *average* mass of the naturally occurring mixture of isotopes. For example, the natural abundances of carbon-12 and carbon-13 are 98.90 percent and 1.10 percent, respectively. The atomic mass of carbon-13 has been determined to be 13.00335 amu. Thus, the average atomic mass of carbon can be calculated as follows:

$$\begin{aligned} \text{average atomic mass} \\ \text{of natural carbon} &= (0.9890)(12.00000 \text{ amu}) + (0.0110)(13.00335 \text{ amu}) \\ &= 12.01 \text{ amu} \end{aligned}$$

Note that in calculations involving percentages, we need to convert percentages to fractions. For example, 98.90 percent becomes  $98.90/100$ , or 0.9890. Because there are many more carbon-12 atoms than carbon-13 atoms in naturally occurring carbon, the average atomic mass is much closer to 12 amu than to 13 amu.

It is important to understand that when we say that the atomic mass of carbon is 12.01 amu, we are referring to the *average* value. If carbon atoms could be examined individually, we would find either an atom of atomic mass 12.00000 amu or one of 13.00335 amu, but never one of 12.01 amu.



Natural abundances of C-12 and C-13 isotopes.



Copper.

**Similar problems:** 3.5, 3.6.

### Example 3.1

Copper, a metal known since ancient times, is used in electrical cables and pennies, among other things. The atomic masses of its two stable isotopes,  $^{63}\text{Cu}$  (69.09 percent) and  $^{65}\text{Cu}$  (30.91 percent), are 62.93 amu and 64.9278 amu, respectively. Calculate the average atomic mass of copper. The relative abundances are given in parentheses.

**Strategy** Each isotope contributes to the average atomic mass based on its relative abundance. Multiplying the mass of an isotope by its fractional abundance (not percent) will give the contribution to the average atomic mass of that particular isotope.

**Solution** First the percents are converted to fractions: 69.09 percent to 69.09/100 or 0.6909 and 30.91 percent to 30.91/100 or 0.3091. We find the contribution to the average atomic mass for each isotope, then add the contributions together to obtain the average atomic mass.

$$(0.6909)(62.93 \text{ amu}) + (0.3091)(64.9278 \text{ amu}) = 63.55 \text{ amu}$$

**Check** The average atomic mass should be between the two isotopic masses; therefore, the answer is reasonable. Note that because there are more  $^{63}\text{Cu}$  than  $^{65}\text{Cu}$  isotopes, the average atomic mass is closer to 62.93 amu than to 64.9278 amu.

**Practice Exercise** The atomic masses of the two stable isotopes of boron,  $^{10}\text{B}$  (19.78 percent) and  $^{11}\text{B}$  (80.22 percent), are 10.0129 amu and 11.0093 amu, respectively. Calculate the average atomic mass of boron.

The atomic masses of many elements have been accurately determined to five or six significant figures. However, for our purposes we will normally use atomic masses accurate only to four significant figures (see table of atomic masses inside the front cover). For simplicity, we will omit the word “average” when we discuss the atomic masses of the elements.

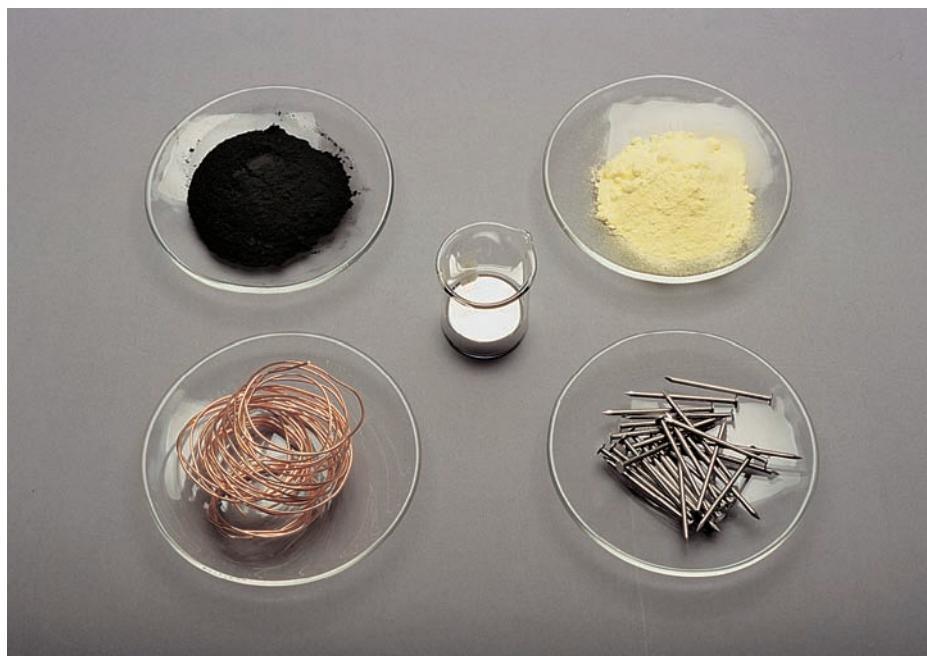
## 3.2 Avogadro’s Number and the Molar Mass of an Element

Atomic mass units provide a relative scale for the masses of the elements. But because atoms have such small masses, no usable scale can be devised to weigh them in calibrated units of atomic mass units. In any real situation, we deal with macroscopic samples containing enormous numbers of atoms. Therefore, it is convenient to have a special unit to describe a very large number of atoms. The idea of a unit to denote a particular number of objects is not new. For example, the pair (2 items), the dozen (12 items), and the gross (144 items) are all familiar units. Chemists measure atoms and molecules in moles.

In the SI system the **mole (mol)** is *the amount of a substance that contains as many elementary entities (atoms, molecules, or other particles) as there are atoms in exactly 12 g (or 0.012 kg) of the carbon-12 isotope*. The actual number of atoms in 12 g of carbon-12 is determined experimentally. This number is called **Avogadro’s number ( $N_A$ )**, in honor of the Italian scientist Amedeo Avogadro. The currently accepted value is

$$N_A = 6.0221415 \times 10^{23}$$

**The adjective formed from the noun “mole” is “molar.”**



**Figure 3.1**  
One mole each of several common elements. Carbon (black charcoal powder), sulfur (yellow powder), iron (as nails), copper (wires), and mercury (shiny liquid metal).

Generally, we round Avogadro's number to  $6.022 \times 10^{23}$ . Thus, just as one dozen oranges contains 12 oranges, 1 mole of hydrogen atoms contains  $6.022 \times 10^{23}$  H atoms. Figure 3.1 shows samples containing 1 mole each of several common elements.

The enormity of Avogadro's number is difficult to imagine. For example, spreading  $6.022 \times 10^{23}$  oranges over the entire surface of Earth would produce a layer 9 mi into space! Because atoms (and molecules) are so tiny, we need a huge number to study them in manageable quantities.

We have seen that 1 mole of carbon-12 atoms has a mass of exactly 12 g and contains  $6.022 \times 10^{23}$  atoms. This mass of carbon-12 is its **molar mass** ( $M$ ), defined as *the mass (in grams or kilograms) of 1 mole of units* (such as atoms or molecules) of a substance. Note that the molar mass of carbon-12 (in grams) is numerically equal to its atomic mass in amu. Likewise, the atomic mass of sodium (Na) is 22.99 amu and its molar mass is 22.99 g; the atomic mass of phosphorus is 30.97 amu and its molar mass is 30.97 g; and so on. If we know the atomic mass of an element, we also know its molar mass.

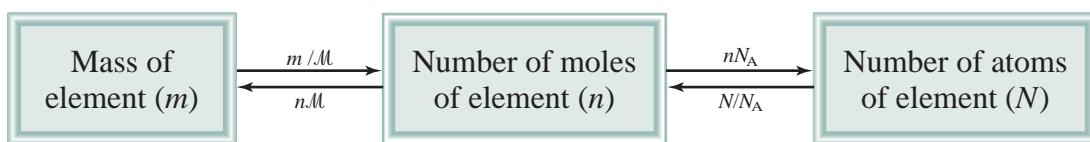
In calculations, the units of molar mass are g/mol or kg/mol.

Knowing the molar mass and Avogadro's number, we can calculate the mass of a single atom in grams. For example, we know the molar mass of carbon-12 is 12.00 g and there are  $6.022 \times 10^{23}$  carbon-12 atoms in 1 mole of the substance; therefore, the mass of one carbon-12 atom is given by

$$\frac{12.00 \text{ g carbon-12 atoms}}{6.022 \times 10^{23} \text{ carbon-12 atoms}} = 1.993 \times 10^{-23} \text{ g}$$

We can use the preceding result to determine the relationship between atomic mass units and grams. Because the mass of every carbon-12 atom is exactly 12 amu, the number of atomic mass units equivalent to 1 gram is

$$\begin{aligned} \frac{\text{amu}}{\text{gram}} &= \frac{12 \text{ amu}}{1 \text{ carbon-12 atom}} \times \frac{1 \text{ carbon-12 atom}}{1.993 \times 10^{-23} \text{ g}} \\ &= 6.022 \times 10^{23} \text{ amu/g} \end{aligned}$$

**Figure 3.2**

The relationships between mass ( $m$  in grams) of an element and number of moles of an element ( $n$ ) and between number of moles of an element and number of atoms ( $N$ ) of an element.  $M$  is the molar mass (g/mol) of the element and  $N_A$  is Avogadro's number.

Thus,

$$1 \text{ g} = 6.022 \times 10^{23} \text{ amu}$$

and

$$1 \text{ amu} = 1.661 \times 10^{-24} \text{ g}$$

This example shows that Avogadro's number can be used to convert from the atomic mass units to mass in grams and vice versa.

The notions of Avogadro's number and molar mass enable us to carry out conversions between mass and moles of atoms and between moles and number of atoms (Figure 3.2). We will employ the following conversion factors in the calculations:

$$\frac{1 \text{ mol X}}{\text{molar mass of X}} \quad \text{and} \quad \frac{1 \text{ mol X}}{6.022 \times 10^{23} \text{ X atoms}}$$

where X represents the symbol of an element. Using the proper conversion factors we can convert one quantity to another, as Examples 3.2–3.4 show.



Zinc.

### Example 3.2

Zinc (Zn) is a silvery metal that is used in making brass (with copper) and in plating iron to prevent corrosion. How many moles of Zn are there in 23.3 g of Zn?

**Strategy** We are trying to solve for moles of Zn. What conversion factor do we need to convert between grams and moles? Arrange the appropriate conversion factor so that grams cancel and the unit mol is obtained for your answer.

**Solution** The conversion factor needed to convert between grams and moles is the molar mass. In the periodic table (see inside front cover) we see that the molar mass of Zn is 65.39 g. This can be expressed as

$$1 \text{ mol Zn} = 65.39 \text{ g Zn}$$

From this equality, we can write the two conversion factors

$$\frac{1 \text{ mol Zn}}{65.39 \text{ g Zn}} \quad \text{and} \quad \frac{65.39 \text{ g Zn}}{1 \text{ mol Zn}}$$

The conversion factor on the left is the correct one. Grams will cancel, leaving unit of mol for the answer. The number of moles of Zn is

$$23.3 \text{ g Zn} \times \frac{1 \text{ mol Zn}}{65.39 \text{ g Zn}} = 0.356 \text{ mol Zn}$$

(Continued)

Thus, there is 0.356 mole of Zn in 23.3 g of Zn.

**Check** Because 23.3 g is less than the molar mass of Zn, we expect the result to be less than 1 mole.

**Practice Exercise** Calculate the number of grams of lead (Pb) in 12.4 moles of lead.

**Similar problem:** 3.15.

### Example 3.3

Sulfur (S) is a nonmetallic element that is present in coal. When coal is burned, sulfur is converted to sulfur dioxide and eventually to sulfuric acid that gives rise to the acid rain phenomenon. How many atoms are in 16.3 g of S?

**Strategy** The question asks for atoms of sulfur. We cannot convert directly from grams to atoms of sulfur. What unit do we need to convert grams of sulfur to in order to convert to atoms? What does Avogadro's number represent?

**Solution** We need two conversions: first from grams to moles and then from moles to number of particles (atoms). The first step is similar to Example 3.2. Because

$$1 \text{ mol S} = 32.07 \text{ g S}$$

the conversion factor is

$$\frac{1 \text{ mol S}}{32.07 \text{ g S}}$$

Avogadro's number is the key to the second step. We have

$$1 \text{ mol} = 6.022 \times 10^{23} \text{ particles (atoms)}$$

and the conversion factors are

$$\frac{6.022 \times 10^{23} \text{ S atoms}}{1 \text{ mol S}} \quad \text{and} \quad \frac{1 \text{ mol S}}{6.022 \times 10^{23} \text{ S atoms}}$$

The conversion factor on the left is the one we need because it has the number of S atoms in the numerator. We can solve the problem by first calculating the number of moles contained in 16.3 g of S, and then calculating the number of S atoms from the number of moles of S:



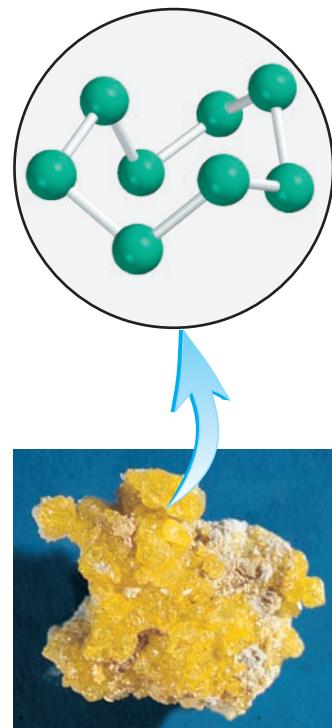
We can combine these conversions in one step as follows:

$$16.3 \text{ g S} \times \frac{1 \text{ mol S}}{32.07 \text{ g S}} \times \frac{6.022 \times 10^{23} \text{ S atoms}}{1 \text{ mol S}} = 3.06 \times 10^{23} \text{ S atoms}$$

Thus, there are  $3.06 \times 10^{23}$  atoms of S in 16.3 g of S.

**Check** Should 16.3 g of S contain fewer than Avogadro's number of atoms? What mass of S would contain Avogadro's number of atoms?

**Practice Exercise** Calculate the number of atoms in 0.551 g of potassium (K).



Elemental sulfur ( $\text{S}_8$ ) consists of eight S atoms joined in a ring.

**Similar problems:** 3.20, 3.21.



Silver.

**Similar problem:** 3.17.



**Interactivity:**  
Molecular Mass  
ARIS, Interactives

### Example 3.4

Silver (Ag) is a precious metal used mainly in jewelry. What is the mass (in grams) of one Ag atom?

**Strategy** The question asks for the mass of one Ag atom. How many Ag atoms are in 1 mole of Ag and what is the molar mass of Ag?

**Solution** Because 1 mole of Ag atom contains  $6.022 \times 10^{23}$  Ag atoms and weighs 107.9 g, we can calculate the mass of one Ag atom as follows:

$$1 \text{ Ag atom} \times \frac{1 \text{ mol Ag}}{6.022 \times 10^{23} \text{ Ag atoms}} \times \frac{107.9 \text{ g}}{1 \text{ mol Ag}} = 1.792 \times 10^{-22} \text{ g}$$

**Practice Exercise** What is the mass (in grams) of one iodine (I) atom?

### 3.3 Molecular Mass

If we know the atomic masses of the component atoms, we can calculate the mass of a molecule. The **molecular mass** (sometimes called *molecular weight*) is *the sum of the atomic masses (in amu) in the molecule*. For example, the molecular mass of H<sub>2</sub>O is

$$2(\text{atomic mass of H}) + \text{atomic mass of O}$$

$$\text{or} \quad 2(1.008 \text{ amu}) + 16.00 \text{ amu} = 18.02 \text{ amu}$$

In general, we need to multiply the atomic mass of each element by the number of atoms of that element present in the molecule and sum over all the elements.



### Example 3.5

Calculate the molecular masses (in amu) of the following compounds: (a) sulfur dioxide (SO<sub>2</sub>) and (b) caffeine (C<sub>8</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub>)

**Strategy** How do atomic masses of different elements combine to give the molecular mass of a compound?

**Solution** To calculate molecular mass, we need to sum all the atomic masses in the molecule. For each element, we multiply the atomic mass of the element by the number of atoms of that element in the molecule. We find atomic masses in the periodic table (inside front cover).

(a) There are two O atoms and one S atom in SO<sub>2</sub>, so that

$$\begin{aligned} \text{molecular mass of SO}_2 &= 32.07 \text{ amu} + 2(16.00 \text{ amu}) \\ &= 64.07 \text{ amu} \end{aligned}$$

(b) There are eight C atoms, ten H atoms, four N atoms, and two O atoms in caffeine, so the molecular mass of C<sub>8</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub> is given by

$$8(12.01 \text{ amu}) + 10(1.008 \text{ amu}) + 4(14.01 \text{ amu}) + 2(16.00 \text{ amu}) = 194.20 \text{ amu}$$

**Similar problems:** 3.23, 3.24.

**Practice Exercise** What is the molecular mass of methanol (CH<sub>4</sub>O)?

From the molecular mass we can determine the molar mass of a molecule or compound. The molar mass of a compound (in grams) is numerically equal to its molecular mass (in amu). For example, the molecular mass of water is 18.02 amu, so its molar mass is 18.02 g. Note that 1 mole of water weighs 18.02 g and contains  $6.022 \times 10^{23}$  H<sub>2</sub>O molecules, just as 1 mole of elemental carbon contains  $6.022 \times 10^{23}$  carbon atoms.

As Examples 3.6 and 3.7 show, a knowledge of the molar mass enables us to calculate the numbers of moles and individual atoms in a given quantity of a compound.

### Example 3.6

Methane (CH<sub>4</sub>) is the principal component of natural gas. How many moles of CH<sub>4</sub> are present in 6.07 g of CH<sub>4</sub>?

**Strategy** We are given grams of CH<sub>4</sub> and asked to solve for moles of CH<sub>4</sub>. What conversion factor do we need to convert between grams and moles? Arrange the appropriate conversion factor so that grams cancel and the unit moles are obtained for your answer.

**Solution** The conversion factor needed to convert between grams and moles is the molar mass. First we need to calculate the molar mass of CH<sub>4</sub>, following the procedure in Example 3.5:

$$\begin{aligned}\text{molar mass of CH}_4 &= 12.01 \text{ g} + 4(1.008 \text{ g}) \\ &= 16.04 \text{ g}\end{aligned}$$

Because

$$1 \text{ mol CH}_4 = 16.04 \text{ g CH}_4$$

the conversion factor we need should have grams in the denominator so that the unit g will cancel, leaving the unit mol in the numerator:

$$\frac{1 \text{ mol CH}_4}{16.04 \text{ g CH}_4}$$

We now write

$$6.07 \text{ g CH}_4 \times \frac{1 \text{ mol CH}_4}{16.04 \text{ g CH}_4} = 0.378 \text{ mol CH}_4$$

Thus, there is 0.378 mole of CH<sub>4</sub> in 6.07 g of CH<sub>4</sub>.

**Check** Should 6.07 g of CH<sub>4</sub> equal less than 1 mole of CH<sub>4</sub>? What is the mass of 1 mole of CH<sub>4</sub>?

**Practice Exercise** Calculate the number of moles of chloroform (CHCl<sub>3</sub>) in 198 g of chloroform.



Methane gas burning on a cooking range.



Urea.

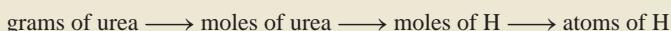
### Example 3.7

How many hydrogen atoms are present in 25.6 g of urea [(NH<sub>2</sub>)<sub>2</sub>CO], which is used as a fertilizer, in animal feed, and in the manufacture of polymers? The molar mass of urea is 60.06 g.

**Strategy** We are asked to solve for atoms of hydrogen in 25.6 g of urea. We cannot convert directly from grams of urea to atoms of hydrogen. How should molar mass and Avogadro's number be used in this calculation? How many moles of H are in 1 mole of urea?

(Continued)

**Solution** To calculate number of H atoms, we first must convert grams of urea to moles of urea using the molar mass of urea. This part is similar to Example 3.2. The molecular formula of urea shows there are four moles of H atoms in one mole of urea molecule, so the mole ratio is 4:1. Finally, knowing the number of moles of H atoms, we can calculate the number of H atoms using Avogadro's number. We need two conversion factors: molar mass and Avogadro's number. We can combine these conversions



into one step:

$$25.6 \cancel{\text{g} (\text{NH}_2)_2\text{CO}} \times \frac{1 \text{ mol} (\text{NH}_2)_2\text{CO}}{60.06 \cancel{\text{g} (\text{NH}_2)_2\text{CO}}} \times \frac{4 \text{ mol H}}{1 \text{ mol} (\text{NH}_2)_2\text{CO}} \times \frac{6.022 \times 10^{23} \text{ H atoms}}{1 \text{ mol H}} \\ = 1.03 \times 10^{24} \text{ H atoms}$$

**Check** Does the answer look reasonable? How many atoms of H would 60.06 g of urea contain?

Similar problems: 3.27, 3.28.

**Practice Exercise** How many H atoms are in 72.5 g of isopropanol (rubbing alcohol), C<sub>3</sub>H<sub>8</sub>O?

For molecules, formula mass and molecular mass refer to the same quantity.

Finally, note that for ionic compounds like NaCl and MgO that do not contain discrete molecular units, we use the term *formula mass* instead. The formula unit of NaCl consists of one Na<sup>+</sup> ion and one Cl<sup>-</sup> ion. Thus, the formula mass of NaCl is the mass of one formula unit:

$$\begin{aligned} \text{formula mass of NaCl} &= 22.99 \text{ amu} + 35.45 \text{ amu} \\ &= 58.44 \text{ amu} \end{aligned}$$

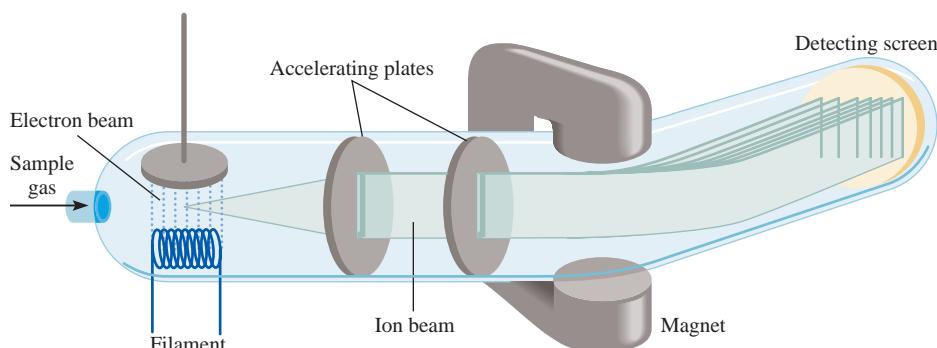
and its molar mass is 58.44 g.

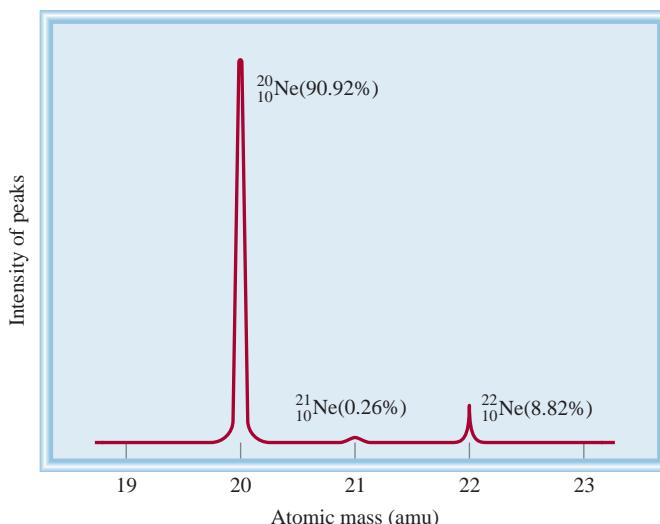
### 3.4 The Mass Spectrometer

The most direct and most accurate method for determining atomic and molecular masses is mass spectrometry, which is depicted in Figure 3.3. In a *mass spectrometer*, a gaseous sample is bombarded by a stream of high-energy electrons. Collisions

**Figure 3.3**

Schematic diagram of one type of mass spectrometer.





**Figure 3.4**  
The mass spectrum of the three isotopes of neon.

between the electrons and the gaseous atoms (or molecules) produce positive ions by dislodging an electron from each atom or molecule. These positive ions (of mass  $m$  and charge  $e$ ) are accelerated by two oppositely charged plates as they pass through the plates. The emerging ions are deflected into a circular path by a magnet. The radius of the path depends on the charge-to-mass ratio (that is,  $e/m$ ). Ions of smaller  $e/m$  ratio trace a wider curve than those having a larger  $e/m$  ratio, so that ions with equal charges but different masses are separated from one another. The mass of each ion (and hence its parent atom or molecule) is determined from the magnitude of its deflection. Eventually the ions arrive at the detector, which registers a current for each type of ion. The amount of current generated is directly proportional to the number of ions, so it enables us to determine the relative abundance of isotopes.

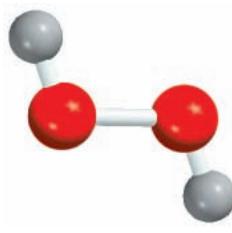
The first mass spectrometer, developed in the 1920s by the English physicist F. W. Aston, was crude by today's standards. Nevertheless, it provided indisputable evidence of the existence of isotopes—neon-20 (atomic mass 19.9924 amu and natural abundance 90.92 percent) and neon-22 (atomic mass 21.9914 amu and natural abundance 8.82 percent). When more sophisticated and sensitive mass spectrometers became available, scientists were surprised to discover that neon has a third stable isotope with an atomic mass of 20.9940 amu and natural abundance 0.257 percent (Figure 3.4). This example illustrates how very important experimental accuracy is to a quantitative science like chemistry. Early experiments failed to detect neon-21 because its natural abundance is just 0.257 percent. In other words, only 26 in 10,000 Ne atoms are neon-21. The masses of molecules can be determined in a similar manner by the mass spectrometer.

### 3.5 Percent Composition of Compounds

As we have seen, the formula of a compound tells us the numbers of atoms of each element in a unit of the compound. However, suppose we needed to verify the purity of a compound for use in a laboratory experiment. We could calculate what percent of the total mass of the compound is contributed by each element from the formula. Then, by comparing the result to the percent composition obtained experimentally for our sample, we could determine the purity of the sample.

The **percent composition** is the *percent by mass of each element in a compound*. Percent composition is obtained by dividing the mass of each element in 1 mole of the compound by the molar mass of the compound and multiplying by 100 percent. Mathematically, the percent composition of an element in a compound is expressed as

$$\text{percent composition of an element} = \frac{n \times \text{molar mass of element}}{\text{molar mass of compound}} \times 100\% \quad (3.1)$$

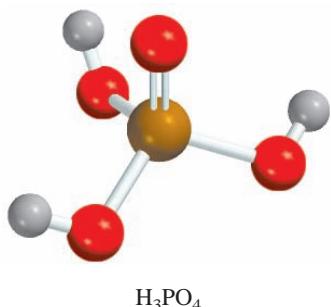


where  $n$  is the number of moles of the element in 1 mole of the compound. For example, in 1 mole of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) there are 2 moles of H atoms and 2 moles of O atoms. The molar masses of  $\text{H}_2\text{O}_2$ , H, and O are 34.02 g, 1.008 g, and 16.00 g, respectively. Therefore, the percent composition of  $\text{H}_2\text{O}_2$  is calculated as follows:

$$\% \text{H} = \frac{2 \times 1.008 \text{ g}}{34.02 \text{ g}} \times 100\% = 5.926\%$$

$$\% \text{O} = \frac{2 \times 16.00 \text{ g}}{34.02 \text{ g}} \times 100\% = 94.06\%$$

The sum of the percentages is 5.926 percent + 94.06 percent = 99.99 percent. The small discrepancy from 100 percent is due to the way we rounded off the molar masses of the elements. Note that the empirical formula (HO) would give us the same results.



### Example 3.8

Phosphoric acid ( $\text{H}_3\text{PO}_4$ ) is a colorless, syrupy liquid used in detergents, fertilizers, toothpastes, and in carbonated beverages for a “tangy” flavor. Calculate the percent composition by mass of H, P, and O in this compound.

**Strategy** Recall the procedure for calculating a percentage. Assume that we have 1 mole of  $\text{H}_3\text{PO}_4$ . The percent by mass of each element (H, P, and O) is given by the combined molar mass of the atoms of the element in 1 mole of  $\text{H}_3\text{PO}_4$  divided by the molar mass of  $\text{H}_3\text{PO}_4$ , then multiplied by 100 percent.

**Solution** The molar mass of  $\text{H}_3\text{PO}_4$  is 97.99 g. The percent by mass of each of the elements in  $\text{H}_3\text{PO}_4$  is calculated as follows:

$$\% \text{H} = \frac{3(1.008 \text{ g}) \text{ H}}{97.99 \text{ g } \text{H}_3\text{PO}_4} \times 100\% = 3.086\%$$

$$\% \text{P} = \frac{30.97 \text{ g } \text{P}}{97.99 \text{ g } \text{H}_3\text{PO}_4} \times 100\% = 31.61\%$$

$$\% \text{O} = \frac{4(16.00 \text{ g}) \text{ O}}{97.99 \text{ g } \text{H}_3\text{PO}_4} \times 100\% = 65.31\%$$

**Check** Do the percentages add to 100 percent? The sum of the percentages is  $(3.086\% + 31.61\% + 65.31\%) = 100.01\%$ . The small discrepancy from 100 percent is due to the way we rounded off.

**Similar problem:** 3.40.

**Practice Exercise** Calculate the percent composition by mass of each of the elements in sulfuric acid ( $\text{H}_2\text{SO}_4$ ).

The procedure used in Example 3.8 can be reversed if necessary. Given the percent composition by mass of a compound, we can determine the empirical formula of the compound (Figure 3.5). Because we are dealing with percentages and the sum of all the percentages is 100 percent, it is convenient to assume that we started with 100 g of a compound, as Example 3.9 shows.

### Example 3.9

Ascorbic acid (vitamin C) cures scurvy. It is composed of 40.92 percent carbon (C), 4.58 percent hydrogen (H), and 54.50 percent oxygen (O) by mass. Determine its empirical formula.

**Strategy** In a chemical formula, the subscripts represent the ratio of the number of moles of each element that combine to form one mole of the compound. How can we convert from mass percent to moles? If we assume an exactly 100-g sample of the compound, do we know the mass of each element in the compound? How do we then convert from grams to moles?

**Solution** If we have 100 g of ascorbic acid, then each percentage can be converted directly to grams. In this sample, there will be 40.92 g of C, 4.58 g of H, and 54.50 g of O. Because the subscripts in the formula represent a mole ratio, we need to convert the grams of each element to moles. The conversion factor needed is the molar mass of each element. Let  $n$  represent the number of moles of each element so that

$$\begin{aligned} n_C &= 40.92 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 3.407 \text{ mol C} \\ n_H &= 4.58 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 4.54 \text{ mol H} \\ n_O &= 54.50 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 3.406 \text{ mol O} \end{aligned}$$

Thus, we arrive at the formula  $\text{C}_{3.407}\text{H}_{4.54}\text{O}_{3.406}$ , which gives the identity and the mole ratios of atoms present. However, chemical formulas are written with whole numbers. Try to convert to whole numbers by dividing all the subscripts by the smallest subscript (3.406):

$$\text{C: } \frac{3.407}{3.406} \approx 1 \quad \text{H: } \frac{4.54}{3.406} = 1.33 \quad \text{O: } \frac{3.406}{3.406} = 1$$

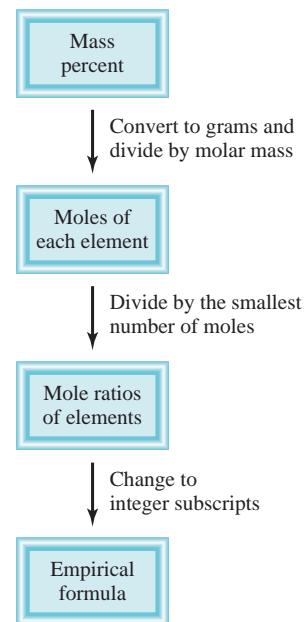
where the  $\approx$  sign means “approximately equal to.” This gives  $\text{CH}_{1.33}\text{O}$  as the formula for ascorbic acid. Next, we need to convert 1.33, the subscript for H, into an integer. This can be done by a trial-and-error procedure:

$$\begin{aligned} 1.33 \times 1 &= 1.33 \\ 1.33 \times 2 &= 2.66 \\ 1.33 \times 3 &= 3.99 \approx 4 \end{aligned}$$

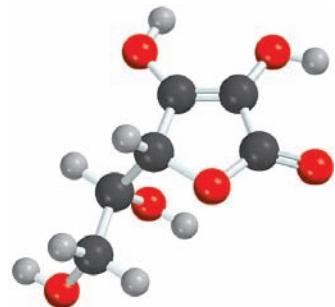
Because  $1.33 \times 3$  gives us an integer (4), we multiply all the subscripts by 3 and obtain  $\text{C}_3\text{H}_4\text{O}_3$  as the empirical formula for ascorbic acid.

**Check** Are the subscripts in  $\text{C}_3\text{H}_4\text{O}_3$  reduced to the smallest whole numbers?

**Practice Exercise** Determine the empirical formula of a compound having the following percent composition by mass: K: 24.75 percent; Mn: 34.77 percent; O: 40.51 percent.



**Figure 3.5**  
Procedure for calculating the empirical formula of a compound from its percent compositions.



The molecular formula of ascorbic acid is  $\text{C}_6\text{H}_8\text{O}_6$ .

Similar problems 3.49, 3.50.

Chemists often want to know the actual mass of an element in a certain mass of a compound. For example, in the mining industry, this information will tell the scientists about the quality of the ore. Because the percent composition by mass of the elements in the substance can be readily calculated, such a problem can be solved in a rather direct way.



Chalcopyrite.

### Example 3.10

Chalcopyrite ( $\text{CuFeS}_2$ ) is a principal mineral of copper. Calculate the number of kilograms of Cu in  $3.71 \times 10^3$  kg of chalcopyrite.

**Strategy** Chalcopyrite is composed of Cu, Fe, and S. The mass due to Cu is based on its percentage by mass in the compound. How do we calculate mass percent of an element?

**Solution** The molar masses of Cu and  $\text{CuFeS}_2$  are 63.55 g and 183.5 g, respectively. The mass percent of Cu is therefore

$$\begin{aligned}\% \text{ Cu} &= \frac{\text{molar mass of Cu}}{\text{molar mass of } \text{CuFeS}_2} \times 100\% \\ &= \frac{63.55 \text{ g}}{183.5 \text{ g}} \times 100\% = 34.63\%\end{aligned}$$

To calculate the mass of Cu in a  $3.71 \times 10^3$  kg sample of  $\text{CuFeS}_2$ , we need to convert the percentage to a fraction (that is, convert 34.63 percent to  $34.63/100$ , or 0.3463) and write

$$\text{mass of Cu in } \text{CuFeS}_2 = 0.3463 \times (3.71 \times 10^3 \text{ kg}) = 1.28 \times 10^3 \text{ kg}$$

We can also solve the problem by reading the formula as the ratio of moles of chalcopyrite to moles of copper using the following conversions:

grams of chalcopyrite  $\longrightarrow$  moles of chalcopyrite  $\longrightarrow$  moles of Cu  $\longrightarrow$  grams of Cu

Try it.

**Check** As a ballpark estimate, note that the mass percent of Cu is roughly 33 percent, so that a third of the mass should be Cu; that is,  $\frac{1}{3} \times 3.71 \times 10^3 \text{ kg} \approx 1.24 \times 10^3 \text{ kg}$ . This quantity is quite close to the answer.

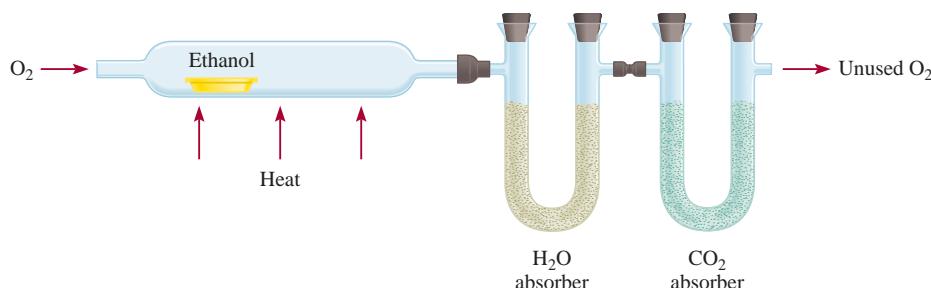
**Similar problem:** 3.45.

**Practice Exercise** Calculate the number of grams of Al in 371 g of  $\text{Al}_2\text{O}_3$ .

## 3.6 Experimental Determination of Empirical Formulas

The fact that we can determine the empirical formula of a compound if we know the percent composition enables us to identify compounds experimentally. The procedure is as follows. First, chemical analysis tells us the number of grams of each element present in a given amount of a compound. Then, we convert the quantities in grams to number of moles of each element. Finally, using the method given in Example 3.9, we find the empirical formula of the compound.

As a specific example, let us consider the compound ethanol. When ethanol is burned in an apparatus such as that shown in Figure 3.6, carbon dioxide ( $\text{CO}_2$ ) and water ( $\text{H}_2\text{O}$ ) are given off. Because neither carbon nor hydrogen was in the inlet gas,



**Figure 3.6**  
Apparatus for determining the empirical formula of ethanol. The absorbers are substances that can retain water and carbon dioxide, respectively.

we can conclude that both carbon (C) and hydrogen (H) were present in ethanol and that oxygen (O) may also be present. (Molecular oxygen was added in the combustion process, but some of the oxygen may also have come from the original ethanol sample.)

The masses of CO<sub>2</sub> and of H<sub>2</sub>O produced can be determined by measuring the increase in mass of the CO<sub>2</sub> and H<sub>2</sub>O absorbers, respectively. Suppose that in one experiment the combustion of 11.5 g of ethanol produced 22.0 g of CO<sub>2</sub> and 13.5 g of H<sub>2</sub>O. We can calculate the mass of carbon and hydrogen in the original 11.5-g sample of ethanol as follows:

$$\begin{aligned}\text{mass of C} &= 22.0 \cancel{\text{g CO}_2} \times \frac{1 \cancel{\text{mol CO}_2}}{44.01 \cancel{\text{g CO}_2}} \times \frac{1 \cancel{\text{mol C}}}{1 \cancel{\text{mol CO}_2}} \times \frac{12.01 \text{ g C}}{1 \cancel{\text{mol C}}} \\ &= 6.00 \text{ g C} \\ \text{mass of H} &= 13.5 \cancel{\text{g H}_2\text{O}} \times \frac{1 \cancel{\text{mol H}_2\text{O}}}{18.02 \cancel{\text{g H}_2\text{O}}} \times \frac{2 \cancel{\text{mol H}}}{1 \cancel{\text{mol H}_2\text{O}}} \times \frac{1.008 \text{ g H}}{1 \cancel{\text{mol H}}} \\ &= 1.51 \text{ g H}\end{aligned}$$

Thus, 11.5 g of ethanol contains 6.00 g of carbon and 1.51 g of hydrogen. The remainder must be oxygen, whose mass is

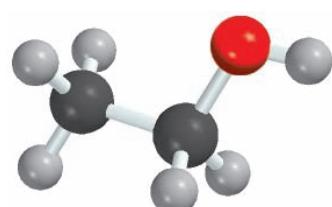
$$\begin{aligned}\text{mass of O} &= \text{mass of sample} - (\text{mass of C} + \text{mass of H}) \\ &= 11.5 \text{ g} - (6.00 \text{ g} + 1.51 \text{ g}) \\ &= 4.0 \text{ g}\end{aligned}$$

The number of moles of each element present in 11.5 g of ethanol is

$$\begin{aligned}\text{moles of C} &= 6.00 \cancel{\text{g C}} \times \frac{1 \text{ mol C}}{12.01 \cancel{\text{g C}}} = 0.500 \text{ mol C} \\ \text{moles of H} &= 1.51 \cancel{\text{g H}} \times \frac{1 \text{ mol H}}{1.008 \cancel{\text{g H}}} = 1.50 \text{ mol H} \\ \text{moles of O} &= 4.0 \cancel{\text{g O}} \times \frac{1 \text{ mol O}}{16.00 \cancel{\text{g O}}} = 0.25 \text{ mol O}\end{aligned}$$

The formula of ethanol is therefore C<sub>0.50</sub>H<sub>1.5</sub>O<sub>0.25</sub> (we round off the number of moles to two significant figures). Because the number of atoms must be an integer, we divide the subscripts by 0.25, the smallest subscript, and obtain for the empirical formula C<sub>2</sub>H<sub>6</sub>O.

Now we can better understand the word “empirical,” which literally means “based only on observation and measurement.” The empirical formula of ethanol is determined from analysis of the compound in terms of its component elements. No knowledge of how the atoms are linked together in the compound is required.



It happens that the molecular formula of ethanol is the same as its empirical formula.

## Determination of Molecular Formulas

Note that the molar mass of a compound can be determined experimentally even if we do not know its molecular formula.

The formula calculated from percent composition by mass is always the empirical formula because the subscripts in the formula are always reduced to the smallest whole numbers. To calculate the actual, molecular formula we must know the *approximate* molar mass of the compound in addition to its empirical formula. Knowing that the molar mass of a compound must be an integral multiple of the molar mass of its empirical formula, we can use the molar mass to find the molecular formula, as Example 3.11 demonstrates.

### Example 3.11

A sample of a compound contains 1.52 g of nitrogen (N) and 3.47 g of oxygen (O). The molar mass of this compound is between 90 g and 95 g. Determine the molecular formula and the accurate molar mass of the compound.

**Strategy** To determine the molecular formula, we first need to determine the empirical formula. How do we convert between grams and moles? Comparing the empirical molar mass to the experimentally determined molar mass will reveal the relationship between the empirical formula and molecular formula.

**Solution** We are given grams of N and O. Use molar mass as a conversion factor to convert grams to moles of each element. Let  $n$  represent the number of moles of each element. We write

$$n_N = \frac{1.52 \text{ g N}}{14.01 \text{ g N}} = 0.108 \text{ mol N}$$

$$n_O = \frac{3.47 \text{ g O}}{16.00 \text{ g O}} = 0.217 \text{ mol O}$$

Thus, we arrive at the formula  $\text{N}_{0.108}\text{O}_{0.217}$ , which gives the identity and the ratios of atoms present. However, chemical formulas are written with whole numbers. Try to convert to whole numbers by dividing the subscripts by the smaller subscript (0.108). After rounding off, we obtain  $\text{NO}_2$  as the empirical formula.

The molecular formula might be the same as the empirical formula or some integral multiple of it (for example, two, three, four, or more times the empirical formula). Comparing the ratio of the molar mass to the molar mass of the empirical formula will show the integral relationship between the empirical and molecular formulas. The molar mass of the empirical formula  $\text{NO}_2$  is

$$\text{empirical molar mass} = 14.01 \text{ g} + 2(16.00 \text{ g}) = 46.01 \text{ g}$$

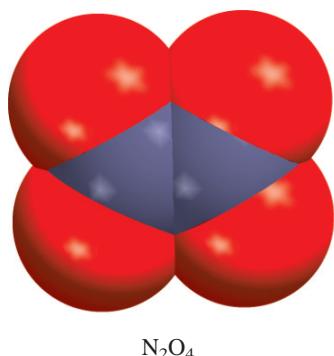
Next, we determine the ratio between the molar mass and the empirical molar mass

$$\frac{\text{molar mass}}{\text{empirical molar mass}} = \frac{90 \text{ g}}{46.01 \text{ g}} \approx 2$$

The molar mass is twice the empirical molar mass. This means that there are two  $\text{NO}_2$  units in each molecule of the compound, and the molecular formula is  $(\text{NO}_2)_2$  or  $\text{N}_2\text{O}_4$ .

The actual molar mass of the compound is two times the empirical molar mass, that is,  $2(46.01 \text{ g})$  or  $92.02 \text{ g}$ , which is between 90 g and 95 g.

**Check** Note that in determining the molecular formula from the empirical formula, we need only know the *approximate* molar mass of the compound. The reason is that the true molar mass is an integral multiple ( $1\times, 2\times, 3\times, \dots$ ) of the empirical molar mass. Therefore, the ratio (molar mass/empirical molar mass) will always be close to an integer.



Similar problems: 3.52, 3.53, 3.54.

(Continued)

**Practice Exercise** A sample of a compound containing boron (B) and hydrogen (H) contains 6.444 g of B and 1.803 g of H. The molar mass of the compound is about 30 g. What is its molecular formula?

## 3.7 Chemical Reactions and Chemical Equations

Having discussed the masses of atoms and molecules, we turn next to what happens to atoms and molecules in a *chemical reaction*, *a process in which a substance (or substances) is changed into one or more new substances*. To communicate with one another about chemical reactions, chemists have devised a standard way to represent them using chemical equations. A *chemical equation* uses chemical symbols to show *what happens during a chemical reaction*. In this section we will learn how to write chemical equations and balance them.

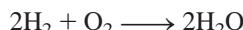
### Writing Chemical Equations

Consider what happens when hydrogen gas ( $\text{H}_2$ ) burns in air (which contains oxygen,  $\text{O}_2$ ) to form water ( $\text{H}_2\text{O}$ ). This reaction can be represented by the chemical equation



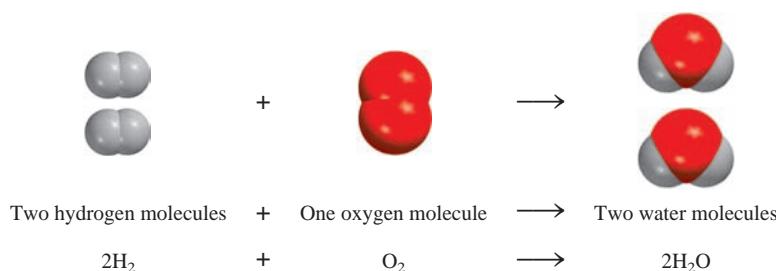
where the “plus” sign means “reacts with” and the arrow means “to yield.” Thus, this symbolic expression can be read: “Molecular hydrogen reacts with molecular oxygen to yield water.” The reaction is assumed to proceed from left to right as the arrow indicates.

Equation (3.2) is not complete, however, because there are twice as many oxygen atoms on the left side of the arrow (two) as on the right side (one). To conform with the law of conservation of mass, there must be the same number of each type of atom on both sides of the arrow; that is, we must have as many atoms after the reaction ends as we did before it started. We can *balance* Equation (3.2) by placing the appropriate coefficient (2 in this case) in front of  $\text{H}_2$  and  $\text{H}_2\text{O}$ :



When the coefficient is 1, as in the case of  $\text{O}_2$ , it is not shown.

This *balanced chemical equation* shows that “two hydrogen molecules can combine or react with one oxygen molecule to form two water molecules” (Figure 3.7). Because the ratio of the number of molecules is equal to the ratio of the number of moles, the equation can also be read as “2 moles of hydrogen molecules react with 1 mole of oxygen molecules to produce 2 moles of water molecules.” We know the



**Figure 3.7**

Three ways of representing the combustion of hydrogen. In accordance with the law of conservation of mass, the number of each type of atom must be the same on both sides of the equation.

**TABLE 3.1** Interpretation of a Chemical Equation

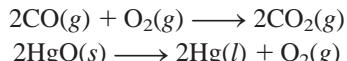
$2\text{H}_2$	$+ \text{O}_2$	$\longrightarrow 2\text{H}_2\text{O}$
Two molecules	+ one molecule	$\longrightarrow$ two molecules
2 moles	+ 1 mole	$\longrightarrow$ 2 moles
$2(2.02 \text{ g}) = 4.04 \text{ g}$	$+ 32.00 \text{ g}$	$\longrightarrow 2(18.02 \text{ g}) = 36.04 \text{ g}$
36.04 g reactants		36.04 g product

mass of a mole of each of these substances, so we can also interpret the equation as “4.04 g of  $\text{H}_2$  react with 32.00 g of  $\text{O}_2$  to give 36.04 g of  $\text{H}_2\text{O}$ .” These three ways of reading the equation are summarized in Table 3.1.

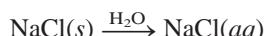
We refer to  $\text{H}_2$  and  $\text{O}_2$  in Equation (3.2) as **reactants**, which are *the starting materials in a chemical reaction*. Water is the **product**, which is *the substance formed as a result of a chemical reaction*. A chemical equation, then, is just the chemist’s short-hand description of a reaction. In a chemical equation the reactants are conventionally written on the left and the products on the right of the arrow:



To provide additional information, chemists often indicate the physical states of the reactants and products by using the letters *g*, *l*, and *s* to denote gas, liquid, and solid, respectively. For example,



To represent what happens when sodium chloride ( $\text{NaCl}$ ) is added to water, we write



where *aq* denotes the aqueous (that is, water) environment. Writing  $\text{H}_2\text{O}$  above the arrow symbolizes the physical process of dissolving a substance in water, although it is sometimes left out for simplicity.

## Balancing Chemical Equations

Suppose we want to write an equation to describe a chemical reaction that we have just carried out in the laboratory. How should we go about doing it? Because we know the identities of the reactants, we can write their chemical formulas. The identities of products are more difficult to establish. For simple reactions, it is often possible to guess the product(s). For more complicated reactions involving three or more products, chemists may need to perform further tests to establish the presence of specific compounds.

Once we have identified all the reactants and products and have written the correct formulas for them, we assemble them in the conventional sequence—reactants on the left separated by an arrow from products on the right. The equation written at this point is likely to be *unbalanced*; that is, the number of each type of atom on one side of the arrow differs from the number on the other side. In general, we can balance a chemical equation by the following steps:

1. Identify all reactants and products and write their correct formulas on the left side and right side of the equation, respectively.



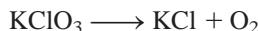
Interactivity:  
Balance the Equation  
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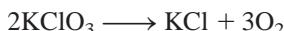
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- Begin balancing the equation by trying different coefficients to make the number of atoms of each element the same on both sides of the equation. We can change the coefficients (the numbers preceding the formulas) but not the subscripts (the numbers within formulas). Changing the subscripts would change the identity of the substance. For example,  $2\text{NO}_2$  means “two molecules of nitrogen dioxide,” but if we double the subscripts, we have  $\text{N}_2\text{O}_4$ , which is the formula of dinitrogen tetroxide, a completely different compound.
- First, look for elements that appear only once on each side of the equation with the same number of atoms on each side: The formulas containing these elements must have the same coefficient. Therefore, there is no need to adjust the coefficients of these elements at this point. Next, look for elements that appear only once on each side of the equation but in unequal numbers of atoms. Balance these elements. Finally, balance elements that appear in two or more formulas on the same side of the equation.
- Check your balanced equation to be sure that you have the same total number of each type of atoms on both sides of the equation arrow.

Let's consider a specific example. In the laboratory, small amounts of oxygen gas can be prepared by heating potassium chlorate ( $\text{KClO}_3$ ). The products are oxygen gas ( $\text{O}_2$ ) and potassium chloride (KCl). From this information, we write



(For simplicity, we omit the physical states of reactants and products.) All three elements (K, Cl, and O) appear only once on each side of the equation, but only for K and Cl do we have equal numbers of atoms on both sides. Thus,  $\text{KClO}_3$  and KCl must have the same coefficient. The next step is to make the number of O atoms the same on both sides of the equation. Because there are three O atoms on the left and two O atoms on the right of the equation, we can balance the O atoms by placing a 2 in front of  $\text{KClO}_3$  and a 3 in front of  $\text{O}_2$ .



Finally, we balance the K and Cl atoms by placing a 2 in front of KCl:



As a final check, we can draw up a balance sheet for the reactants and products where the number in parentheses indicates the number of atoms of each element:

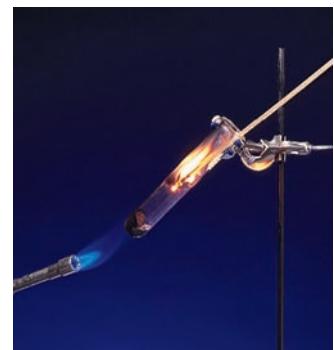
Reactants	Products
K (2)	K (2)
Cl (2)	Cl (2)
O (6)	O (6)

Note that this equation could also be balanced with coefficients that are multiples of 2 (for  $\text{KClO}_3$ ), 2 (for KCl), and 3 (for  $\text{O}_2$ ); for example,

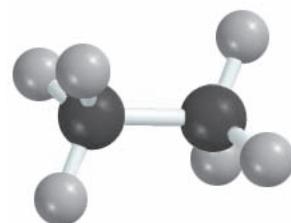


However, it is common practice to use the *simplest* possible set of whole-number coefficients to balance the equation. Equation (3.3) conforms to this convention.

Now let us consider the combustion (that is, burning) of the natural gas component ethane ( $\text{C}_2\text{H}_6$ ) in oxygen or air, which yields carbon dioxide ( $\text{CO}_2$ ) and water. The unbalanced equation is



Heating potassium chlorate produces oxygen, which supports the combustion of wood splint.



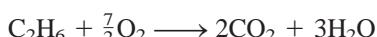
We see that the number of atoms is not the same on both sides of the equation for any of the elements (C, H, and O). In addition, C and H appear only once on each side of the equation; O appears in two compounds on the right side ( $\text{CO}_2$  and  $\text{H}_2\text{O}$ ). To balance the C atoms, we place a 2 in front of  $\text{CO}_2$ :



To balance the H atoms, we place a 3 in front of  $\text{H}_2\text{O}$ :



At this stage, the C and H atoms are balanced, but the O atoms are not because there are seven O atoms on the right-hand side and only two O atoms on the left-hand side of the equation. This inequality of O atoms can be eliminated by writing  $\frac{7}{2}$  in front of the  $\text{O}_2$  on the left-hand side:



The “logic” for using  $\frac{7}{2}$  as a coefficient is that there were seven oxygen atoms on the right-hand side of the equation, but only a pair of oxygen atoms ( $\text{O}_2$ ) on the left. To balance them we ask how many *pairs* of oxygen atoms are needed to equal seven oxygen atoms. Just as 3.5 pairs of shoes equal seven shoes,  $\frac{7}{2}\text{O}_2$  molecules equal seven O atoms. As the following tally shows, the equation is now balanced:

Reactants	Products
C (2)	C (2)
H (6)	H (6)
O (7)	O (7)

However, we normally prefer to express the coefficients as whole numbers rather than as fractions. Therefore, we multiply the entire equation by 2 to convert  $\frac{7}{2}$  to 7:



The final tally is

Reactants	Products
C (4)	C (4)
H (12)	H (12)
O (14)	O (14)

Note that the coefficients used in balancing the last equation are the smallest possible set of whole numbers.

### Example 3.12

When aluminum metal is exposed to air, a protective layer of aluminum oxide ( $\text{Al}_2\text{O}_3$ ) forms on its surface. This layer prevents further reaction between aluminum and oxygen, and it is the reason that aluminum beverage cans do not corrode. [In the case of iron, the rust, or iron(III) oxide, that forms is too porous to protect the iron metal underneath, so rusting continues.] Write a balanced equation for the formation of  $\text{Al}_2\text{O}_3$ .

(Continued)

**Strategy** Remember that the formula of an element or compound cannot be changed when balancing a chemical equation. The equation is balanced by placing the appropriate coefficients in front of the formulas. Follow the procedure described on p. 74.

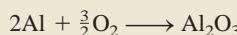
**Solution** The unbalanced equation is



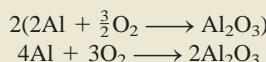
In a balanced equation, the number and types of atoms on each side of the equation must be the same. We see that there is one Al atom on the reactants side and there are two Al atoms on the product side. We can balance the Al atoms by placing a coefficient of 2 in front of Al on the reactants side.



There are two O atoms on the reactants side, and three O atoms on the product side of the equation. We can balance the O atoms by placing a coefficient of  $\frac{3}{2}$  in front of  $\text{O}_2$  on the reactants side.



This is a balanced equation. However, equations are normally balanced with the smallest set of *whole* number coefficients. Multiplying both sides of the equation by 2 gives whole number coefficients.



**Check** For an equation to be balanced, the number and types of atoms on each side of the equation must be the same. The final tally is

Reactants	Products
Al (4)	Al (4)
O (6)	O (6)

The equation is balanced.

Similar problems: 3.59, 3.60.

**Practice Exercise** Balance the equation representing the reaction between iron(III) oxide,  $\text{Fe}_2\text{O}_3$ , and carbon monoxide (CO) to yield iron (Fe) and carbon dioxide ( $\text{CO}_2$ ).

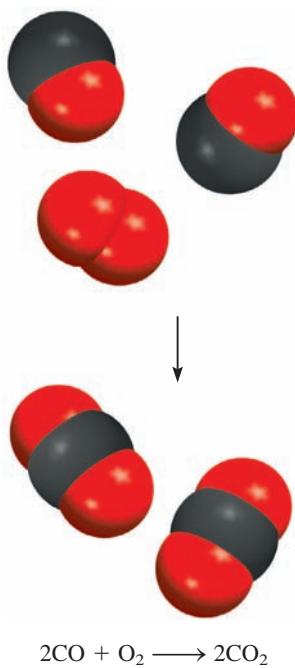
## 3.8 Amounts of Reactants and Products

A basic question raised in the chemical laboratory is “How much product will be formed from specific amounts of starting materials (reactants)?” Or in some cases, we might ask the reverse question: “How much starting material must be used to obtain a specific amount of product?” To interpret a reaction quantitatively, we need to apply our knowledge of molar masses and the mole concept. **Stoichiometry** is the quantitative study of reactants and products in a chemical reaction.

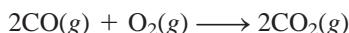
Whether the units given for reactants (or products) are moles, grams, liters (for gases), or some other units, we use moles to calculate the amount of product formed in a reaction. This approach is called the **mole method**, which means simply that the stoichiometric coefficients in a chemical equation can be interpreted as the number



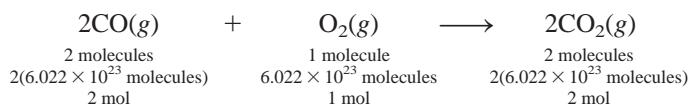
Interactivity:  
The Mole Method  
ARIS, Interactives



of moles of each substance. For example, the combustion of carbon monoxide in air produces carbon dioxide:



The stoichiometric coefficients show that two molecules of CO react with one molecule of O<sub>2</sub> to form two molecules of CO<sub>2</sub>. It follows that the relative numbers of moles are the same as the relative numbers of molecules:



Thus, this equation can also be read as “2 moles of carbon monoxide gas combine with 1 mole of oxygen gas to form 2 moles of carbon dioxide gas.” In stoichiometric calculations, we say that two moles of CO are equivalent to two moles of CO<sub>2</sub>, that is,

$$2 \text{ mol CO} \simeq 2 \text{ mol CO}_2$$

where the symbol  $\simeq$  means “stoichiometrically equivalent to” or simply “equivalent to.” The mole ratio between CO and CO<sub>2</sub> is 2:2 or 1:1, meaning that if 10 moles of CO are reacted, 10 moles of CO<sub>2</sub> will be produced. Likewise, if 0.20 mole of CO is reacted, 0.20 mole of CO<sub>2</sub> will be formed. This relationship enables us to write the conversion factors

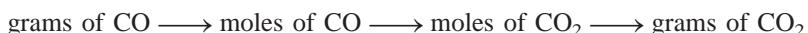
$$\frac{2 \text{ mol CO}}{2 \text{ mol CO}_2} \quad \text{and} \quad \frac{2 \text{ mol CO}_2}{2 \text{ mol CO}}$$

Similarly, we have  $1 \text{ mol O}_2 \simeq 2 \text{ mol CO}_2$  and  $2 \text{ mol CO} \simeq 1 \text{ mol O}_2$ .

Let's consider a simple example in which 4.8 moles of CO react completely with O<sub>2</sub> to form CO<sub>2</sub>. To calculate the amount of CO<sub>2</sub> produced in moles, we use the conversion factor that has CO in the denominator and write

$$\begin{aligned} \text{moles of CO}_2 \text{ produced} &= 4.8 \cancel{\text{mol CO}} \times \frac{2 \text{ mol CO}_2}{2 \cancel{\text{mol CO}}} \\ &= 4.8 \text{ mol CO}_2 \end{aligned}$$

Now suppose 10.7 g of CO react completely with O<sub>2</sub> to form CO<sub>2</sub>. How many grams of CO<sub>2</sub> will be formed? To do this calculation, we note that the link between CO and CO<sub>2</sub> is the mole ratio from the balanced equation. So we need to first convert grams of CO to moles of CO, then to moles of CO<sub>2</sub>, and finally to grams of CO<sub>2</sub>. The conversion steps are

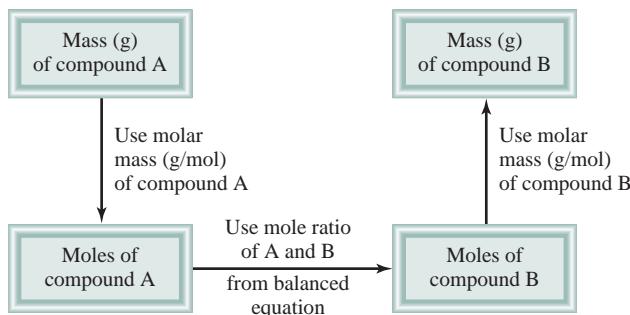


First we convert 10.7 g of CO to number of moles of CO, using the molar mass of CO as the conversion factor:

$$\begin{aligned} \text{moles of CO} &= 10.7 \cancel{\text{g CO}} \times \frac{1 \text{ mol CO}}{28.01 \cancel{\text{g CO}}} \\ &= 0.382 \text{ mol CO} \end{aligned}$$

Next we calculate the number of moles of CO<sub>2</sub> produced:

$$\begin{aligned} \text{moles of CO}_2 &= 0.382 \cancel{\text{mol CO}} \times \frac{2 \text{ mol CO}_2}{2 \cancel{\text{mol CO}}} \\ &= 0.382 \text{ mol CO}_2 \end{aligned}$$



Finally, we calculate the mass of  $\text{CO}_2$  produced in grams using the molar mass of  $\text{CO}_2$  as the conversion factor:

$$\begin{aligned}\text{grams of } \text{CO}_2 &= 0.382 \cancel{\text{mol CO}_2} \times \frac{44.01 \text{ g CO}_2}{1 \cancel{\text{mol CO}_2}} \\ &= 16.8 \text{ g CO}_2\end{aligned}$$

These three separate calculations can be combined in a single step as follows:

$$\begin{aligned}\text{grams of } \text{CO}_2 &= 10.7 \cancel{\text{g CO}} \times \frac{1 \cancel{\text{mol CO}}}{28.01 \cancel{\text{g CO}}} \times \frac{2 \cancel{\text{mol CO}_2}}{2 \cancel{\text{mol CO}}} \times \frac{44.01 \text{ g CO}_2}{1 \cancel{\text{mol CO}_2}} \\ &= 16.8 \text{ g CO}_2\end{aligned}$$

Similarly, we can calculate the mass of  $\text{O}_2$  in grams consumed in this reaction. By using the relationship  $2 \text{ mol CO} \approx 1 \text{ mol O}_2$ , we write

$$\begin{aligned}\text{grams of } \text{O}_2 &= 10.7 \cancel{\text{g CO}} \times \frac{1 \cancel{\text{mol CO}}}{28.01 \cancel{\text{g CO}}} \times \frac{1 \cancel{\text{mol O}_2}}{2 \cancel{\text{mol CO}}} \times \frac{32.00 \text{ g O}_2}{1 \cancel{\text{mol O}_2}} \\ &= 6.11 \text{ g O}_2\end{aligned}$$

Figure 3.8 shows the steps involved in stoichiometric calculations using the mole method.

### Example 3.13

The food we eat is degraded, or broken down, in our bodies to provide energy for growth and function. A general overall equation for this very complex process represents the degradation of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) to carbon dioxide ( $\text{CO}_2$ ) and water ( $\text{H}_2\text{O}$ ):



If 856 g of  $\text{C}_6\text{H}_{12}\text{O}_6$  is consumed by a person over a certain period, what is the mass of  $\text{CO}_2$  produced?

**Strategy** Looking at the balanced equation, how do we compare the amount of  $\text{C}_6\text{H}_{12}\text{O}_6$  and  $\text{CO}_2$ ? We can compare them based on the *mole ratio* from the balanced equation. Starting with grams of  $\text{C}_6\text{H}_{12}\text{O}_6$ , how do we convert to moles of  $\text{C}_6\text{H}_{12}\text{O}_6$ ? Once moles of  $\text{CO}_2$  are determined using the mole ratio from the balanced equation how do we convert to grams of  $\text{CO}_2$ ?

**Solution** We follow the preceding steps and Figure 3.8.

*Step 1:* The balanced equation is given in the problem.

**Figure 3.8**  
*The mole method. First convert the quantity of reactant A (in grams or other units) to number of moles. Next, use the mole ratio in the balanced equation to calculate the number of moles of product B formed. Finally, convert moles of product to grams of product.*



(Continued)

*Step 2:* To convert grams of C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> to moles of C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, we write

$$856 \text{ g C}_6\text{H}_{12}\text{O}_6 \times \frac{1 \text{ mol C}_6\text{H}_{12}\text{O}_6}{180.2 \text{ g C}_6\text{H}_{12}\text{O}_6} = 4.750 \text{ mol C}_6\text{H}_{12}\text{O}_6$$

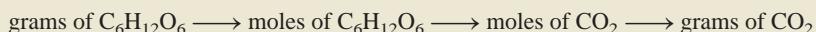
*Step 3:* From the mole ratio, we see that 1 mol C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> ≈ 6 mol CO<sub>2</sub>. Therefore, the number of moles of CO<sub>2</sub> formed is

$$4.750 \text{ mol C}_6\text{H}_{12}\text{O}_6 \times \frac{6 \text{ mol CO}_2}{1 \text{ mol C}_6\text{H}_{12}\text{O}_6} = 28.50 \text{ mol CO}_2$$

*Step 4:* Finally, the number of grams of CO<sub>2</sub> formed is given by

$$28.50 \text{ mol CO}_2 \times \frac{44.01 \text{ g CO}_2}{1 \text{ mol CO}_2} = 1.25 \times 10^3 \text{ g CO}_2$$

After some practice, we can combine the conversion steps



into one equation:

$$\begin{aligned} \text{mass of CO}_2 &= 856 \text{ g C}_6\text{H}_{12}\text{O}_6 \times \frac{1 \text{ mol C}_6\text{H}_{12}\text{O}_6}{180.2 \text{ g C}_6\text{H}_{12}\text{O}_6} \times \frac{6 \text{ mol CO}_2}{1 \text{ mol C}_6\text{H}_{12}\text{O}_6} \times \frac{44.01 \text{ g CO}_2}{1 \text{ mol CO}_2} \\ &= 1.25 \times 10^3 \text{ g CO}_2 \end{aligned}$$

**Check** Does the answer seem reasonable? Should the mass of CO<sub>2</sub> produced be larger than the mass of C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> reacted, even though the molar mass of CO<sub>2</sub> is considerably less than the molar mass of C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>? What is the mole ratio between CO<sub>2</sub> and C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>?

**Similar problem:** 3.72.

**Practice Exercise** Methanol (CH<sub>3</sub>OH) burns in air according to the equation



If 209 g of methanol are used up in a combustion process, what is the mass of H<sub>2</sub>O produced?



Lithium reacting with water to produce hydrogen gas.

### Example 3.14

All alkali metals react with water to produce hydrogen gas and the corresponding alkali metal hydroxide. A typical reaction is that between lithium and water:



How many grams of Li are needed to produce 9.89 g of H<sub>2</sub>?

**Strategy** The question asks for number of grams of reactant (Li) to form a specific amount of product (H<sub>2</sub>). Therefore, we need to reverse the steps shown in Figure 3.8. From the equation we see that 2 mol Li ≈ 1 mol H<sub>2</sub>.

**Solution** The conversion steps are



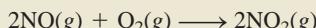
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Combining these steps into one equation, we write

$$9.89 \text{ g H}_2 \times \frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2} \times \frac{2 \text{ mol Li}}{1 \text{ mol H}_2} \times \frac{6.941 \text{ g Li}}{1 \text{ mol Li}} = 68.1 \text{ g Li}$$

**Check** There are roughly 5 moles of H<sub>2</sub> in 9.89 g H<sub>2</sub>, so we need 10 moles of Li. From the approximate molar mass of Li (7 g), does the answer seem reasonable?

**Practice Exercise** The reaction between nitric oxide (NO) and oxygen to form nitrogen dioxide (NO<sub>2</sub>) is a key step in photochemical smog formation:



How many grams of O<sub>2</sub> are needed to produce 2.21 g of NO<sub>2</sub>?

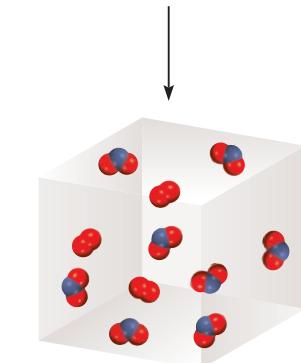
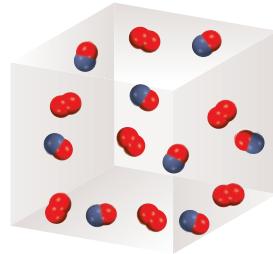
Similar problems: 3.65, 3.71.



**Animation:**  
Limiting Reagent  
ARIS, Animations



Before reaction has started



After reaction is complete



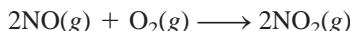
**Figure 3.9**  
At the start of the reaction, there were eight NO molecules and seven O<sub>2</sub> molecules. At the end, all the NO molecules are gone and only three O<sub>2</sub> molecules are left. Therefore, NO is the limiting reagent and O<sub>2</sub> is the excess reagent. Each molecule can also be treated as one mole of the substance in this reaction.

## 3.9 Limiting Reagents

When a chemist carries out a reaction, the reactants are usually not present in exact **stoichiometric amounts**, that is, *in the proportions indicated by the balanced equation*. Because the goal of a reaction is to produce the maximum quantity of a useful compound from the starting materials, frequently a large excess of one reactant is supplied to ensure that the more expensive reactant is completely converted to the desired product. Consequently, some reactant will be left over at the end of the reaction. *The reactant used up first in a reaction* is called the **limiting reagent**, because the maximum amount of product formed depends on how much of this reactant was originally present. When this reactant is used up, no more product can be formed. **Excess reagents** are the *reactants present in quantities greater than necessary to react with the quantity of the limiting reagent*.

The concept of the limiting reagent is analogous to the relationship between men and women in a dance contest at a club. If there are 14 men and only 9 women, then only 9 female/male pairs can compete. Five men will be left without partners. The number of women thus *limits* the number of men that can dance in the contest, and there is an *excess* of men.

Consider the formation of nitrogen dioxide (NO<sub>2</sub>) from nitric oxide (NO) and oxygen:



Suppose initially we have 8 moles of NO and 7 moles of O<sub>2</sub> (Figure 3.9). One way to determine which of the two reactants is the limiting reagent is to calculate the number of moles of NO<sub>2</sub> obtained based on the initial quantities of NO and O<sub>2</sub>. From the preceding definition, we see that only the limiting reagent will yield the smaller amount of the product. Starting with 8 moles of NO, we find the number of moles of NO<sub>2</sub> produced is

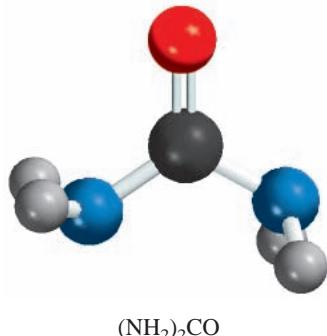
$$8 \cancel{\text{mol NO}} \times \frac{2 \text{ mol NO}_2}{2 \cancel{\text{mol NO}}} = 8 \text{ mol NO}_2$$

and starting with 7 moles of O<sub>2</sub>, the number of moles of NO<sub>2</sub> formed is

$$7 \cancel{\text{mol O}_2} \times \frac{2 \text{ mol NO}_2}{1 \cancel{\text{mol O}_2}} = 14 \text{ mol NO}_2$$

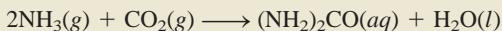
Because NO results in a smaller amount of NO<sub>2</sub>, it must be the limiting reagent. Therefore, O<sub>2</sub> is the excess reagent.

In stoichiometric calculations involving limiting reagents, the first step is to decide which reactant is the limiting reagent. After the limiting reagent has been identified, the rest of the problem can be solved as outlined in Section 3.8. Example 3.15 illustrates this approach.



### Example 3.15

Urea  $[(\text{NH}_2)_2\text{CO}]$  is prepared by reacting ammonia with carbon dioxide:



In one process, 637.2 g of  $\text{NH}_3$  are treated with 1142 g of  $\text{CO}_2$ . (a) Which of the two reactants is the limiting reagent? (b) Calculate the mass of  $(\text{NH}_2)_2\text{CO}$  formed. (c) How much excess reagent (in grams) is left at the end of the reaction?

**(a) Strategy** The reactant that produces fewer moles of product is the limiting reagent because it limits the amount of product that can be formed. How do we convert from the amount of reactant to amount of product? Perform this calculation for each reactant, then compare the moles of product,  $(\text{NH}_2)_2\text{CO}$ , formed by the given amounts of  $\text{NH}_3$  and  $\text{CO}_2$  to determine which reactant is the limiting reagent.

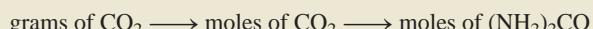
**Solution** We carry out two separate calculations. First, starting with 637.2 g of  $\text{NH}_3$ , we calculate the number of moles of  $(\text{NH}_2)_2\text{CO}$  that could be produced if all the  $\text{NH}_3$  reacted according to the following conversions:



Combining these conversions in one step, we write

$$\begin{aligned}\text{moles of } (\text{NH}_2)_2\text{CO} &= 637.2 \text{ g } \cancel{\text{NH}_3} \times \frac{1 \text{ mol } \text{NH}_3}{17.03 \text{ g } \cancel{\text{NH}_3}} \times \frac{1 \text{ mol } (\text{NH}_2)_2\text{CO}}{2 \text{ mol } \cancel{\text{NH}_3}} \\ &= 18.71 \text{ mol } (\text{NH}_2)_2\text{CO}\end{aligned}$$

Second, for 1142 g of  $\text{CO}_2$ , the conversions are



The number of moles of  $(\text{NH}_2)_2\text{CO}$  that could be produced if all the  $\text{CO}_2$  reacted is

$$\begin{aligned}\text{moles of } (\text{NH}_2)_2\text{CO} &= 1142 \text{ g } \cancel{\text{CO}_2} \times \frac{1 \text{ mol } \text{CO}_2}{44.01 \text{ g } \cancel{\text{CO}_2}} \times \frac{1 \text{ mol } (\text{NH}_2)_2\text{CO}}{1 \text{ mol } \cancel{\text{CO}_2}} \\ &= 25.95 \text{ mol } (\text{NH}_2)_2\text{CO}\end{aligned}$$

It follows, therefore, that  $\text{NH}_3$  must be the limiting reagent because it produces a smaller amount of  $(\text{NH}_2)_2\text{CO}$ .

**(b) Strategy** We determined the moles of  $(\text{NH}_2)_2\text{CO}$  produced in part (a), using  $\text{NH}_3$  as the limiting reagent. How do we convert from moles to grams?

**Solution** The molar mass of  $(\text{NH}_2)_2\text{CO}$  is 60.06 g. We use this as a conversion factor to convert from moles of  $(\text{NH}_2)_2\text{CO}$  to grams of  $(\text{NH}_2)_2\text{CO}$ :

$$\begin{aligned}\text{mass of } (\text{NH}_2)_2\text{CO} &= 18.71 \text{ mol } \cancel{(\text{NH}_2)_2\text{CO}} \times \frac{60.06 \text{ g } (\text{NH}_2)_2\text{CO}}{1 \text{ mol } \cancel{(\text{NH}_2)_2\text{CO}}} \\ &= 1124 \text{ g } (\text{NH}_2)_2\text{CO}\end{aligned}$$

(Continued)

**Check** Does your answer seem reasonable? 18.71 moles of product are formed. What is the mass of 1 mole of  $(\text{NH}_2)_2\text{CO}$ ?

**(c) Strategy** Working backward, we can determine the amount of  $\text{CO}_2$  that reacted to produce 18.71 moles of  $(\text{NH}_2)_2\text{CO}$ . The amount of  $\text{CO}_2$  left over is the difference between the initial amount and the amount reacted.

**Solution** Starting with 18.71 moles of  $(\text{NH}_2)_2\text{CO}$ , we can determine the mass of  $\text{CO}_2$  that reacted using the mole ratio from the balanced equation and the molar mass of  $\text{CO}_2$ . The conversion steps are



so that

$$\begin{aligned}\text{mass of } \text{CO}_2 \text{ reacted} &= 18.71 \cancel{\text{mol } (\text{NH}_2)_2\text{CO}} \times \frac{1 \cancel{\text{mol } \text{CO}_2}}{1 \cancel{\text{mol } (\text{NH}_2)_2\text{CO}}} \times \frac{44.01 \text{ g } \text{CO}_2}{1 \cancel{\text{mol } \text{CO}_2}} \\ &= 823.4 \text{ g } \text{CO}_2\end{aligned}$$

The amount of  $\text{CO}_2$  remaining (in excess) is the difference between the initial amount (1142 g) and the amount reacted (823.4 g):

$$\text{mass of } \text{CO}_2 \text{ remaining} = 1142 \text{ g} - 823.4 \text{ g} = 319 \text{ g}$$

**Similar problem:** 3.86.

**Practice Exercise** The reaction between aluminum and iron(III) oxide can generate temperatures approaching  $3000^\circ\text{C}$  and is used in welding metals:



In one process, 124 g of Al are reacted with 601 g of  $\text{Fe}_2\text{O}_3$ . (a) Calculate the mass (in grams) of  $\text{Al}_2\text{O}_3$  formed. (b) How much of the excess reagent is left at the end of the reaction?

Example 3.15 brings out an important point. In practice, chemists usually choose the more expensive chemical as the limiting reagent so that all or most of it will be consumed in the reaction. In the synthesis of urea,  $\text{NH}_3$  is invariably the limiting reagent because it is much more expensive than  $\text{CO}_2$ .

## 3.10 Reaction Yield

The amount of limiting reagent present at the start of a reaction determines the **theoretical yield** of the reaction, that is, *the amount of product that would result if all the limiting reagent reacted*. The theoretical yield, then, is the *maximum obtainable yield*, predicted by the balanced equation. In practice, the **actual yield**, or *the amount of product actually obtained from a reaction*, is almost always less than the theoretical yield. There are many reasons for the difference between actual and theoretical yields. For instance, many reactions are reversible, and so they do not proceed 100 percent from left to right. Even when a reaction is 100 percent complete, it may be difficult to recover all of the product from the reaction medium (say, from an aqueous solution). Some reactions are complex in the sense that the products formed may react further among themselves or with the reactants to form still other products. These additional reactions will reduce the yield of the first reaction.

To determine how efficient a given reaction is, chemists often figure the ***percent yield***, which describes *the proportion of the actual yield to the theoretical yield*. It is calculated as follows:

$$\% \text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% \quad (3.4)$$

Percent yields may range from a fraction of 1 percent to 100 percent. Chemists strive to maximize the percent yield in a reaction. Factors that can affect the percent yield include temperature and pressure. We will study these effects later.

In Example 3.16 we will calculate the yield of an industrial process.



The frame of this bicycle is made of titanium.

### Example 3.16

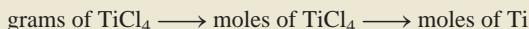
Titanium is a strong, lightweight, corrosion-resistant metal that is used in rockets, aircraft, jet engines, and bicycle frames. It is prepared by the reaction of titanium(IV) chloride with molten magnesium between 950°C and 1150°C:



In a certain industrial operation  $3.54 \times 10^7$  g of  $\text{TiCl}_4$  are reacted with  $1.13 \times 10^7$  g of Mg. (a) Calculate the theoretical yield of Ti in grams. (b) Calculate the percent yield if  $7.91 \times 10^6$  g of Ti are actually obtained.

**(a) Strategy** Because there are two reactants, this is likely to be a limiting reagent problem. The reactant that produces fewer moles of product is the limiting reagent. How do we convert from amount of reactant to amount of product? Perform this calculation for each reactant, then compare the moles of product, Ti, formed.

**Solution** Carry out two separate calculations to see which of the two reactants is the limiting reagent. First, starting with  $3.54 \times 10^7$  g of  $\text{TiCl}_4$ , calculate the number of moles of Ti that could be produced if all the  $\text{TiCl}_4$  reacted. The conversions are



so that

$$\begin{aligned} \text{moles of Ti} &= 3.54 \times 10^7 \cancel{\text{g TiCl}_4} \times \frac{1 \text{ mol TiCl}_4}{189.7 \cancel{\text{g TiCl}_4}} \times \frac{1 \text{ mol Ti}}{1 \cancel{\text{mol TiCl}_4}} \\ &= 1.87 \times 10^5 \text{ mol Ti} \end{aligned}$$

Next, we calculate the number of moles of Ti formed from  $1.13 \times 10^7$  g of Mg. The conversion steps are



and we write

$$\begin{aligned} \text{moles of Ti} &= 1.13 \times 10^7 \cancel{\text{g Mg}} \times \frac{1 \text{ mol Mg}}{24.31 \cancel{\text{g Mg}}} \times \frac{1 \text{ mol Ti}}{2 \cancel{\text{mol Mg}}} \\ &= 2.32 \times 10^5 \text{ mol Ti} \end{aligned}$$

(Continued)

Therefore,  $\text{TiCl}_4$  is the limiting reagent because it produces a smaller amount of Ti. The mass of Ti formed is

$$1.87 \times 10^5 \text{ mol Ti} \times \frac{47.88 \text{ g Ti}}{1 \text{ mol Ti}} = 8.95 \times 10^6 \text{ g Ti}$$

**(b) Strategy** The mass of Ti determined in part (a) is the theoretical yield. The amount given in part (b) is the actual yield of the reaction.

**Solution** The percent yield is given by

$$\begin{aligned}\% \text{ yield} &= \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% \\ &= \frac{7.91 \times 10^6 \text{ g}}{8.95 \times 10^6 \text{ g}} \times 100\% \\ &= 88.4\%\end{aligned}$$

**Check** Should the percent yield be less than 100 percent?

**Similar problems:** 3.89, 3.90.

**Practice Exercise** Industrially, vanadium metal, which is used in steel alloys, can be obtained by reacting vanadium(V) oxide with calcium at high temperatures:



In one process,  $1.54 \times 10^3$  g of  $\text{V}_2\text{O}_5$  react with  $1.96 \times 10^3$  g of Ca. (a) Calculate the theoretical yield of V. (b) Calculate the percent yield if 803 g of V are obtained.

## KEY EQUATIONS

$$\text{percent composition of an element in a compound} = \frac{n \times \text{molar mass of element}}{\text{molar mass of compound}} \times 100\% \quad (3.1)$$

$$\% \text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% \quad (3.4)$$

## SUMMARY OF FACTS AND CONCEPTS

- Atomic masses are measured in atomic mass units (amu), a relative unit based on a value of exactly 12 for the C-12 isotope. The atomic mass given for the atoms of a particular element is the average of the naturally occurring isotope distribution of that element. The molecular mass of a molecule is the sum of the atomic masses of the atoms in the molecule. Both atomic mass and molecular mass can be accurately determined with a mass spectrometer.
- A mole is Avogadro's number ( $6.022 \times 10^{23}$ ) of atoms, molecules, or other particles. The molar mass (in grams) of an element or a compound is numerically equal to its mass in atomic mass units (amu) and contains Avogadro's number of atoms (in the case of elements), molecules (in the case of molecular substances), or simplest formula units (in the case of ionic compounds).
- The percent composition by mass of a compound is the percent by mass of each element present. If we know the percent composition by mass of a compound, we can deduce the empirical formula of the compound and also the molecular formula of the compound if the approximate molar mass is known.
- Chemical changes, called chemical reactions, are represented by chemical equations. Substances that undergo change—the reactants—are written on the left and the substances formed—the products—appear to the right of the arrow. Chemical equations must be balanced, in

accordance with the law of conservation of mass. The number of atoms of each element in the reactants must equal the number in the products.

- Stoichiometry is the quantitative study of products and reactants in chemical reactions. Stoichiometric calculations are best done by expressing both the known and unknown quantities in terms of moles and then converting

to other units if necessary. A limiting reagent is the reactant that is present in the smallest stoichiometric amount. It limits the amount of product that can be formed. The amount of product obtained in a reaction (the actual yield) may be less than the maximum possible amount (the theoretical yield). The ratio of the two multiplied by 100 percent is expressed as the percent yield.

## KEY WORDS

Actual yield, p. 83	Chemical reaction, p. 73	Mole method, p. 77	Reactant, p. 73
Atomic mass, p. 59	Excess reagent, p. 81	Molecular mass, p. 64	Stoichiometric amount, p. 81
Atomic mass unit (amu), p. 59	Limiting reagent, p. 81	Percent composition, p. 68	Stoichiometry, p. 77
Avogadro's number ( $N_A$ ), p. 60	Molar mass ( $M$ ), p. 61	Percent yield, p. 84	Theoretical yield, p. 83
Chemical equation, p. 73	Mole (mol), p. 60	Product, p. 73	

## QUESTIONS AND PROBLEMS

### Atomic Mass

#### Review Questions

- What is an atomic mass unit? Why is it necessary to introduce such a unit?
- What is the mass (in amu) of a carbon-12 atom? Why is the atomic mass of carbon listed as 12.01 amu in the table on the inside front cover of this book?
- Explain clearly what is meant by the statement “The atomic mass of gold is 197.0 amu.”
- What information would you need to calculate the average atomic mass of an element?

#### Problems

- The atomic masses of  $^{35}_{17}\text{Cl}$  (75.53 percent) and  $^{37}_{17}\text{Cl}$  (24.47 percent) are 34.968 amu and 36.956 amu, respectively. Calculate the average atomic mass of chlorine. The percentages in parentheses denote the relative abundances.
- The atomic masses of  $^6_3\text{Li}$  and  $^7_3\text{Li}$  are 6.0151 amu and 7.0160 amu, respectively. Calculate the natural abundances of these two isotopes. The average atomic mass of Li is 6.941 amu.
- What is the mass in grams of 13.2 amu?
- How many amu are there in 8.4 g?

### Avogadro's Number and Molar Mass

#### Review Questions

- Define the term “mole.” What is the unit for mole in calculations? What does the mole have in common

with the pair, the dozen, and the gross? What does Avogadro's number represent?

- What is the molar mass of an atom? What are the commonly used units for molar mass?

#### Problems

- Earth's population is about 6.5 billion. Suppose that every person on Earth participates in a process of counting identical particles at the rate of two particles per second. How many years would it take to count  $6.0 \times 10^{23}$  particles? Assume that there are 365 days in a year.
- The thickness of a piece of paper is 0.0036 in. Suppose a certain book has an Avogadro's number of pages; calculate the thickness of the book in light-years. (Hint: See Problem 1.38 for the definition of light-year.)
- How many atoms are there in 5.10 moles of sulfur (S)?
- How many moles of cobalt (Co) atoms are there in  $6.00 \times 10^9$  (6 billion) Co atoms?
- How many moles of calcium (Ca) atoms are in 77.4 g of Ca?
- How many grams of gold (Au) are there in 15.3 moles of Au?
- What is the mass in grams of a single atom of each of the following elements? (a) Hg, (b) Ne.
- What is the mass in grams of a single atom of each of the following elements? (a) As, (b) Ni.
- What is the mass in grams of  $1.00 \times 10^{12}$  lead (Pb) atoms?

- 3.20** How many atoms are present in 3.14 g of copper (Cu)?
- 3.21 Which of the following has more atoms: 1.10 g of hydrogen atoms or 14.7 g of chromium atoms?
- 3.22** Which of the following has a greater mass: 2 atoms of lead or  $5.1 \times 10^{-23}$  mole of helium?

## Molecular Mass

### Problems

- 3.23 Calculate the molecular mass or formula mass (in amu) of each of the following substances: (a) CH<sub>4</sub>, (b) NO<sub>2</sub>, (c) SO<sub>3</sub>, (d) C<sub>6</sub>H<sub>6</sub>, (e) NaI, (f) K<sub>2</sub>SO<sub>4</sub>, (g) Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.
- 3.24** Calculate the molar mass of the following substances: (a) Li<sub>2</sub>CO<sub>3</sub>, (b) CS<sub>2</sub>, (c) CHCl<sub>3</sub> (chloroform), (d) C<sub>6</sub>H<sub>8</sub>O<sub>6</sub> (ascorbic acid, or vitamin C), (e) KNO<sub>3</sub>, (f) Mg<sub>3</sub>N<sub>2</sub>.
- 3.25 Calculate the molar mass of a compound if 0.372 mole of it has a mass of 152 g.
- 3.26** How many molecules of ethane (C<sub>2</sub>H<sub>6</sub>) are present in 0.334 g of C<sub>2</sub>H<sub>6</sub>?
- 3.27 Calculate the number of C, H, and O atoms in 1.50 g of glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>), a sugar.
- 3.28** Urea [(NH<sub>2</sub>)<sub>2</sub>CO] is used for fertilizer and many other things. Calculate the number of N, C, O, and H atoms in  $1.68 \times 10^4$  g of urea.
- 3.29 Pheromones are a special type of compound secreted by the females of many insect species to attract the males for mating. One pheromone has the molecular formula C<sub>19</sub>H<sub>38</sub>O. Normally, the amount of this pheromone secreted by a female insect is about  $1.0 \times 10^{-12}$  g. How many molecules are there in this quantity?
- 3.30** The density of water is 1.00 g/mL at 4°C. How many water molecules are present in 2.56 mL of water at this temperature?

## Mass Spectrometry

### Review Questions

- 3.31 Describe the operation of a mass spectrometer.
- 3.32 Describe how you would determine the isotopic abundance of an element from its mass spectrum.

### Problems

- 3.33 Carbon has two stable isotopes, <sup>12</sup>C and <sup>13</sup>C, and fluorine has only one stable isotope, <sup>19</sup>F. How many peaks would you observe in the mass spectrum of the positive ion of CF<sub>4</sub><sup>+</sup>? Assume that the ion does not break up into smaller fragments.
- 3.34** Hydrogen has two stable isotopes, <sup>1</sup>H and <sup>2</sup>H, and sulfur has four stable isotopes, <sup>32</sup>S, <sup>33</sup>S, <sup>34</sup>S, and <sup>36</sup>S. How many peaks would you observe in the mass

spectrum of the positive ion of hydrogen sulfide, H<sub>2</sub>S<sup>+</sup>? Assume no decomposition of the ion into smaller fragments.

## Percent Composition and Chemical Formulas

### Review Questions

- 3.35 Use ammonia (NH<sub>3</sub>) to explain what is meant by the percent composition by mass of a compound.
- 3.36 Describe how the knowledge of the percent composition by mass of an unknown compound can help us identify the compound.
- 3.37 What does the word “empirical” in empirical formula mean?
- 3.38 If we know the empirical formula of a compound, what additional information do we need to determine its molecular formula?

### Problems

- 3.39 Tin (Sn) exists in Earth’s crust as SnO<sub>2</sub>. Calculate the percent composition by mass of Sn and O in SnO<sub>2</sub>.
- 3.40** For many years chloroform (CHCl<sub>3</sub>) was used as an inhalation anesthetic in spite of the fact that it is also a toxic substance that may cause severe liver, kidney, and heart damage. Calculate the percent composition by mass of this compound.
- 3.41 Cinnamic alcohol is used mainly in perfumery, particularly in soaps and cosmetics. Its molecular formula is C<sub>9</sub>H<sub>10</sub>O. (a) Calculate the percent composition by mass of C, H, and O in cinnamic alcohol. (b) How many molecules of cinnamic alcohol are contained in a sample of mass 0.469 g?
- 3.42** All of the substances listed below are fertilizers that contribute nitrogen to the soil. Which of these is the richest source of nitrogen on a mass percentage basis?
- (a) Urea, (NH<sub>2</sub>)<sub>2</sub>CO
  - (b) Ammonium nitrate, NH<sub>4</sub>NO<sub>3</sub>
  - (c) Guanidine, HNC(NH<sub>2</sub>)<sub>2</sub>
  - (d) Ammonia, NH<sub>3</sub>
- 3.43 Allicin is the compound responsible for the characteristic smell of garlic. An analysis of the compound gives the following percent composition by mass: C: 44.4 percent; H: 6.21 percent; S: 39.5 percent; O: 9.86 percent. Calculate its empirical formula. What is its molecular formula given that its molar mass is about 162 g?
- 3.44** Peroxyacetyl nitrate (PAN) is one of the components of smog. It is a compound of C, H, N, and O. Determine the percent composition of oxygen and the empirical formula from the following percent composition by mass: 19.8 percent C, 2.50 percent H, 11.6 percent N. What is its molecular formula given that its molar mass is about 120 g?

- 3.45 The formula for rust can be represented by  $\text{Fe}_2\text{O}_3$ . How many moles of Fe are present in 24.6 g of the compound?
- 3.46 How many grams of sulfur (S) are needed to react completely with 246 g of mercury (Hg) to form  $\text{HgS}$ ?
- 3.47 Calculate the mass in grams of iodine ( $\text{I}_2$ ) that will react completely with 20.4 g of aluminum (Al) to form aluminum iodide ( $\text{AlI}_3$ ).
- 3.48 Tin(II) fluoride ( $\text{SnF}_2$ ) is often added to toothpaste as an ingredient to prevent tooth decay. What is the mass of F in grams in 24.6 g of the compound?
- 3.49 What are the empirical formulas of the compounds with the following compositions? (a) 2.1 percent H, 65.3 percent O, 32.6 percent S, (b) 20.2 percent Al, 79.8 percent Cl.
- 3.50 What are the empirical formulas of the compounds with the following compositions? (a) 40.1 percent C, 6.6 percent H, 53.3 percent O, (b) 18.4 percent C, 21.5 percent N, 60.1 percent K.
- 3.51 The anticaking agent added to Morton salt is calcium silicate,  $\text{CaSiO}_3$ . This compound can absorb up to 2.5 times its mass of water and still remains a free-flowing powder. Calculate the percent composition of  $\text{CaSiO}_3$ .
- 3.52 The empirical formula of a compound is CH. If the molar mass of this compound is about 78 g, what is its molecular formula?
- 3.53 The molar mass of caffeine is 194.19 g. Is the molecular formula of caffeine  $\text{C}_4\text{H}_5\text{N}_2\text{O}$  or  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$ ?
- 3.54 Monosodium glutamate (MSG), a food-flavor enhancer, has been blamed for “Chinese restaurant syndrome,” the symptoms of which are headaches and chest pains. MSG has the following composition by mass: 35.51 percent C, 4.77 percent H, 37.85 percent O, 8.29 percent N, and 13.60 percent Na. What is its molecular formula if its molar mass is about 169 g?
- (a)  $\text{C} + \text{O}_2 \longrightarrow \text{CO}$   
 (b)  $\text{CO} + \text{O}_2 \longrightarrow \text{CO}_2$   
 (c)  $\text{H}_2 + \text{Br}_2 \longrightarrow \text{HBr}$   
 (d)  $\text{K} + \text{H}_2\text{O} \longrightarrow \text{KOH} + \text{H}_2$   
 (e)  $\text{Mg} + \text{O}_2 \longrightarrow \text{MgO}$   
 (f)  $\text{O}_3 \longrightarrow \text{O}_2$   
 (g)  $\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{O}_2$   
 (h)  $\text{N}_2 + \text{H}_2 \longrightarrow \text{NH}_3$   
 (i)  $\text{Zn} + \text{AgCl} \longrightarrow \text{ZnCl}_2 + \text{Ag}$   
 (j)  $\text{S}_8 + \text{O}_2 \longrightarrow \text{SO}_2$   
 (k)  $\text{NaOH} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$   
 (l)  $\text{Cl}_2 + \text{NaI} \longrightarrow \text{NaCl} + \text{I}_2$   
 (m)  $\text{KOH} + \text{H}_3\text{PO}_4 \longrightarrow \text{K}_3\text{PO}_4 + \text{H}_2\text{O}$   
 (n)  $\text{CH}_4 + \text{Br}_2 \longrightarrow \text{CBr}_4 + \text{HBr}$
- 3.60 Balance the following equations using the method outlined in Section 3.7:
- (a)  $\text{N}_2\text{O}_5 \longrightarrow \text{N}_2\text{O}_4 + \text{O}_2$   
 (b)  $\text{KNO}_3 \longrightarrow \text{KNO}_2 + \text{O}_2$   
 (c)  $\text{NH}_4\text{NO}_3 \longrightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$   
 (d)  $\text{NH}_4\text{NO}_2 \longrightarrow \text{N}_2 + \text{H}_2\text{O}$   
 (e)  $\text{NaHCO}_3 \longrightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$   
 (f)  $\text{P}_4\text{O}_{10} + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_4$   
 (g)  $\text{HCl} + \text{CaCO}_3 \longrightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$   
 (h)  $\text{Al} + \text{H}_2\text{SO}_4 \longrightarrow \text{Al}_2(\text{SO}_4)_3 + \text{H}_2$   
 (i)  $\text{CO}_2 + \text{KOH} \longrightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$   
 (j)  $\text{CH}_4 + \text{O}_2 \longrightarrow \text{CO}_2 + \text{H}_2\text{O}$   
 (k)  $\text{Be}_2\text{C} + \text{H}_2\text{O} \longrightarrow \text{Be}(\text{OH})_2 + \text{CH}_4$   
 (l)  $\text{Cu} + \text{HNO}_3 \longrightarrow \text{Cu}(\text{NO}_3)_2 + \text{NO} + \text{H}_2\text{O}$   
 (m)  $\text{S} + \text{HNO}_3 \longrightarrow \text{H}_2\text{SO}_4 + \text{NO}_2 + \text{H}_2\text{O}$   
 (n)  $\text{NH}_3 + \text{CuO} \longrightarrow \text{Cu} + \text{N}_2 + \text{H}_2\text{O}$

## Chemical Reactions and Chemical Equations

### Review Questions

- 3.55 Use the formation of water from hydrogen and oxygen to explain the following terms: chemical reaction, reactant, product.
- 3.56 What is the difference between a chemical reaction and a chemical equation?
- 3.57 Why must a chemical equation be balanced? What law is obeyed by a balanced chemical equation?
- 3.58 Write the symbols used to represent gas, liquid, solid, and the aqueous phase in chemical equations.

### Problems

- 3.59 Balance the following equations using the method outlined in Section 3.7:

- (a)  $\text{C} + \text{O}_2 \longrightarrow \text{CO}$   
 (b)  $\text{CO} + \text{O}_2 \longrightarrow \text{CO}_2$   
 (c)  $\text{H}_2 + \text{Br}_2 \longrightarrow \text{HBr}$   
 (d)  $\text{K} + \text{H}_2\text{O} \longrightarrow \text{KOH} + \text{H}_2$   
 (e)  $\text{Mg} + \text{O}_2 \longrightarrow \text{MgO}$   
 (f)  $\text{O}_3 \longrightarrow \text{O}_2$   
 (g)  $\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{O}_2$   
 (h)  $\text{N}_2 + \text{H}_2 \longrightarrow \text{NH}_3$   
 (i)  $\text{Zn} + \text{AgCl} \longrightarrow \text{ZnCl}_2 + \text{Ag}$   
 (j)  $\text{S}_8 + \text{O}_2 \longrightarrow \text{SO}_2$   
 (k)  $\text{NaOH} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$   
 (l)  $\text{Cl}_2 + \text{NaI} \longrightarrow \text{NaCl} + \text{I}_2$   
 (m)  $\text{KOH} + \text{H}_3\text{PO}_4 \longrightarrow \text{K}_3\text{PO}_4 + \text{H}_2\text{O}$   
 (n)  $\text{CH}_4 + \text{Br}_2 \longrightarrow \text{CBr}_4 + \text{HBr}$

3.60 Balance the following equations using the method outlined in Section 3.7:

- (a)  $\text{N}_2\text{O}_5 \longrightarrow \text{N}_2\text{O}_4 + \text{O}_2$   
 (b)  $\text{KNO}_3 \longrightarrow \text{KNO}_2 + \text{O}_2$   
 (c)  $\text{NH}_4\text{NO}_3 \longrightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$   
 (d)  $\text{NH}_4\text{NO}_2 \longrightarrow \text{N}_2 + \text{H}_2\text{O}$   
 (e)  $\text{NaHCO}_3 \longrightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$   
 (f)  $\text{P}_4\text{O}_{10} + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_4$   
 (g)  $\text{HCl} + \text{CaCO}_3 \longrightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$   
 (h)  $\text{Al} + \text{H}_2\text{SO}_4 \longrightarrow \text{Al}_2(\text{SO}_4)_3 + \text{H}_2$   
 (i)  $\text{CO}_2 + \text{KOH} \longrightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$   
 (j)  $\text{CH}_4 + \text{O}_2 \longrightarrow \text{CO}_2 + \text{H}_2\text{O}$   
 (k)  $\text{Be}_2\text{C} + \text{H}_2\text{O} \longrightarrow \text{Be}(\text{OH})_2 + \text{CH}_4$   
 (l)  $\text{Cu} + \text{HNO}_3 \longrightarrow \text{Cu}(\text{NO}_3)_2 + \text{NO} + \text{H}_2\text{O}$   
 (m)  $\text{S} + \text{HNO}_3 \longrightarrow \text{H}_2\text{SO}_4 + \text{NO}_2 + \text{H}_2\text{O}$   
 (n)  $\text{NH}_3 + \text{CuO} \longrightarrow \text{Cu} + \text{N}_2 + \text{H}_2\text{O}$

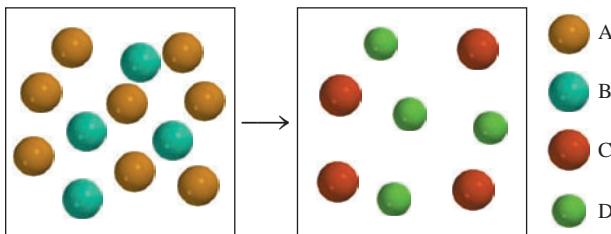
## Amounts of Reactants and Products

### Review Questions

- 3.61 On what law is stoichiometry based? Why is it essential to use balanced equations in solving stoichiometric problems?
- 3.62 Describe the steps involved in the mole method.

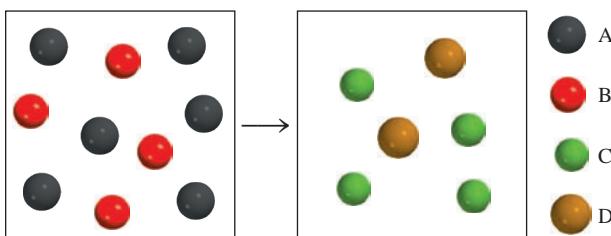
### Problems

- 3.63 Which of the following equations best represents the reaction shown in the diagram?
- (a)  $8\text{A} + 4\text{B} \longrightarrow \text{C} + \text{D}$   
 (b)  $4\text{A} + 8\text{B} \longrightarrow 4\text{C} + 4\text{D}$   
 (c)  $2\text{A} + \text{B} \longrightarrow \text{C} + \text{D}$   
 (d)  $4\text{A} + 2\text{B} \longrightarrow 4\text{C} + 4\text{D}$   
 (e)  $2\text{A} + 4\text{B} \longrightarrow \text{C} + \text{D}$

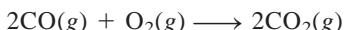


- 3.64** Which of the following equations best represents the reaction shown in the diagram?

- $A + B \longrightarrow C + D$
- $6A + 4B \longrightarrow C + D$
- $A + 2B \longrightarrow 2C + D$
- $3A + 2B \longrightarrow 2C + D$
- $3A + 2B \longrightarrow 4C + 2D$

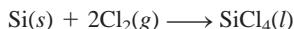


- 3.65** Consider the combustion of carbon monoxide ( $\text{CO}$ ) in oxygen gas



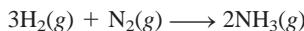
Starting with 3.60 moles of  $\text{CO}$ , calculate the number of moles of  $\text{CO}_2$  produced if there is enough oxygen gas to react with all of the  $\text{CO}$ .

- 3.66** Silicon tetrachloride ( $\text{SiCl}_4$ ) can be prepared by heating Si in chlorine gas:



In one reaction, 0.507 mole of  $\text{SiCl}_4$  is produced. How many moles of molecular chlorine were used in the reaction?

- 3.67** Ammonia is a principal nitrogen fertilizer. It is prepared by the reaction between hydrogen and nitrogen.



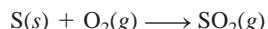
In a particular reaction, 6.0 moles of  $\text{NH}_3$  were produced. How many moles of  $\text{H}_2$  and how many moles of  $\text{N}_2$  were reacted to produce this amount of  $\text{NH}_3$ ?

- 3.68** Consider the combustion of butane ( $\text{C}_4\text{H}_{10}$ ):



In a particular reaction, 5.0 moles of  $\text{C}_4\text{H}_{10}$  are reacted with an excess of  $\text{O}_2$ . Calculate the number of moles of  $\text{CO}_2$  formed.

- 3.69** The annual production of sulfur dioxide from burning coal and fossil fuels, auto exhaust, and other sources is about 26 million tons. The equation for the reaction is



How much sulfur (in tons), present in the original materials, would result in that quantity of  $\text{SO}_2$ ?

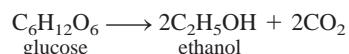
- 3.70** When baking soda (sodium bicarbonate or sodium hydrogen carbonate,  $\text{NaHCO}_3$ ) is heated, it releases carbon dioxide gas, which is responsible for the rising of cookies, donuts, and bread. (a) Write a balanced equation for the decomposition of the compound (one of the products is  $\text{Na}_2\text{CO}_3$ ). (b) Calculate the mass of  $\text{NaHCO}_3$  required to produce 20.5 g of  $\text{CO}_2$ .

- 3.71** When potassium cyanide ( $\text{KCN}$ ) reacts with acids, a deadly poisonous gas, hydrogen cyanide ( $\text{HCN}$ ), is given off. Here is the equation:



If a sample of 0.140 g of  $\text{KCN}$  is treated with an excess of  $\text{HCl}$ , calculate the amount of  $\text{HCN}$  formed, in grams.

- 3.72** Fermentation is a complex chemical process of wine making in which glucose is converted into ethanol and carbon dioxide:



Starting with 500.4 g of glucose, what is the maximum amount of ethanol in grams and in liters that can be obtained by this process? (Density of ethanol = 0.789 g/mL.)

- 3.73** Each copper(II) sulfate unit is associated with five water molecules in crystalline copper(II) sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ). When this compound is heated in air above 100°C, it loses the water molecules and also its blue color:



If 9.60 g of  $\text{CuSO}_4$  are left after heating 15.01 g of the blue compound, calculate the number of moles of  $\text{H}_2\text{O}$  originally present in the compound.

- 3.74** For many years the recovery of gold—that is, the separation of gold from other materials—involved the use of potassium cyanide:

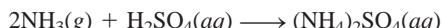


What is the minimum amount of KCN in moles needed to extract 29.0 g (about an ounce) of gold?

**3.75** Limestone ( $\text{CaCO}_3$ ) is decomposed by heating to quicklime ( $\text{CaO}$ ) and carbon dioxide. Calculate how many grams of quicklime can be produced from 1.0 kg of limestone.

**3.76** Nitrous oxide ( $\text{N}_2\text{O}$ ) is also called “laughing gas.” It can be prepared by the thermal decomposition of ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ). The other product is  $\text{H}_2\text{O}$ . (a) Write a balanced equation for this reaction. (b) How many grams of  $\text{N}_2\text{O}$  are formed if 0.46 mole of  $\text{NH}_4\text{NO}_3$  is used in the reaction?

**3.77** The fertilizer ammonium sulfate [ $(\text{NH}_4)_2\text{SO}_4$ ] is prepared by the reaction between ammonia ( $\text{NH}_3$ ) and sulfuric acid:



How many kilograms of  $\text{NH}_3$  are needed to produce  $1.00 \times 10^5$  kg of  $(\text{NH}_4)_2\text{SO}_4$ ?

**3.78** A common laboratory preparation of oxygen gas is the thermal decomposition of potassium chlorate ( $\text{KClO}_3$ ). Assuming complete decomposition, calculate the number of grams of  $\text{O}_2$  gas that can be obtained from 46.0 g of  $\text{KClO}_3$ . (The products are  $\text{KCl}$  and  $\text{O}_2$ .)

## Limiting Reagents

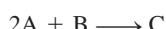
### Review Questions

**3.79** Define limiting reagent and excess reagent. What is the significance of the limiting reagent in predicting the amount of the product obtained in a reaction? Can there be a limiting reagent if only one reactant is present?

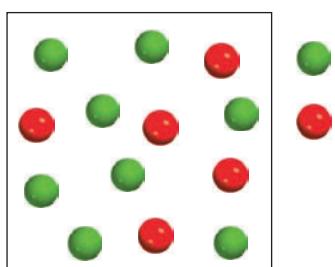
**3.80** Give an everyday example that illustrates the limiting reagent concept.

### Problems

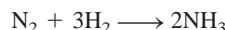
**3.81** Consider the reaction



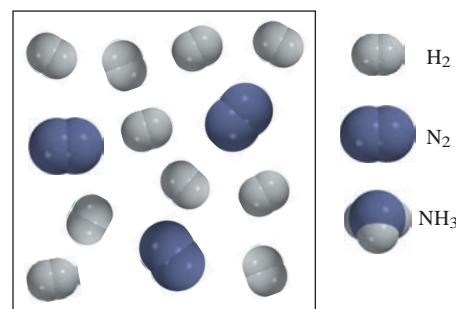
(a) In the diagram here that represents the reaction, which reactant, A or B, is the limiting reagent? (b) Assuming complete reaction, draw a molecular-model representation of the amounts of reactants and products left after the reaction. The atomic arrangement in C is ABA.



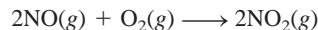
**3.82** Consider the reaction



Assuming each model represents one mole of the substance, show the number of moles of the product and the excess reagent left after the complete reaction.



**3.83** Nitric oxide (NO) reacts with oxygen gas to form nitrogen dioxide ( $\text{NO}_2$ ), a dark-brown gas:



In one experiment 0.886 mole of NO is mixed with 0.503 mole of  $\text{O}_2$ . Calculate which of the two reactants is the limiting reagent. Calculate also the number of moles of  $\text{NO}_2$  produced.

**3.84** The depletion of ozone ( $\text{O}_3$ ) in the stratosphere has been a matter of great concern among scientists in recent years. It is believed that ozone can react with nitric oxide (NO) that is discharged from the high-altitude jet plane, the SST. The reaction is



If 0.740 g of  $\text{O}_3$  reacts with 0.670 g of NO, how many grams of  $\text{NO}_2$  will be produced? Which compound is the limiting reagent? Calculate the number of moles of the excess reagent remaining at the end of the reaction.

**3.85** Propane ( $\text{C}_3\text{H}_8$ ) is a component of natural gas and is used in domestic cooking and heating. (a) Balance the following equation representing the combustion of propane in air:



(b) How many grams of carbon dioxide can be produced by burning 3.65 moles of propane? Assume that oxygen is the excess reagent in this reaction.

**3.86** Consider the reaction



If 0.86 mole of  $\text{MnO}_2$  and 48.2 g of HCl react, which reagent will be used up first? How many grams of  $\text{Cl}_2$  will be produced?

## Reaction Yield

### Review Questions

- 3.87 Why is the theoretical yield of a reaction determined only by the amount of the limiting reagent?
- 3.88 Why is the actual yield of a reaction almost always smaller than the theoretical yield?

### Problems

- 3.89 Hydrogen fluoride is used in the manufacture of Freons (which destroy ozone in the stratosphere) and in the production of aluminum metal. It is prepared by the reaction



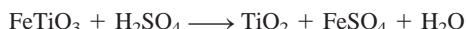
In one process 6.00 kg of  $\text{CaF}_2$  are treated with an excess of  $\text{H}_2\text{SO}_4$  and yield 2.86 kg of HF. Calculate the percent yield of HF.

- 3.90** Nitroglycerin ( $\text{C}_3\text{H}_5\text{N}_3\text{O}_9$ ) is a powerful explosive. Its decomposition can be represented by



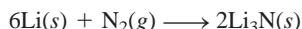
This reaction generates a large amount of heat and many gaseous products. It is the sudden formation of these gases, together with their rapid expansion, that produces the explosion. (a) What is the maximum amount of  $\text{O}_2$  in grams that can be obtained from  $2.00 \times 10^2$  g of nitroglycerin? (b) Calculate the percent yield in this reaction if the amount of  $\text{O}_2$  generated is found to be 6.55 g.

- 3.91 Titanium(IV) oxide ( $\text{TiO}_2$ ) is a white substance produced by the action of sulfuric acid on the mineral ilmenite ( $\text{FeTiO}_3$ ):



Its opaque and nontoxic properties make it suitable as a pigment in plastics and paints. In one process  $8.00 \times 10^3$  kg of  $\text{FeTiO}_3$  yielded  $3.67 \times 10^3$  kg of  $\text{TiO}_2$ . What is the percent yield of the reaction?

- 3.92** When heated, lithium reacts with nitrogen to form lithium nitride:

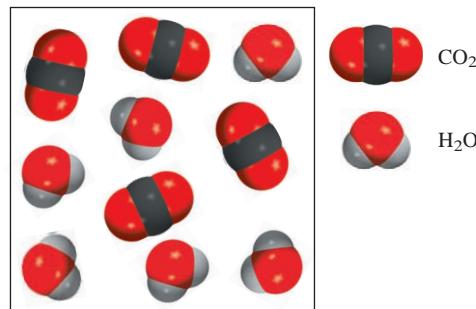


What is the theoretical yield of  $\text{Li}_3\text{N}$  in grams when 12.3 g of Li are heated with 33.6 g of  $\text{N}_2$ ? If the actual yield of  $\text{Li}_3\text{N}$  is 5.89 g, what is the percent yield of the reaction?

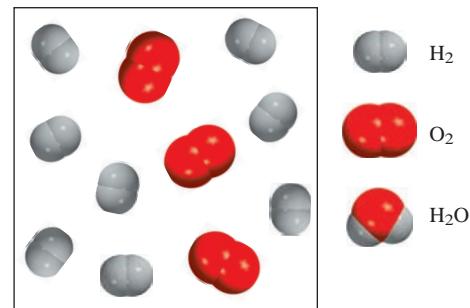
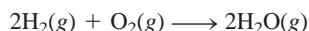
### Additional Problems

- 3.93 The following diagram represents the products ( $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) formed after the combustion of a hydrocarbon (a compound containing only C and H atoms). Write an equation for the reaction.

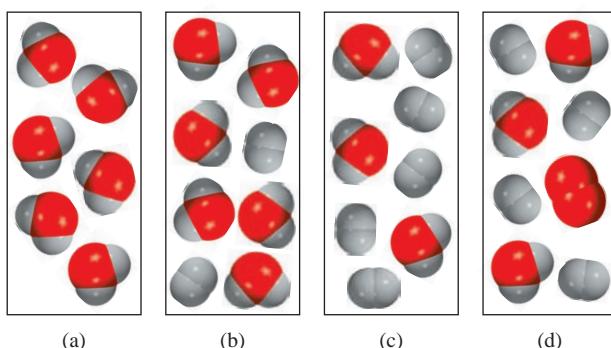
(Hint: The molar mass of the hydrocarbon is about 30 g.)



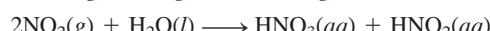
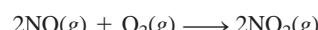
- 3.94** Consider the reaction of hydrogen gas with oxygen gas:



Assuming complete reaction, which of the diagrams shown below represents the amounts of reactants and products left after the reaction?



- 3.95** Industrially, nitric acid is produced by the Ostwald process represented by the following equations:



What mass of  $\text{NH}_3$  (in g) must be used to produce 1.00 ton of  $\text{HNO}_3$  by the above procedure, assuming an 80 percent yield in each step? (1 ton = 2000 lb; 1 lb = 453.6 g.)

- 3.96** A sample of a compound of Cl and O reacts with an excess of  $\text{H}_2$  to give 0.233 g of HCl and 0.403 g of  $\text{H}_2\text{O}$ . Determine the empirical formula of the compound.

- 3.97** The atomic mass of element X is 33.42 amu. A 27.22-g sample of X combines with 84.10 g of another element Y to form a compound XY. Calculate the atomic mass of Y.

- 3.98** The aluminum sulfate hydrate  $[\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}]$  contains 8.20 percent Al by mass. Calculate  $x$ , that is, the number of water molecules associated with each  $\text{Al}_2(\text{SO}_4)_3$  unit.

- 3.99** An iron bar weighed 664 g. After the bar had been standing in moist air for a month, exactly one-eighth of the iron turned to rust ( $\text{Fe}_2\text{O}_3$ ). Calculate the final mass of the iron bar and rust.

- 3.100** A certain metal oxide has the formula MO, where M denotes the metal. A 39.46-g sample of the compound is strongly heated in an atmosphere of hydrogen to remove oxygen as water molecules. At the end, 31.70 g of the metal is left over. If O has an atomic mass of 16.00 amu, calculate the atomic mass of M and identify the element.

- 3.101** An impure sample of zinc (Zn) is treated with an excess of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) to form zinc sulfate ( $\text{ZnSO}_4$ ) and molecular hydrogen ( $\text{H}_2$ ). (a) Write a balanced equation for the reaction. (b) If 0.0764 g of  $\text{H}_2$  is obtained from 3.86 g of the sample, calculate the percent purity of the sample. (c) What assumptions must you make in (b)?

- 3.102** One of the reactions that occurs in a blast furnace, where iron ore is converted to cast iron, is



Suppose that  $1.64 \times 10^3$  kg of Fe are obtained from a  $2.62 \times 10^3$ -kg sample of  $\text{Fe}_2\text{O}_3$ . Assuming that the reaction goes to completion, what is the percent purity of  $\text{Fe}_2\text{O}_3$  in the original sample?

- 3.103** Carbon dioxide ( $\text{CO}_2$ ) is the gas that is mainly responsible for global warming (the greenhouse effect). The burning of fossil fuels is a major cause of the increased concentration of  $\text{CO}_2$  in the atmosphere. Carbon dioxide is also the end product of metabolism (see Example 3.13). Using glucose as an example of food, calculate the annual human production of  $\text{CO}_2$  in grams, assuming that each person consumes  $5.0 \times 10^2$  g of glucose per day. The world's population is 6.5 billion, and there are 365 days in a year.

- 3.104** Carbohydrates are compounds containing carbon, hydrogen, and oxygen in which the hydrogen to oxygen ratio is 2:1. A certain carbohydrate contains 40.0 percent carbon by mass. Calculate the empirical and molecular formulas of the compound if the approximate molar mass is 178 g.

- 3.105** Heating 2.40 g of the oxide of metal X (molar mass of X = 55.9 g/mol) in carbon monoxide (CO) yields the pure metal and carbon dioxide. The mass of the metal product is 1.68 g. From the data given, show that the simplest formula of the oxide is  $\text{X}_2\text{O}_3$  and write a balanced equation for the reaction.

- 3.106** A compound X contains 63.3 percent manganese (Mn) and 36.7 percent O by mass. When X is heated, oxygen gas is evolved and a new compound Y containing 72.0 percent Mn and 28.0 percent O is formed. (a) Determine the empirical formulas of X and Y. (b) Write a balanced equation for the conversion of X to Y.

- 3.107** A sample containing  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{NaNO}_3$  gives the following elemental analysis: Na: 32.08 percent; O: 36.01 percent; Cl: 19.51 percent. Calculate the mass percent of each compound in the sample.

- 3.108** When 0.273 g of Mg is heated strongly in a nitrogen ( $\text{N}_2$ ) atmosphere, a chemical reaction occurs. The product of the reaction weighs 0.378 g. Calculate the empirical formula of the compound containing Mg and N. Name the compound.

- 3.109** A mixture of methane ( $\text{CH}_4$ ) and ethane ( $\text{C}_2\text{H}_6$ ) of mass 13.43 g is completely burned in oxygen. If the total mass of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  produced is 64.84 g, calculate the fraction of  $\text{CH}_4$  in the mixture.

- 3.110** The following is a crude but effective method for estimating the *order of magnitude* of Avogadro's number using stearic acid ( $\text{C}_{18}\text{H}_{36}\text{O}_2$ ). When stearic acid is added to water, its molecules collect at the surface and form a monolayer; that is, the layer is only one molecule thick. The cross-sectional area of each stearic acid molecule has been measured to be  $0.21 \text{ nm}^2$ . In one experiment it is found that  $1.4 \times 10^{-4}$  g of stearic acid is needed to form a monolayer over water in a dish of diameter 20 cm. Based on these measurements, what is Avogadro's number? (The area of a circle of radius  $r$  is  $\pi r^2$ .)

- 3.111** Octane ( $\text{C}_8\text{H}_{18}$ ) is a component of gasoline. Complete combustion of octane yields  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . Incomplete combustion produces  $\text{H}_2\text{O}$  and CO, which not only reduces the efficiency of the engine using the fuel but is also toxic. In a certain test run, 1.000 gallon of octane is burned in an engine. The total mass of CO,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  produced is 11.53 kg. Calculate the efficiency of the process; that is, calculate the fraction of octane converted to  $\text{CO}_2$ . The density of octane is 2.650 kg/gallon.

**3.112** A reaction having a 90 percent yield may be considered a successful experiment. However, in the synthesis of complex molecules such as chlorophyll and many anticancer drugs, a chemist often has to carry out multiple-step synthesis. What is the overall percent yield for such a synthesis, assuming it is a 30-step reaction with a 90 percent yield at each step?

**3.113** A mixture of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  is heated until all the water is lost. If 5.020 g of the mixture gives 2.988 g of the anhydrous salts, what is the percent by mass of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in the mixture?

## SPECIAL PROBLEMS

- 3.114** (a) A research chemist used a mass spectrometer to study the two isotopes of an element. Over time, she recorded a number of mass spectra of these isotopes. On analysis, she noticed that the ratio of the taller peak (the more abundant isotope) to the shorter peak (the less abundant isotope) gradually increased with time. Assuming that the mass spectrometer was functioning normally, what do you think was causing this change?  
 (b) Mass spectrometry can be used to identify the formulas of molecules having small molecular masses. To illustrate this point, identify the molecule which most likely accounts for the observation of a peak in a mass spectrum at: 16 amu, 17 amu, 18 amu, and 64 amu.  
 (c) Note that there are (among others) two likely molecules that would give rise to a peak at 44 amu, namely,  $\text{C}_3\text{H}_8$  and  $\text{CO}_2$ . In such cases, a chemist might try to look for other peaks generated when some of the molecules break apart in the spectrometer. For example, if a chemist sees a peak at 44 amu and also one at 15 amu, which molecule is producing the 44-amu peak? Why?  
 (d) Using the following precise atomic masses:  ${}^1\text{H}$ (1.00797 amu),  ${}^{12}\text{C}$ (12.00000 amu), and  ${}^{16}\text{O}$ (15.99491 amu), how precisely must the masses of  $\text{C}_3\text{H}_8$  and  $\text{CO}_2$  be measured to distinguish between them?  
 (e) Every year millions of dollars' worth of gold is stolen. In most cases the gold is melted down and shipped abroad. This way the gold retains its value while losing all means of identification. Gold is a highly unreactive metal that exists in

nature in the uncombined form. During the mineralization of gold, that is, the formation of gold nuggets from microscopic gold particles, various elements such as cadmium (Cd), lead (Pb), and zinc (Zn) are incorporated into the nuggets. The amounts and types of the impurities or trace elements in gold vary according to the location where it was mined. Based on this knowledge, describe how you would identify the source of a piece of gold suspected of being stolen from Fort Knox, the federal gold depository.

- 3.115** Potash is any potassium mineral that is used for its potassium content. Most of the potash produced in the United States goes into fertilizer. The major sources of potash are potassium chloride ( $\text{KCl}$ ) and potassium sulfate ( $\text{K}_2\text{SO}_4$ ). Potash production is often reported as the potassium oxide ( $\text{K}_2\text{O}$ ) equivalent or the amount of  $\text{K}_2\text{O}$  that could be made from a given mineral. (a) If  $\text{KCl}$  costs \$0.055 per kg, for what price (dollar per kg) must  $\text{K}_2\text{SO}_4$  be sold in order to supply the same amount of potassium on a per dollar basis?  
 (b) What mass (in kg) of  $\text{K}_2\text{O}$  contains the same number of moles of K atoms as 1.00 kg of  $\text{KCl}$ ?  
**3.116** A sample of iron weighing 15.0 g was heated with potassium chlorate ( $\text{KClO}_3$ ) in an evacuated container. The oxygen generated from the decomposition of  $\text{KClO}_3$  converted some of the Fe to  $\text{Fe}_2\text{O}_3$ . If the combined mass of Fe and  $\text{Fe}_2\text{O}_3$  was 17.9 g, calculate the mass of  $\text{Fe}_2\text{O}_3$  formed and the mass of  $\text{KClO}_3$  decomposed.  
**3.117** A certain metal M forms a bromide containing 53.79 percent Br by mass. What is the chemical formula of the compound?

## ANSWERS TO PRACTICE EXERCISES

- 3.1** 10.81 amu. **3.2**  $2.57 \times 10^3$  g. **3.3**  $8.49 \times 10^{21}$  K atoms.  
**3.4**  $2.107 \times 10^{-22}$  g. **3.5** 32.04 amu. **3.6** 1.66 moles.  
**3.7**  $5.81 \times 10^{24}$  H atoms. **3.8** H: 2.055%; S: 32.69%; O: 65.25%. **3.9**  $\text{KMnO}_4$  (potassium permanganate).

- 3.10** 196 g. **3.11**  $\text{B}_2\text{H}_6$ . **3.12**  $\text{Fe}_2\text{O}_3 + 3\text{CO} \longrightarrow 2\text{Fe} + 3\text{CO}_2$ . **3.13** 235 g. **3.14** 0.769 g. **3.15** (a) 234 g, (b) 234 g. **3.16** (a) 863 g, (b) 93.0%.



"Black smoker," insoluble metal sulfides formed on the ocean floor through the lava on a mid-ocean-ridge volcano.

## Reactions in Aqueous Solutions

### CHAPTER OUTLINE

- 4.1** General Properties of Aqueous Solutions 95  
Electrolytes versus Nonelectrolytes
- 4.2** Precipitation Reactions 97  
Solubility • Molecular Equations, Ionic Equations, and Net Ionic Equations
- 4.3** Acid-Base Reactions 101  
General Properties of Acids and Bases • Brønsted Acids and Bases • Acid-Base Neutralization • Acid-Base Reactions Leading to Gas Formation
- 4.4** Oxidation-Reduction Reactions 106  
Oxidation Number • Some Common Oxidation-Reduction Reactions
- 4.5** Concentration of Solutions 114  
Dilution of Solutions
- 4.6** Solution Stoichiometry 118  
Gravimetric Analysis • Acid-Base Titrations

### ESSENTIAL CONCEPTS

**Reactions in Aqueous Solution** Many chemical and almost all biological reactions occur in the aqueous medium. Substances (solute) that dissolve in water (solvent) can be divided into two categories: electrolytes and nonelectrolytes, depending on their ability to conduct electricity.

**Three Major Types of Reactions** In a precipitation reaction, the product, an insoluble substance, separates from solution. Acid-base reactions involve the transfer of a proton ( $H^+$ ) from an acid to a base. In an oxidation-reduction reaction, or redox reaction, electrons are transferred from a reducing agent to an oxidizing agent. These three types of reactions represent the majority of reactions in chemical and biological systems.

**Solution Stoichiometry** Quantitative studies of reactions in solution require that we know the concentration of the solution, which is usually represented by the molarity unit. These studies include gravimetric analysis, which involves the measurement of mass, and titrations in which the unknown concentration of a solution is determined by reaction with a solution of known concentration.



### Interactive Activity Summary

- 1. Animation: Strong Electrolytes, Weak Electrolytes, and Nonelectrolytes (4.1)
- 2. Animation: Hydration (4.1)
- 3. Animation: Precipitation Reactions (4.2)
- 4. Interactivity: Construct a Net Ionic Equation (4.2)
- 5. Animation: Neutralization Reactions (4.3)
- 6. Animation: Oxidation-Reduction Reactions (4.4)
- 7. Animation: Making a Solution (4.5)
- 8. Animation: Preparing a Solution by Dilution (4.5)

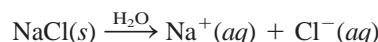
## 4.1 General Properties of Aqueous Solutions

Many chemical reactions and virtually all biological processes take place in an aqueous environment. Therefore, it is important to understand the properties of different substances in solution with water. To start with, what exactly is a solution? A **solution** is a *homogeneous mixture of two or more substances*. The substance present in a smaller amount is called the **solute**, whereas the substance present in a larger amount is called the **solvent**. A solution may be gaseous (such as air), solid (such as an alloy), or liquid (seawater, for example). In this section we will discuss only **aqueous solutions**, in which the solute initially is a liquid or a solid and the solvent is water.

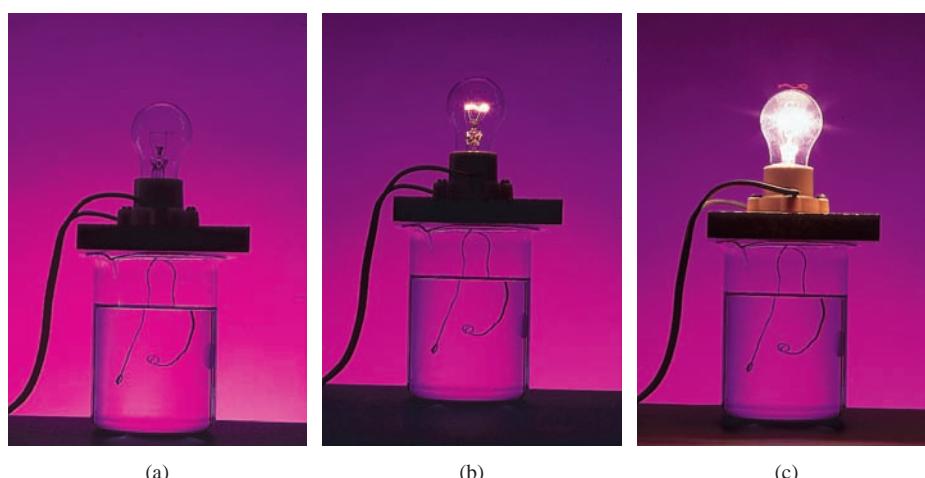
### Electrolytes versus Nonelectrolytes

All solutes that dissolve in water fit into one of two categories: electrolytes and nonelectrolytes. An **electrolyte** is a substance that, when dissolved in water, results in a solution that can conduct electricity. A **nonelectrolyte** does not conduct electricity when dissolved in water. Figure 4.1 shows an easy and straightforward method of distinguishing between electrolytes and nonelectrolytes. A pair of platinum electrodes is immersed in a beaker of water. To light the bulb, electric current must flow from one electrode to the other, thus completing the circuit. Pure water is a very poor conductor of electricity. However, if we add a small amount of sodium chloride (NaCl), the bulb will glow as soon as the salt dissolves in the water. Solid NaCl, an ionic compound, breaks up into  $\text{Na}^+$  and  $\text{Cl}^-$  ions when it dissolves in water. The  $\text{Na}^+$  ions are attracted to the negative electrode and the  $\text{Cl}^-$  ions to the positive electrode. This movement sets up an electrical current that is equivalent to the flow of electrons along a metal wire. Because the NaCl solution conducts electricity, we say that NaCl is an electrolyte. Pure water contains very few ions, so it cannot conduct electricity.

Comparing the lightbulb's brightness for the *same molar amounts* of dissolved substances helps us distinguish between strong and weak electrolytes. A characteristic of strong electrolytes is that the solute is assumed to be 100 percent dissociated into ions in solution. (By *dissociation* we mean the breaking up of the compound into cations and anions.) Thus, we can represent sodium chloride dissolving in water as



What this equation says is that all the sodium chloride that enters the aqueous solution ends up as  $\text{Na}^+$  and  $\text{Cl}^-$  ions; there are no undissociated NaCl units in solution.



**Animation:**  
Strong Electrolytes, Weak  
Electrolytes, and Nonelectrolytes  
ARIS, Animations

**Figure 4.1**  
An arrangement for distinguishing between electrolytes and nonelectrolytes. A solution's ability to conduct electricity depends on the number of ions it contains. (a) A nonelectrolyte solution does not contain ions, and the lightbulb is not lit. (b) A weak electrolyte solution contains a small number of ions, and the lightbulb is dimly lit. (c) A strong electrolyte solution contains a large number of ions, and the lightbulb is brightly lit. The molar amounts of the dissolved solutes are equal in all three cases.

**TABLE 4.1 Classification of Solutes in Aqueous Solution**

Strong Electrolyte	Weak Electrolyte	Nonelectrolyte
HCl	CH <sub>3</sub> COOH	(NH <sub>2</sub> ) <sub>2</sub> CO (urea)
HNO <sub>3</sub>	HF	CH <sub>3</sub> OH (methanol)
HClO <sub>4</sub>	HNO <sub>2</sub>	C <sub>2</sub> H <sub>5</sub> OH (ethanol)
H <sub>2</sub> SO <sub>4</sub> *	NH <sub>3</sub>	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> (glucose)
NaOH	H <sub>2</sub> O <sup>†</sup>	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> (sucrose)
Ba(OH) <sub>2</sub>		
Ionic compounds		

\*H<sub>2</sub>SO<sub>4</sub> has two ionizable H<sup>+</sup> ions.

<sup>†</sup>Pure water is an extremely weak electrolyte.

Table 4.1 lists examples of strong electrolytes, weak electrolytes, and nonelectrolytes. Ionic compounds, such as sodium chloride, potassium iodide (KI), and calcium nitrate [Ca(NO<sub>3</sub>)<sub>2</sub>], are strong electrolytes. It is interesting to note that human body fluids contain many strong and weak electrolytes.

Water is a very effective solvent for ionic compounds. Although water is an electrically neutral molecule, it has a positive end (the H atoms) and a negative end (the O atom), or positive and negative “poles”; for this reason, it is often referred to as a *polar* solvent. When an ionic compound such as sodium chloride dissolves in water, the three-dimensional network of the ions in the solid is destroyed, and the Na<sup>+</sup> and Cl<sup>-</sup> ions are separated from each other. In solution, each Na<sup>+</sup> ion is surrounded by a number of water molecules orienting their negative ends toward the cation. Similarly, each Cl<sup>-</sup> ion is surrounded by water molecules with their positive ends oriented toward the anion (Figure 4.2). *The process in which an ion is surrounded by water molecules arranged in a specific manner is called hydration.* Hydration helps to stabilize ions in solution and prevents cations from combining with anions.

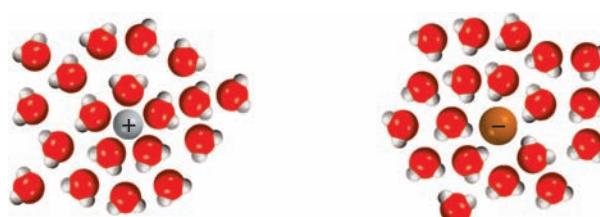
Acids and bases are also electrolytes. Some acids, including hydrochloric acid (HCl) and nitric acid (HNO<sub>3</sub>), are strong electrolytes. These acids ionize completely in water; for example, when hydrogen chloride gas dissolves in water, it forms hydrated H<sup>+</sup> and Cl<sup>-</sup> ions:



In other words, *all* the dissolved HCl molecules separate into hydrated H<sup>+</sup> and Cl<sup>-</sup> ions in solution. Thus, when we write HCl(aq), it is understood that it is a solution of only H<sup>+</sup>(aq) and Cl<sup>-</sup>(aq) ions and there are no hydrated HCl molecules present. On the other hand, certain acids, such as acetic acid (CH<sub>3</sub>COOH), which is found in vinegar, ionize to a much lesser extent. We represent the ionization of acetic acid as



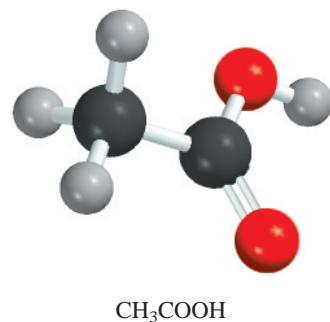
**Figure 4.2**  
*Hydration of Na<sup>+</sup> and Cl<sup>-</sup> ions.*



in which  $\text{CH}_3\text{COO}^-$  is called the acetate ion. (In this book we will use the term *dissociation* for ionic compounds and *ionization* for acids and bases.) By writing the formula of acetic acid as  $\text{CH}_3\text{COOH}$  we indicate that the ionizable proton is in the COOH group.

The double arrow  $\rightleftharpoons$  in an equation means that the reaction is **reversible**; that is, the *reaction can occur in both directions*. Initially, a number of  $\text{CH}_3\text{COOH}$  molecules break up to yield  $\text{CH}_3\text{COO}^-$  and  $\text{H}^+$  ions. As time goes on, some of the  $\text{CH}_3\text{COO}^-$  and  $\text{H}^+$  ions recombine to form  $\text{CH}_3\text{COOH}$  molecules. Eventually, a state is reached in which the acid molecules break up as fast as the ions recombine. Such a *chemical state, in which no net change can be observed* (although continuous activity is taking place on the molecular level), is called **chemical equilibrium**. Acetic acid, then, is a weak electrolyte because its ionization in water is incomplete. By contrast, in a hydrochloric acid solution, the  $\text{H}^+$  and  $\text{Cl}^-$  ions have no tendency to recombine to form molecular HCl. We use the single arrow to represent complete ionizations.

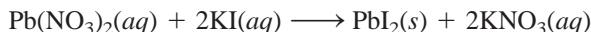
In Sections 4.2–4.4 we will study three types of reactions in the aqueous medium (precipitation, acid-base, and oxidation-reduction) that are of great importance to industrial, environmental, and biological processes. They also play a role in our daily experience.



**There are different types of chemical equilibrium. We will return to this very important topic in Chapter 15.**

## 4.2 Precipitation Reactions

One common type of reaction that occurs in aqueous solution is the **precipitation reaction**, which *results in the formation of an insoluble product, or precipitate*. A **precipitate** is *an insoluble solid that separates from the solution*. Precipitation reactions usually involve ionic compounds. For example, when an aqueous solution of lead(II) nitrate  $[\text{Pb}(\text{NO}_3)_2]$  is added to an aqueous solution of potassium iodide (KI), a yellow precipitate of lead iodide ( $\text{PbI}_2$ ) is formed:

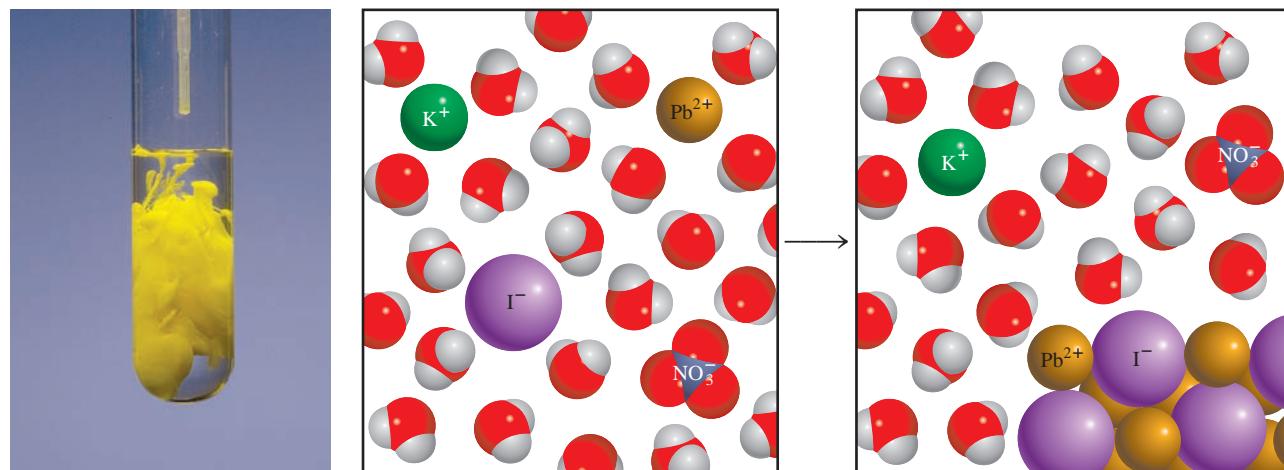


Potassium nitrate remains in solution. Figure 4.3 shows this reaction in progress.

The preceding reaction is an example of a **metathesis reaction** (also called a double displacement reaction), *a reaction that involves the exchange of parts between two*



**Animation:**  
Precipitation Reactions  
ARIS, Animations



**Figure 4.3**

Formation of yellow  $\text{PbI}_2$  precipitate as a solution of  $\text{Pb}(\text{NO}_3)_2$  is added to a solution of KI.

**TABLE 4.2 Solubility Rules for Common Ionic Compounds in Water at 25°C**

Soluble Compounds	Exceptions
Compounds containing alkali metal ions ( $\text{Li}^+$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Rb}^+$ , $\text{Cs}^+$ ) and the ammonium ion ( $\text{NH}_4^+$ )	
Nitrates ( $\text{NO}_3^-$ ), bicarbonates ( $\text{HCO}_3^-$ ), and chlorates ( $\text{ClO}_3^-$ )	
Halides ( $\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$ )	Halides of $\text{Ag}^+$ , $\text{Hg}_2^{2+}$ , and $\text{Pb}^{2+}$
Sulfates ( $\text{SO}_4^{2-}$ )	Sulfates of $\text{Ag}^+$ , $\text{Ca}^{2+}$ , $\text{Sr}^{2+}$ , $\text{Ba}^{2+}$ , $\text{Hg}_2^{2+}$ , and $\text{Pb}^{2+}$
Insoluble Compounds	Exceptions
Carbonates ( $\text{CO}_3^{2-}$ ), phosphates ( $\text{PO}_4^{3-}$ ), chromates ( $\text{CrO}_4^{2-}$ ), and sulfides ( $\text{S}^{2-}$ )	Compounds containing alkali metal ions and the ammonium ion
Hydroxides ( $\text{OH}^-$ )	Compounds containing alkali metal ions and the $\text{Ba}^{2+}$ ion

compounds. (In this case, the compounds exchange the  $\text{NO}_3^-$  and  $\text{I}^-$  ions.) As we will see, the precipitation reactions discussed in this chapter are examples of metathesis reactions.

## Solubility

How can we predict whether a precipitate will form when a compound is added to a solution or when two solutions are mixed? It depends on the **solubility** of the solute, which is defined as *the maximum amount of solute that will dissolve in a given quantity of solvent at a specific temperature*. Chemists refer to substances as soluble, slightly soluble, or insoluble in a qualitative sense. A substance is said to be soluble if a fair amount of it visibly dissolves when added to water. If not, the substance is described as slightly soluble or insoluble. All ionic compounds are strong electrolytes, but they are not equally soluble.

Table 4.2 classifies a number of common ionic compounds as soluble or insoluble. Keep in mind, however, that even insoluble compounds dissolve to a certain extent. Figure 4.4 shows several precipitates.

### Example 4.1

Classify the following ionic compounds as soluble or insoluble: (a) silver sulfate ( $\text{Ag}_2\text{SO}_4$ ), (b) calcium carbonate ( $\text{CaCO}_3$ ), (c) sodium phosphate ( $\text{Na}_3\text{PO}_4$ ).

**Strategy** Although it is not necessary to memorize the solubilities of compounds, you should keep in mind the following useful rules: all ionic compounds containing alkali metal cations; the ammonium ion; and the nitrate, bicarbonate, and chloride ions are soluble. For other compounds we need to refer to Table 4.2.

(Continued)



**Figure 4.4**  
Appearance of several precipitates. From left to right: CdS, PbS, Ni(OH)<sub>2</sub>, Al(OH)<sub>3</sub>.

- Solution** (a) According to Table 4.2, Ag<sub>2</sub>SO<sub>4</sub> is insoluble.  
 (b) This is a carbonate and Ca is a Group 2A metal. Therefore, CaCO<sub>3</sub> is insoluble.  
 (c) Sodium is an alkali metal (Group 1A) so Na<sub>3</sub>PO<sub>4</sub> is soluble.

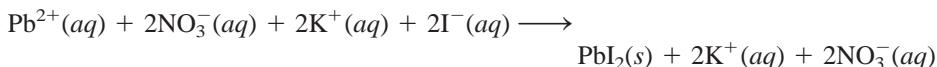
Similar problems: 4.19, 4.20.

- Practice Exercise** Classify the following ionic compounds as soluble or insoluble:  
 (a) CuS, (b) Mg(OH)<sub>2</sub>, (c) Zn(NO<sub>3</sub>)<sub>2</sub>.

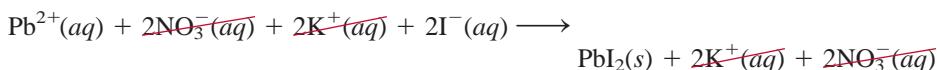
## Molecular Equations, Ionic Equations, and Net Ionic Equations

The equation describing the precipitation of lead iodide on page 97 is called a **molecular equation** because *the formulas of the compounds are written as though all species existed as molecules or whole units*. A molecular equation is useful because it identifies the reagents (that is, lead nitrate and potassium iodide). If we wanted to bring about this reaction in the laboratory, we would use the molecular equation. However, a molecular equation does not describe in detail what actually is happening in solution.

As pointed out earlier, when ionic compounds dissolve in water, they break apart into their component cations and anions. To be more realistic, the equations should show the dissociation of dissolved ionic compounds into ions. Therefore, returning to the reaction between potassium iodide and lead nitrate, we would write



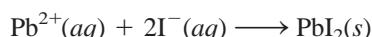
The preceding equation is an example of an **ionic equation**, which *shows dissolved species as free ions*. To see whether a precipitate might form from this solution, we first combine the cation and anion from different compounds; that is, PbI<sub>2</sub> and KNO<sub>3</sub>. Referring to Table 4.2, we see that PbI<sub>2</sub> is an insoluble compound and KNO<sub>3</sub> is soluble. Therefore, the dissolved KNO<sub>3</sub> remains in solution as separate K<sup>+</sup> and NO<sub>3</sub><sup>-</sup> ions, which are called **spectator ions**, or *ions that are not involved in the overall reaction*. Because spectator ions appear on both sides of an equation, they can be eliminated from the ionic equation





**Figure 4.5**  
Formation of  $\text{BaSO}_4$  precipitate.

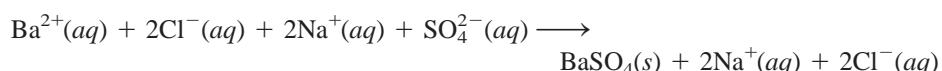
Finally, we end up with the **net ionic equation**, which shows only the species that actually take part in the reaction:



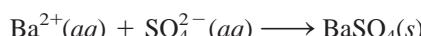
Looking at another example, we find that when an aqueous solution of barium chloride ( $\text{BaCl}_2$ ) is added to an aqueous solution of sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), a white precipitate is formed (Figure 4.5). Treating this as a metathesis reaction, the products are  $\text{BaSO}_4$  and  $\text{NaCl}$ . From Table 4.2 we see that only  $\text{BaSO}_4$  is insoluble. Therefore, we write the molecular equation as



The ionic equation for the reaction is



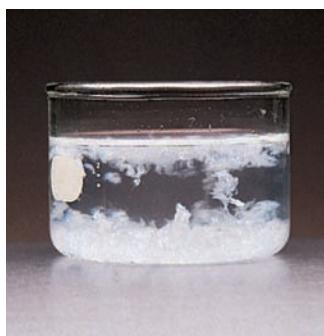
Cancelling the spectator ions ( $\text{Na}^+$  and  $\text{Cl}^-$ ) on both sides of the equation gives us the net ionic equation



**Interactivity:**  
Construct a Net Ionic Equation  
ARIS, Interactives

The following four steps summarize the procedure for writing ionic and net ionic equations:

1. Write a balanced molecular equation for the reaction, using the correct formulas for the reactant and product ionic compounds. Refer to Table 4.2 to decide which of the products is insoluble and therefore will appear as a precipitate.
2. Write the ionic equation for the reaction. The compound that does not appear as the precipitate should be shown as free ions.
3. Identify and cancel the spectator ions on both sides of the equation. Write the net ionic equation for the reaction.
4. Check that the charges and number of atoms balance in the net ionic equation.

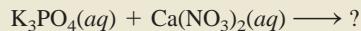


Precipitate formed by the reaction between  $\text{K}_3\text{PO}_4(aq)$  and  $\text{Ca}(\text{NO}_3)_2(aq)$ .

### Example 4.2

Predict what happens when a potassium phosphate ( $\text{K}_3\text{PO}_4$ ) solution is mixed with a calcium nitrate [ $\text{Ca}(\text{NO}_3)_2$ ] solution. Write a net ionic equation for the reaction.

**Strategy** From the given information, it is useful to first write the unbalanced equation



What happens when ionic compounds dissolve in water? What ions are formed from the dissociation of  $\text{K}_3\text{PO}_4$  and  $\text{Ca}(\text{NO}_3)_2$ ? What happens when the cations encounter the anions in solution?

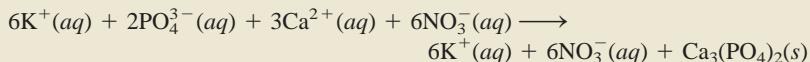
**Solution** In solution,  $\text{K}_3\text{PO}_4$  dissociates into  $\text{K}^+$  and  $\text{PO}_4^{3-}$  ions and  $\text{Ca}(\text{NO}_3)_2$  dissociates into  $\text{Ca}^{2+}$  and  $\text{NO}_3^-$  ions. According to Table 4.2, calcium ions ( $\text{Ca}^{2+}$ ) and phosphate ions ( $\text{PO}_4^{3-}$ ) will form an insoluble compound, calcium phosphate [ $\text{Ca}_3(\text{PO}_4)_2$ ], while the other product,  $\text{KNO}_3$ , is soluble and remains in solution. Therefore, this is a precipitation reaction. We follow the stepwise procedure just outlined.

(Continued)

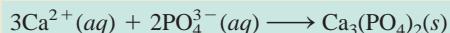
*Step 1:* The balanced molecular equation for this reaction is



*Step 2:* To write the ionic equation, the soluble compounds are shown as dissociated ions:



*Step 3:* Canceling the spectator ions ( $\text{K}^+$  and  $\text{NO}_3^-$ ) on each side of the equation, we obtain the net ionic equation:



*Step 4:* Note that because we balanced the molecular equation first, the net ionic equation is balanced as to the number of atoms on each side and the number of positive (+6) and negative (-6) charges on the left-hand side is the same.

Similar problems: 4.21, 4.22.

**Practice Exercise** Predict the precipitate produced by mixing an  $\text{Al}(\text{NO}_3)_3$  solution with a  $\text{NaOH}$  solution. Write the net ionic equation for the reaction.

## 4.3 Acid-Base Reactions

Acids and bases are as familiar as aspirin and milk of magnesia although many people do not know their chemical names—acetylsalicylic acid (aspirin) and magnesium hydroxide (milk of magnesia). In addition to being the basis of many medicinal and household products, acid-base chemistry is important in industrial processes and essential in sustaining biological systems. Before we can discuss acid-base reactions, we need to know more about acids and bases themselves.

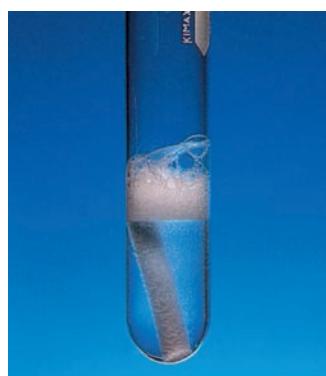
### General Properties of Acids and Bases

In Section 2.7 we defined acids as substances that ionize in water to produce  $\text{H}^+$  ions and bases as substances that ionize in water to produce  $\text{OH}^-$  ions. These definitions were formulated in the late nineteenth century by the Swedish chemist Svante Arrhenius to classify substances whose properties in aqueous solutions were well known.

#### Acids

- Acids have a sour taste; for example, vinegar owes its sourness to acetic acid, and lemons and other citrus fruits contain citric acid.
- Acids cause color changes in plant dyes; for example, they change the color of litmus from blue to red.
- Acids react with certain metals, such as zinc, magnesium, and iron, to produce hydrogen gas. A typical reaction is that between hydrochloric acid and magnesium:



**Figure 4.6**

A piece of blackboard chalk, which is mostly  $\text{CaCO}_3$ , reacts with hydrochloric acid to produce carbon dioxide gas.

- Acids react with carbonates and bicarbonates, such as  $\text{Na}_2\text{CO}_3$ ,  $\text{CaCO}_3$ , and  $\text{NaHCO}_3$ , to produce carbon dioxide gas (Figure 4.6). For example,



- Aqueous acid solutions conduct electricity.

### Bases

- Bases have a bitter taste.
- Bases feel slippery; for example, soaps, which contain bases, exhibit this property.
- Bases cause color changes in plant dyes; for example, they change the color of litmus from red to blue.
- Aqueous base solutions conduct electricity.

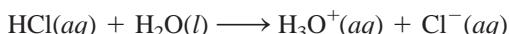
### Brønsted Acids and Bases

Arrhenius's definitions of acids and bases are limited in that they apply only to aqueous solutions. Broader definitions were proposed by the Danish chemist Johannes Brønsted in 1932; a **Brønsted acid** is a proton donor, and a **Brønsted base** is a proton acceptor. Note that Brønsted's definitions do not require acids and bases to be in aqueous solution.

Hydrochloric acid is a Brønsted acid because it donates a proton in water:

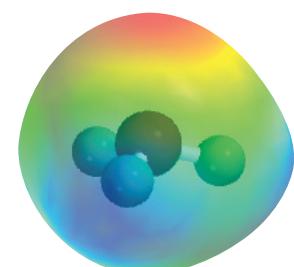


Note that the  $\text{H}^+$  ion is a hydrogen atom that has lost its electron; that is, it is just a bare proton. The size of a proton is about  $10^{-15}\text{m}$ , compared to a diameter of  $10^{-10}\text{m}$  for an average atom or ion. Such an exceedingly small charged particle cannot exist as a separate entity in aqueous solution owing to its strong attraction for the negative pole (the O atom) in  $\text{H}_2\text{O}$ . Consequently, the proton exists in the hydrated form, as shown in Figure 4.7. Therefore, the ionization of hydrochloric acid should be written as



The *hydrated proton*,  $\text{H}_3\text{O}^+$ , is called the **hydronium ion**. This equation shows a reaction in which a Brønsted acid ( $\text{HCl}$ ) donates a proton to a Brønsted base ( $\text{H}_2\text{O}$ ).

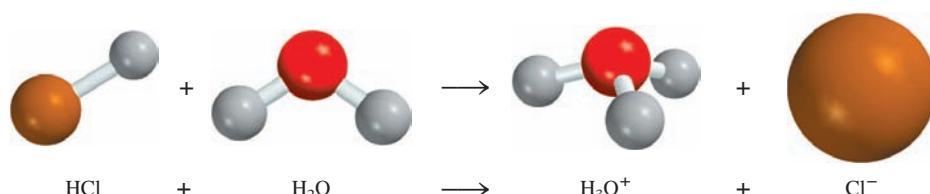
Experiments show that the hydronium ion is further hydrated so that the proton may have several water molecules associated with it. Because the acidic properties of the proton are unaffected by the degree of hydration, in this text we will generally use  $\text{H}^+(aq)$  to represent the hydrated proton. This notation is for convenience, but  $\text{H}_3\text{O}^+$  is closer to reality. Keep in mind that both notations represent the same species in aqueous solution.



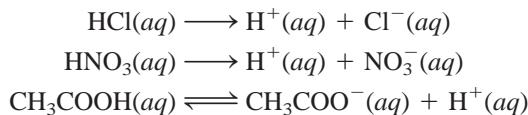
Electrostatic potential map of the  $\text{H}_3\text{O}^+$  ion. In the rainbow color spectrum representation, the most electron-rich region is red and the most electron-poor region is blue.

**Figure 4.7**

*Ionization of HCl in water to form the hydronium ion and the chloride ion.*

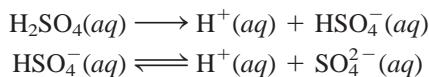


Acids commonly used in the laboratory include hydrochloric acid (HCl), nitric acid ( $\text{HNO}_3$ ), acetic acid ( $\text{CH}_3\text{COOH}$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), and phosphoric acid ( $\text{H}_3\text{PO}_4$ ). The first three are ***monoprotic acids***; that is, *each unit of the acid yields one hydrogen ion upon ionization*:



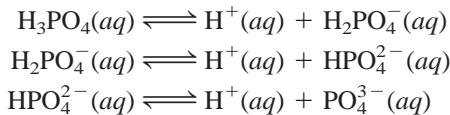
As mentioned earlier, because the ionization of acetic acid is incomplete (note the double arrows), it is a weak electrolyte. For this reason it is called a weak acid (see Table 4.1). On the other hand, HCl and  $\text{HNO}_3$  are strong acids because they are strong electrolytes, so they are completely ionized in solution (note the use of single arrows).

Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is a ***diprotic acid*** because *each unit of the acid gives up two  $\text{H}^+$  ions*, in two separate steps:



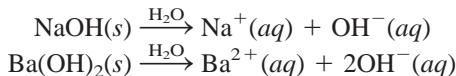
$\text{H}_2\text{SO}_4$  is a strong electrolyte or strong acid (the first step of ionization is complete), but  $\text{HSO}_4^-$  is a weak acid or weak electrolyte, and we need a double arrow to represent its incomplete ionization.

***Triprotic acids***, which *yield three  $\text{H}^+$  ions*, are relatively few in number. The best known triprotic acid is phosphoric acid, whose ionizations are

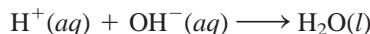


All three species ( $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{HPO}_4^{2-}$ ) in this case are weak acids, and we use the double arrows to represent each ionization step. Anions such as  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  are found in aqueous solutions of phosphates such as  $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$ .

Table 4.1 shows that sodium hydroxide ( $\text{NaOH}$ ) and barium hydroxide [ $\text{Ba}(\text{OH})_2$ ] are strong electrolytes. This means that they are completely ionized in solution:



The  $\text{OH}^-$  ion can accept a proton as follows:



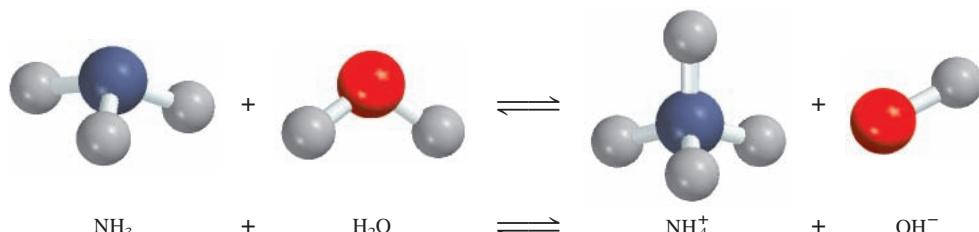
Thus,  $\text{OH}^-$  is a Brønsted base.

Ammonia ( $\text{NH}_3$ ) is classified as a Brønsted base because it can accept a  $\text{H}^+$  ion (Figure 4.8):

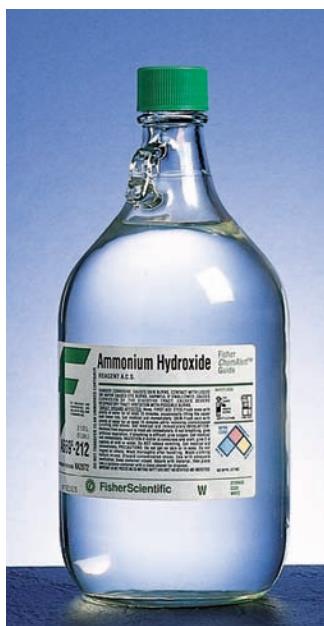


Ammonia is a weak electrolyte (and therefore a weak base) because only a small fraction of dissolved  $\text{NH}_3$  molecules react with water to form  $\text{NH}_4^+$  and  $\text{OH}^-$  ions.

The most commonly used strong base in the laboratory is sodium hydroxide. It is cheap and soluble. (In fact, all of the alkali metal hydroxides are soluble.) The most

**Figure 4.8**

*Ionization of ammonia in water to form the ammonium ion and the hydroxide ion.*



A bottle of aqueous ammonia, which is sometimes erroneously called ammonium hydroxide.

commonly used weak base is aqueous ammonia solution, which is sometimes erroneously called ammonium hydroxide; there is no evidence that the species  $\text{NH}_4\text{OH}$  actually exists other than the  $\text{NH}_4^+$  and  $\text{OH}^-$  ions in solution. All of the Group 2A elements form hydroxides of the type  $\text{M(OH)}_2$ , where M denotes an alkaline earth metal. Of these hydroxides, only  $\text{Ba(OH)}_2$  is soluble. Magnesium and calcium hydroxides are used in medicine and industry. Hydroxides of other metals, such as  $\text{Al(OH)}_3$  and  $\text{Zn(OH)}_2$  are insoluble and are not used as bases.

Example 4.3 classifies substances as Brønsted acids or Brønsted bases.

### Example 4.3

Classify each of the following species in aqueous solution as a Brønsted acid or base:  
(a)  $\text{HBr}$ , (b)  $\text{NO}_2^-$ , (c)  $\text{HCO}_3^-$ .

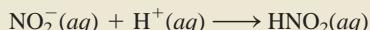
**Strategy** What are the characteristics of a Brønsted acid? Does it contain at least an H atom? With the exception of ammonia, most Brønsted bases that you will encounter at this stage are anions.

**Solution** (a) We know that  $\text{HCl}$  is an acid. Because Br and Cl are both halogens (Group 7A), we expect  $\text{HBr}$ , like  $\text{HCl}$ , to ionize in water as follows:



Therefore,  $\text{HBr}$  is a Brønsted acid.

(b) In solution the nitrite ion can accept a proton from water to form nitrous acid:

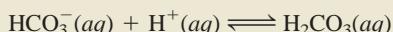


This property makes  $\text{NO}_2^-$  a Brønsted base.

(c) The bicarbonate ion is a Brønsted acid because it ionizes in solution as follows:



It is also a Brønsted base because it can accept a proton to form carbonic acid:



**Comment** The  $\text{HCO}_3^-$  species is said to be *amphoteric* because it possesses both acidic and basic properties. The double arrows show that this is a reversible reaction.

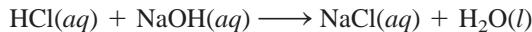
**Practice Exercise** Classify each of the following species as a Brønsted acid or base:  
(a)  $\text{SO}_4^{2-}$ , (b)  $\text{HI}$ , (c)  $\text{H}_2\text{PO}_4^-$ .

## Acid-Base Neutralization

A **neutralization reaction** is a reaction between an acid and a base. Generally, aqueous acid-base reactions produce water and a **salt**, which is an ionic compound made up of a cation other than  $H^+$  and an anion other than  $OH^-$  or  $O^{2-}$ :

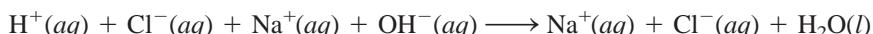


For example, when a HCl solution is mixed with a NaOH solution, the following reaction occurs:

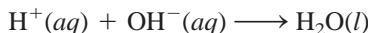


Acid-base reactions generally go to completion.

However, because both the acid and the base are strong electrolytes, they are completely ionized in solution. The ionic equation is



Therefore, the reaction can be represented by the net ionic equation

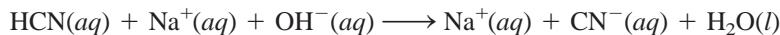


Both  $\text{Na}^+$  and  $\text{Cl}^-$  are spectator ions.

Now consider the reaction between NaOH with hydrocyanic acid (HCN), which is a weak acid:



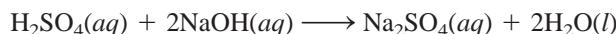
In this case, the ionic equation is



and the net ionic equation is



The following are also examples of acid-base neutralization reactions, represented by molecular equations:



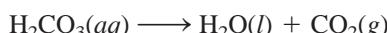
## Acid-Base Reactions Leading to Gas Formation

Certain salts like carbonates (containing the  $\text{CO}_3^{2-}$  ion), bicarbonates (containing the  $\text{HCO}_3^-$  ion), sulfites (containing the  $\text{SO}_3^{2-}$  ion), and sulfides (containing the  $\text{S}^{2-}$  ion) react with acids to form gaseous products. For example, the molecular equation for the reaction between sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and  $\text{HCl}(aq)$  is

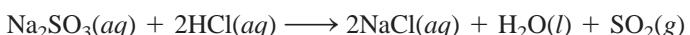
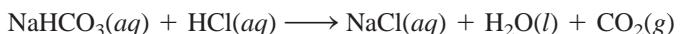


See Figure 4.6 on p. 102.

Carbonic acid is unstable and if present in solution in sufficient concentrations decomposes as follows:



Similar reactions involving other mentioned salts are



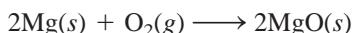
## 4.4 Oxidation-Reduction Reactions



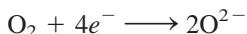
**Animation:**  
Oxidation-Reduction Reactions  
ARIS, Animations

Whereas acid-base reactions can be characterized as proton-transfer processes, the class of reactions called **oxidation-reduction**, or **redox, reactions** are considered *electron-transfer reactions*. Oxidation-reduction reactions are very much a part of the world around us. They range from the burning of fossil fuels to the action of household bleach. Additionally, most metallic and nonmetallic elements are obtained from their ores by the process of oxidation or reduction.

Many important redox reactions take place in water, but not all redox reactions occur in aqueous solution. Nonaqueous redox reactions are less cumbersome to deal with, so we will begin our discussion with a reaction in which two elements combine to form a compound. Consider the formation of magnesium oxide ( $\text{MgO}$ ) from magnesium and oxygen (Figure 4.9):

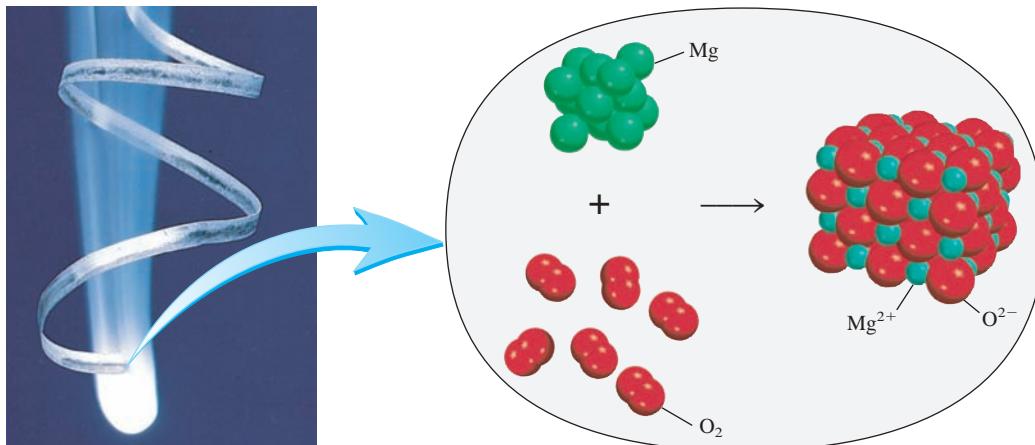
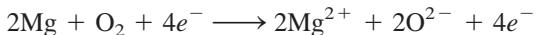


Magnesium oxide ( $\text{MgO}$ ) is an ionic compound made up of  $\text{Mg}^{2+}$  and  $\text{O}^{2-}$  ions. In this reaction, two Mg atoms give up or transfer four electrons to two O atoms (in  $\text{O}_2$ ). For convenience, we can think of this process as two separate steps, one involving the loss of four electrons by the two Mg atoms and the other being the gain of four electrons by an  $\text{O}_2$  molecule:



In oxidation half-reaction, electrons appear as the product; in reduction half-reaction, electrons appear as the reactant.

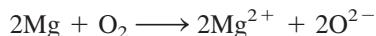
Each of these steps is called a **half-reaction**, which *explicitly shows the electrons involved in a redox reaction*. The sum of the half-reactions gives the overall reaction:



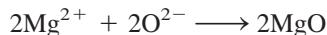
**Figure 4.9**

Magnesium burns in oxygen to form magnesium oxide.

or, if we cancel the electrons that appear on both sides of the equation,



Finally, the  $\text{Mg}^{2+}$  and  $\text{O}^{2-}$  ions combine to form  $\text{MgO}$ :



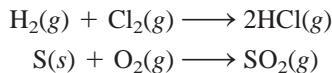
The term **oxidation reaction** refers to the *half-reaction that involves loss of electrons*. Chemists originally used “oxidation” to denote the combination of elements with oxygen. However, it now has a broader meaning that includes reactions not involving oxygen. A **reduction reaction** is a *half-reaction that involves gain of electrons*. In the formation of magnesium oxide, magnesium is oxidized. It is said to act as a **reducing agent** because it *donates electrons* to oxygen and causes oxygen to be reduced. Oxygen is reduced and acts as an **oxidizing agent** because it *accepts electrons* from magnesium, causing magnesium to be oxidized. Note that the extent of oxidation in a redox reaction must be equal to the extent of reduction; that is, the number of electrons lost by a reducing agent must be equal to the number of electrons gained by an oxidizing agent.

A useful mnemonic for redox is OILRIG:  
Oxidation Is Loss (of electrons) and  
Reduction Is Gain (of electrons).

Oxidizing agents are always reduced, and  
reducing agents are always oxidized. This  
statement may be somewhat confusing,  
but it is simply a consequence of the  
definitions of the two processes.

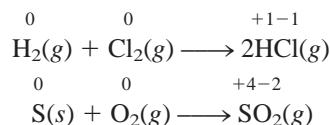
## Oxidation Number

The definitions of oxidation and reduction in terms of loss and gain of electrons apply to the formation of ionic compounds such as  $\text{MgO}$ . However, these definitions do not accurately characterize the formation of hydrogen chloride ( $\text{HCl}$ ) and sulfur dioxide ( $\text{SO}_2$ ):



Because  $\text{HCl}$  and  $\text{SO}_2$  are not ionic but molecular compounds, no electrons are actually transferred in the formation of these compounds, as they are in the case of  $\text{MgO}$ . Nevertheless, chemists find it convenient to treat these reactions as redox reactions because experimental measurements show that there is a partial transfer of electrons (from H to Cl in  $\text{HCl}$  and from S to O in  $\text{SO}_2$ ).

To keep track of electrons in redox reactions, it is useful to assign oxidation numbers to the reactants and products. An atom's **oxidation number**, also called **oxidation state**, signifies the *number of charges the atom would have in a molecule (or an ionic compound) if electrons were transferred completely*. For example, we can rewrite the preceding equations for the formation of  $\text{HCl}$  and  $\text{SO}_2$  as follows:



The numbers above the element symbols are the oxidation numbers. In both of the reactions shown, there is no charge on the atoms in the reactant molecules. Thus, their oxidation number is zero. For the product molecules, however, it is assumed that complete electron transfer has taken place and that atoms have gained or lost electrons. The oxidation numbers reflect the number of electrons “transferred.”

Oxidation numbers enable us to identify elements that are oxidized and reduced at a glance. The elements that show an increase in oxidation number—hydrogen and sulfur in the preceding examples—are oxidized. Chlorine and oxygen are reduced, so

their oxidation numbers show a decrease from their initial values. Note that the sum of the oxidation numbers of H and Cl in HCl (+1 and  $-1$ ) is zero. Likewise, if we add the charges on S (+4) and two atoms of O [ $2 \times (-2)$ ], the total is zero. The reason is that the HCl and SO<sub>2</sub> molecules are neutral, so the charges must cancel.

We use the following rules to assign oxidation numbers:

1. In free elements (that is, in the uncombined state), each atom has an oxidation number of zero. Thus, each atom in H<sub>2</sub>, Br<sub>2</sub>, Na, Be, K, O<sub>2</sub>, and P<sub>4</sub> has the same oxidation number: zero.
2. For ions composed of only one atom (that is, monatomic ions), the oxidation number is equal to the charge on the ion. Thus, Li<sup>+</sup> ion has an oxidation number of +1; Ba<sup>2+</sup> ion, +2; Fe<sup>3+</sup> ion, +3; I<sup>-</sup> ion, -1; O<sup>2-</sup> ion, -2; and so on. All alkali metals have an oxidation number of +1 and all alkaline earth metals have an oxidation number of +2 in their compounds. Aluminum has an oxidation number of +3 in all its compounds.
3. The oxidation number of oxygen in most compounds (for example, MgO and H<sub>2</sub>O) is -2, but in hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and peroxide ion (O<sub>2</sub><sup>2-</sup>), it is -1.
4. The oxidation number of hydrogen is +1, except when it is bonded to metals in binary compounds. In these cases (for example, LiH, NaH, CaH<sub>2</sub>), its oxidation number is -1.
5. Fluorine has an oxidation number of -1 in *all* its compounds. Other halogens (Cl, Br, and I) have negative oxidation numbers when they occur as halide ions in their compounds. When combined with oxygen—for example in oxoacids and oxoanions (see Section 2.7)—they have positive oxidation numbers.
6. In a neutral molecule, the sum of the oxidation numbers of all the atoms must be zero. In a polyatomic ion, the sum of oxidation numbers of all the elements in the ion must be equal to the net charge of the ion. For example, in the ammonium ion, NH<sub>4</sub><sup>+</sup>, the oxidation number of N is -3 and that of H is +1. Thus, the sum of the oxidation numbers is  $-3 + 4(+1) = +1$ , which is equal to the net charge of the ion.
7. Oxidation numbers do not have to be integers. For example, the oxidation number of O in the superoxide ion, O<sub>2</sub><sup>-</sup>, is  $-\frac{1}{2}$ .

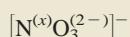
### Example 4.4

Assign oxidation numbers to all the elements in the following compounds and ion:  
 (a) Li<sub>2</sub>O, (b) HNO<sub>3</sub>, (c) Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>.

**Strategy** In general, we follow the rules just listed for assigning oxidation numbers. Remember that all alkali metals have an oxidation number of +1, and in most cases hydrogen has an oxidation number of +1 and oxygen has an oxidation number of -2 in their compounds.

**Solution** (a) By rule 2 we see that lithium has an oxidation number of +1 (Li<sup>+</sup>) and oxygen's oxidation number is -2 (O<sup>2-</sup>).

(b) This is the formula for nitric acid, which yields a H<sup>+</sup> ion and a NO<sub>3</sub><sup>-</sup> ion in solution. From rule 4 we see that H has an oxidation number of +1. Thus, the other group (the nitrate ion) must have a net oxidation number of -1. Oxygen has an oxidation number of -2, and if we use  $x$  to represent the oxidation number of nitrogen, then the nitrate ion can be written as

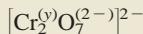


(Continued)

so that  
or

$$x + 3(-2) = -1 \\ x = +5$$

- (c) From rule 6 we see that the sum of the oxidation numbers in the dichromate ion  $\text{Cr}_2\text{O}_7^{2-}$  must be  $-2$ . We know that the oxidation number of O is  $-2$ , so all that remains is to determine the oxidation number of Cr, which we call  $y$ . The dichromate ion can be written as



so that  
or

$$2(y) + 7(-2) = -2 \\ y = +6$$

**Check** In each case, does the sum of the oxidation numbers of all the atoms equal the net charge on the species?

Similar problems: 4.43, 4.45.

**Practice Exercise** Assign oxidation numbers to all the elements in the following compound and ion: (a)  $\text{PF}_3$ , (b)  $\text{MnO}_4^-$ .

Figure 4.10 on p. 110 shows the known oxidation numbers of the familiar elements, arranged according to their positions in the periodic table. We can summarize the content of this figure as follows:

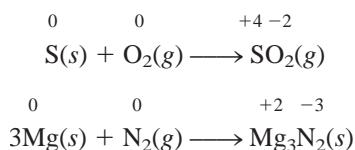
- Metallic elements have only positive oxidation numbers, whereas nonmetallic elements may have either positive or negative oxidation numbers.
- The highest oxidation number an element in Groups 1A–7A can have is its group number. For example, the halogens are in Group 7A, so their highest possible oxidation number is  $+7$ .
- The transition metals (Groups 1B, 3B–8B) usually have several possible oxidation numbers.

## Some Common Oxidation-Reduction Reactions

Among the most common oxidation-reduction reactions are combination, decomposition, combustion, and displacement reactions.

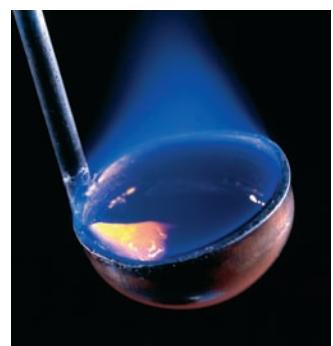
### Combination Reactions

A **combination reaction** is a reaction in which two or more substances combine to form a single product. For example,



### Decomposition Reactions

Decomposition reactions are the opposite of combination reactions. Specifically, a **decomposition reaction** is the breakdown of a compound into two or more components.



Sulfur burning in air to form sulfur dioxide.

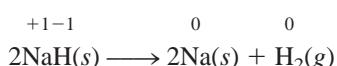
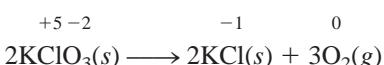
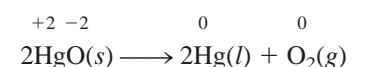
1 1A H +1 -1	2 2A Be +2	3 Li +1	4 Be +2	5 B +3	6 C +4 +2 -4	7 N +5 +4 +3 +2 -1 -2	8 O +2 -2 -1 -2	9 F -1	10 Ne								
11 Na +1	12 Mg +2	3 3B Sc +3	4 4B Ti +4 +3 +2	5 5B V +5 +4 +3 +2	6 6B Cr +6 +5 +4 +3 +2	7 7B Mn +7 +6 +5 +4 +3 +2	8 8B Fe +3 +2	9 Co +3 +2	10 Ni +2 +1	11 1B Cu +2 +1	12 2B Zn +2	13 Al +3	14 Si +4 -4	15 P +5 +3 -3	16 S +6 +4 +2	17 Cl +7 +6 +5 +4 +3 +1 -1	18 Ar
19 K +1	20 Ca +2	21 Sc +3	22 Ti +4 +3 +2	23 V +5 +4 +3 +2	24 Cr +6 +5 +4 +3 +2	25 Mn +7 +6 +5 +4 +3 +2	26 Fe +3 +2	27 Co +3 +2	28 Ni +2 +1	29 Cu +2 +1	30 Zn +2	31 Ga +3	32 Ge +4 -4	33 As +5 +3 -3	34 Se +6 +4 -2	35 Br +5 +3 +1 -1	36 Kr +4 +2
37 Rb +1	38 Sr +2	39 Y +3	40 Zr +4	41 Nb +5 +4 +3	42 Mo +6 +4 +3	43 Tc +7 +6 +4 +3	44 Ru +8 +6 +4 +3	45 Rh +4 +3 +2	46 Pd +4 +2	47 Ag +1	48 Cd +2	49 In +3	50 Sn +4 +2	51 Sb +5 +3 -3	52 Te +6 +4 -2	53 I +7 +5 +1 -1	54 Xe +6 +4 +2
55 Cs +1	56 Ba +2	57 La +3	72 Hf +4	73 Ta +5	74 W +6 +4	75 Re +7 +6 +4	76 Os +8 +4	77 Ir +4 +3	78 Pt +4 +2	79 Au +3 +1	80 Hg +2 +1	81 Tl +3 +1	82 Pb +4 +2	83 Bi +5 +3	84 Po +2	85 At -1	86 Rn

**Figure 4.10**

The oxidation numbers of elements in their compounds. The more common oxidation numbers are in color.



For example,

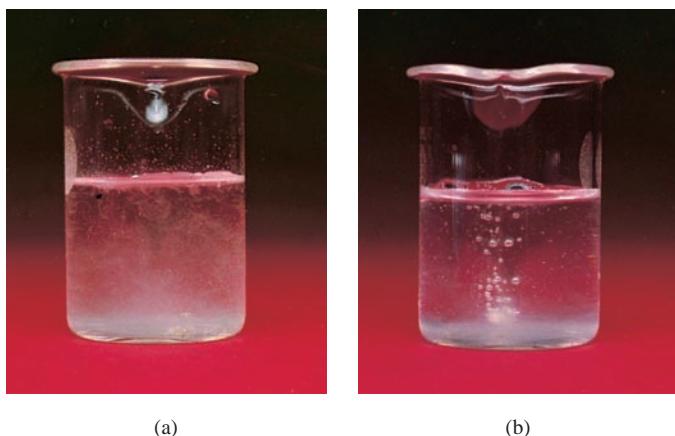


On heating,  $\text{HgO}$  decomposes to give  $\text{Hg}$  and  $\text{O}_2$ .

Note that we show oxidation numbers only for elements that are oxidized or reduced.

## *Combustion Reactions*

A **combustion reaction** is a reaction in which a substance reacts with oxygen, usually with the release of heat and light to produce a flame. The reactions between magnesium



**Figure 4.11**  
Reactions of (a) sodium (Na) and (b) calcium (Ca) with cold water. Note that the reaction is more vigorous with Na than with Ca.

and sulfur with oxygen described earlier are combustion reactions. Another example is the burning of propane ( $C_3H_8$ ), a component of natural gas that is used for domestic heating and cooking:

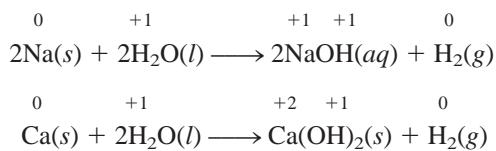


All combustions are redox reactions.

### Displacement Reactions

In a *displacement reaction*, an ion (or atom) in a compound is replaced by an ion (or atom) of another element: Most displacement reactions fit into one of three sub-categories: hydrogen displacement, metal displacement, or halogen displacement.

**1. Hydrogen Displacement.** All alkali metals and some alkaline earth metals (Ca, Sr, and Ba), which are the most reactive of the metallic elements, will displace hydrogen from cold water (Figure 4.11):



Many metals, including those that do not react with water, are capable of displacing hydrogen from acids. For example, zinc (Zn) and magnesium (Mg) do not react with cold water but do react with hydrochloric acid, as follows:

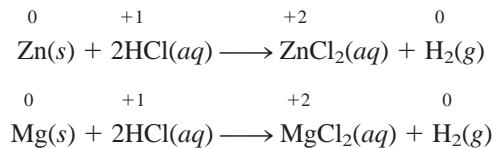
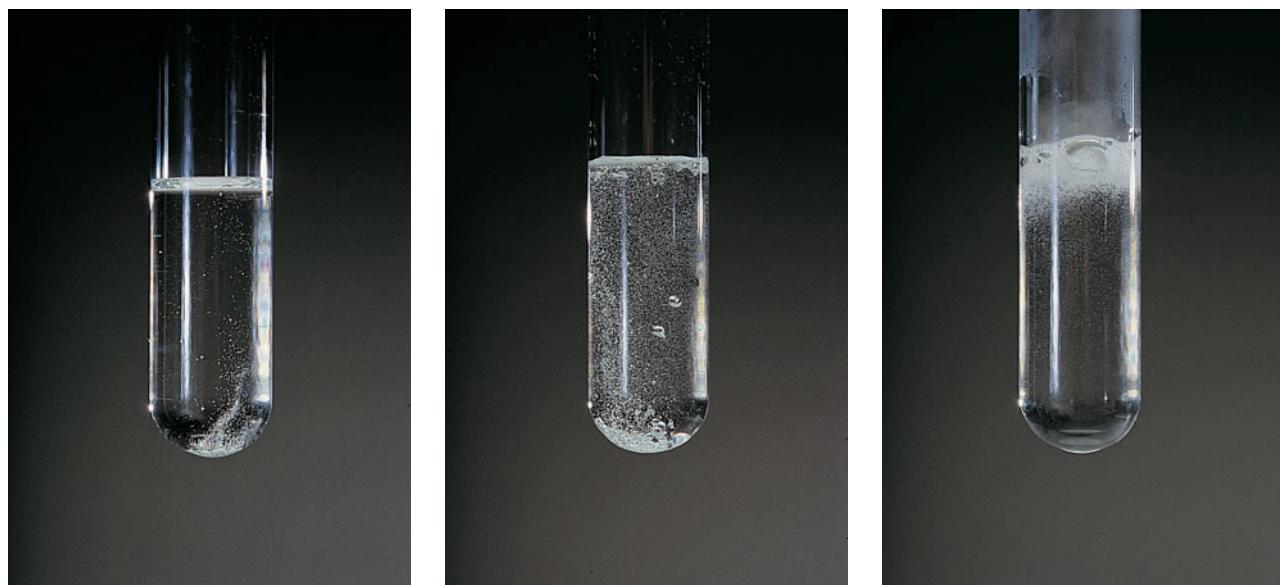


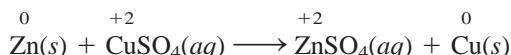
Figure 4.12 shows the reactions between hydrochloric acid (HCl) and iron (Fe), zinc (Zn), and magnesium (Mg). These reactions are used to prepare hydrogen gas in the laboratory.

**2. Metal Displacement.** A metal in a compound can be displaced by another metal in the uncombined state. For example, when metallic zinc is added to a

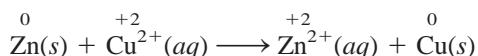
**Figure 4.12**

Left to right: Reactions of iron (Fe), zinc (Zn), and magnesium (Mg) with hydrochloric acid to form hydrogen gas and the metal chlorides ( $\text{FeCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{MgCl}_2$ ). The reactivity of these metals is reflected in the rate of hydrogen gas evolution, which is slowest for the least reactive metal, Fe, and fastest for the most reactive metal, Mg.

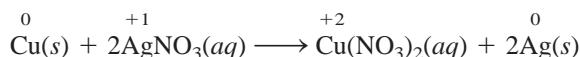
solution containing copper sulfate ( $\text{CuSO}_4$ ), it displaces  $\text{Cu}^{2+}$  ions from the solution (Figure 4.13):



The net ionic equation is



Similarly, metallic copper displaces silver ions from a solution containing silver nitrate ( $\text{AgNO}_3$ ) (also shown in Figure 4.13):

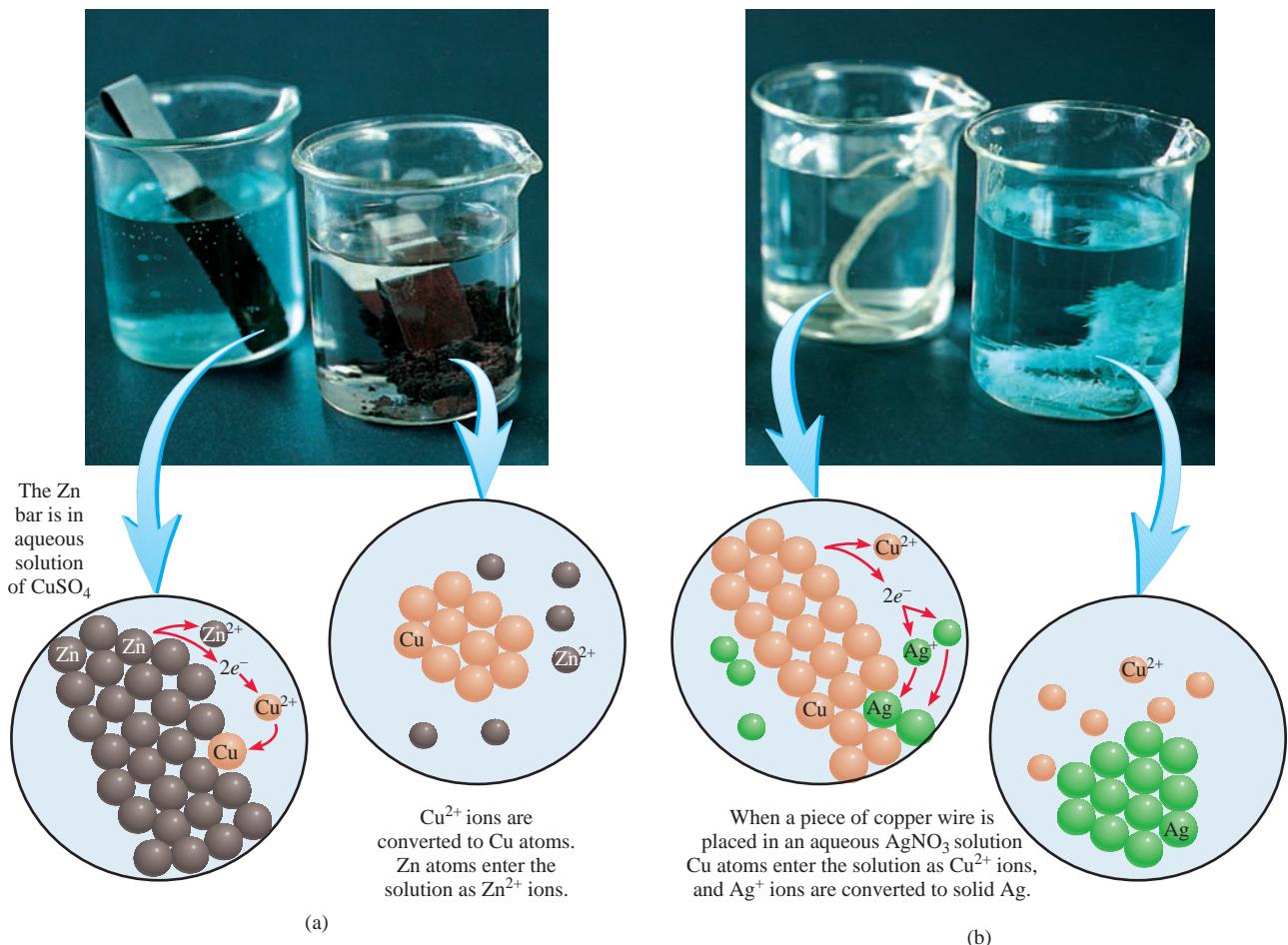


The net ionic equation is



Reversing the roles of the metals would result in no reaction. In other words, copper metal will not displace zinc ions from zinc sulfate, and silver metal will not displace copper ions from copper nitrate.

An easy way to predict whether a metal or hydrogen displacement reaction will actually occur is to refer to an *activity series* (sometimes called the *electrochemical series*), shown in Figure 4.14. Basically, an activity series is a *convenient summary of the results of many possible displacement reactions* similar to the ones already discussed. According to this series, any metal above hydrogen will displace it from water or from an acid,



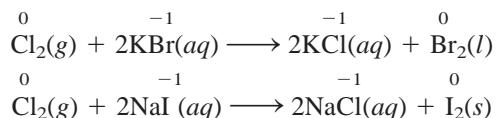
**Figure 4.13**  
Metal displacement reactions in solution.

but metals below hydrogen will not react with either water or an acid. In fact, any metal listed in the series will react with any metal (in a compound) below it. For example, Zn is above Cu, so zinc metal will displace copper ions from copper sulfate.

**3. Halogen Displacement.** Another activity series summarizes the halogens' behavior in halogen displacement reactions:



The power of these elements as oxidizing agents decreases as we move down Group 7A from fluorine to iodine, so molecular fluorine can replace chloride, bromide, and iodide ions in solution. In fact, molecular fluorine is so reactive that it also attacks water; thus, these reactions cannot be carried out in aqueous solutions. On the other hand, molecular chlorine can displace bromide and iodide ions in aqueous solution. The displacement equations are



1A	2A								8A

The halogens.

**Figure 4.14**

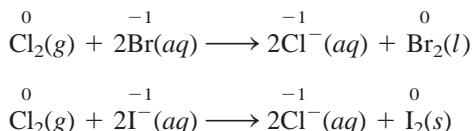
The activity series for metals. The metals are arranged according to their ability to displace hydrogen from an acid or water. Li (lithium) is the most reactive metal, and Au (gold) is the least reactive.

$\text{Li} \rightarrow \text{Li}^+ + e^-$ $\text{K} \rightarrow \text{K}^+ + e^-$ $\text{Ba} \rightarrow \text{Ba}^{2+} + 2e^-$ $\text{Ca} \rightarrow \text{Ca}^{2+} + 2e^-$ $\text{Na} \rightarrow \text{Na}^+ + e^-$ $\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-$ $\text{Al} \rightarrow \text{Al}^{3+} + 3e^-$ $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$ $\text{Cr} \rightarrow \text{Cr}^{3+} + 3e^-$ $\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$ $\text{Cd} \rightarrow \text{Cd}^{2+} + 2e^-$ $\text{Co} \rightarrow \text{Co}^{2+} + 2e^-$ $\text{Ni} \rightarrow \text{Ni}^{2+} + 2e^-$ $\text{Sn} \rightarrow \text{Sn}^{2+} + 2e^-$ $\text{Pb} \rightarrow \text{Pb}^{2+} + 2e^-$ $\text{H}_2 \rightarrow 2\text{H}^+ + 2e^-$ $\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^-$ $\text{Ag} \rightarrow \text{Ag}^+ + e^-$ $\text{Hg} \rightarrow \text{Hg}^{2+} + 2e^-$ $\text{Pt} \rightarrow \text{Pt}^{2+} + 2e^-$ $\text{Au} \rightarrow \text{Au}^{3+} + 3e^-$	React with cold water to produce $\text{H}_2$  React with steam to produce $\text{H}_2$  React with acids to produce $\text{H}_2$  Do not react with water or acids to produce $\text{H}_2$
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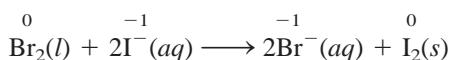


Industrially, bromine (a fuming red liquid) is prepared by the action of chlorine on seawater, which is a rich source of  $\text{Br}^-$  ions.

The ionic equations are



Molecular bromine, in turn, can displace iodide ion in solution:



Reversing the roles of the halogens produces no reaction. Thus, bromine cannot displace chloride ions, and iodine cannot displace bromide and chloride ions.

## 4.5 Concentration of Solutions

To study solution stoichiometry, we must know how much of the reactants are present in a solution and also how to control the amounts of reactants used to bring about a reaction in aqueous solution.

The **concentration of a solution** is the amount of solute present in a given quantity of solution. (For this discussion, we will assume the solute is a liquid or a solid and the solvent is a liquid.) The concentration of a solution can be expressed in many different ways, as we will see in Chapter 12. Here we will consider one of the most commonly used units in chemistry, **molarity ( $M$ )**, or **molar concentration**, which is the number of moles of solute per liter of solution. Molarity is defined as

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of soln}} \quad (4.1)$$

where “soln” denotes “solution.” Equation (4.1) can also be expressed algebraically as

$$M = \frac{n}{V} \quad (4.2)$$

where  $n$  denotes the number of moles of solute and  $V$  is the volume of the solution in liters. Thus, a 1.46 molar glucose ( $C_6H_{12}O_6$ ) solution, written  $1.46\text{ M } C_6H_{12}O_6$ , contains 1.46 moles of the solute ( $C_6H_{12}O_6$ ) in 1 L of the solution; a 0.52 molar urea [ $(NH_2)_2CO$ ] solution, written  $0.52\text{ M } (NH_2)_2CO$ , contains 0.52 mole of  $(NH_2)_2CO$  (the solute) in 1 L of solution; and so on.

Of course, we do not always work with solution volumes of exactly 1 L. This is not a problem as long as we remember to convert the volume of the solution to liters. Thus, a 500-mL solution containing 0.730 mole of  $C_6H_{12}O_6$  also has a concentration of  $1.46\text{ M}$ :

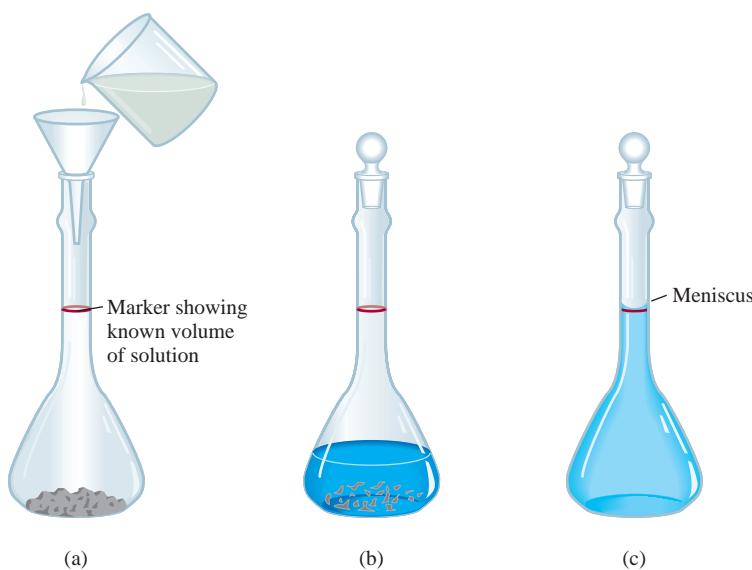
$$\begin{aligned} M = \text{molarity} &= \frac{0.730 \text{ mol}}{0.500 \text{ L}} \\ &= 1.46 \text{ mol/L} = 1.46\text{ M} \end{aligned}$$

As you can see, the unit of molarity is moles per liter, so a 500-mL solution containing 0.730 mole of  $C_6H_{12}O_6$  is equivalent to  $1.46\text{ mol/L}$  or  $1.46\text{ M}$ . Note that concentration, like density, is an intensive property, so its value does not depend on how much of the solution is present.

The procedure for preparing a solution of known molarity is as follows. First, the solute is accurately weighed and transferred to a volumetric flask through a funnel (Figure 4.15). Next, water is added to the flask, which is carefully swirled to dissolve the solid. After *all* the solid has dissolved, more water is added slowly to bring the level of solution exactly to the volume mark. Knowing the volume of the solution in the flask and the quantity of compound (the number of moles) dissolved, we can calculate the molarity of the solution using Equation (4.1). Note that this procedure does not require knowing the amount of water added, as long as the volume of the final solution is known.



**Animation:**  
Making a Solution  
ARIS, Animations



**Figure 4.15**  
*Preparing a solution of known molarity. (a) A known amount of a solid solute is transferred into the volumetric flask; then water is added through a funnel. (b) The solid is slowly dissolved by gently swirling the flask. (c) After the solid has completely dissolved, more water is added to bring the level of solution to the mark. Knowing the volume of the solution and the amount of solute dissolved in it, we can calculate the molarity of the prepared solution.*

A  $\text{K}_2\text{Cr}_2\text{O}_7$  solution.

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### Example 4.5

 ARIS Presentation Center, Worked Examples

How many grams of potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) are required to prepare a 250-mL solution whose concentration is 2.16 M?

**Strategy** How many moles of  $\text{K}_2\text{Cr}_2\text{O}_7$  does a 1-L (or 1000 mL) 2.16 M  $\text{K}_2\text{Cr}_2\text{O}_7$  solution contain? A 250-mL solution? How would you convert moles to grams?

**Solution** The first step is to determine the number of moles of  $\text{K}_2\text{Cr}_2\text{O}_7$  in 250 mL or 0.250 L of a 2.16 M solution:

$$\begin{aligned}\text{moles of } \text{K}_2\text{Cr}_2\text{O}_7 &= 0.250 \text{ L soln} \times \frac{2.16 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7}{1 \text{ L soln}} \\ &= 0.540 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7\end{aligned}$$

The molar mass of  $\text{K}_2\text{Cr}_2\text{O}_7$  is 294.2 g, so we write

$$\begin{aligned}\text{grams of } \text{K}_2\text{Cr}_2\text{O}_7 \text{ needed} &= 0.540 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7 \times \frac{294.2 \text{ g } \text{K}_2\text{Cr}_2\text{O}_7}{1 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7} \\ &= 159 \text{ g } \text{K}_2\text{Cr}_2\text{O}_7\end{aligned}$$

**Check** As a ball-park estimate, the mass should be given by [molarity (mol/L)  $\times$  volume (L)  $\times$  molar mass (g/mol)] or [2 mol/L  $\times$  0.25 L  $\times$  300 g/mol] = 150 g. So the answer is reasonable.

Similar problems: 4.56, 4.57.

**Practice Exercise** What is the molarity of an 85.0-mL ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) solution containing 1.77 g of ethanol?

### Example 4.6

 ARIS Presentation Center, Worked Examples

In a biochemical essay, a chemist needs to add 3.81 g of glucose to a reaction mixture. Calculate the volume in milliliters of a 2.53 M glucose solution she should use for the addition.

**Strategy** We must first determine the number of moles contained in 3.81 g of glucose and then use Equation (4.2) to calculate the volume.

**Solution** From the molar mass of glucose, we write

$$3.81 \text{ g } \text{C}_6\text{H}_{12}\text{O}_6 \times \frac{1 \text{ mol } \text{C}_6\text{H}_{12}\text{O}_6}{180.2 \text{ g } \text{C}_6\text{H}_{12}\text{O}_6} = 2.114 \times 10^{-2} \text{ mol } \text{C}_6\text{H}_{12}\text{O}_6$$

Next, we calculate the volume of the solution that contains  $2.114 \times 10^{-2}$  mole of the solute. Rearranging Equation (4.2) gives

$$\begin{aligned}V &= \frac{n}{M} \\ &= \frac{2.114 \times 10^{-2} \text{ mol } \text{C}_6\text{H}_{12}\text{O}_6}{2.53 \text{ mol } \text{C}_6\text{H}_{12}\text{O}_6/\text{L soln}} \times \frac{1000 \text{ mL soln}}{1 \text{ L soln}} \\ &= 8.36 \text{ mL soln}\end{aligned}$$

**Check** One liter of the solution contains 2.53 moles of  $\text{C}_6\text{H}_{12}\text{O}_6$ . Therefore, the number of moles in 8.36 mL or  $8.36 \times 10^{-3}$  L is  $(2.53 \text{ mol} \times 8.36 \times 10^{-3})$  or  $2.12 \times 10^{-2}$  mol. The small difference is due to the different ways of rounding off.

Similar problem: 4.59.

**Practice Exercise** What volume (in milliliters) of a 0.315 M NaOH solution contains 6.22 g of NaOH?

## Dilution of Solutions

Concentrated solutions are often stored in the laboratory stockroom for use as needed. Frequently we dilute these “stock” solutions before working with them. **Dilution** is the procedure for preparing a less concentrated solution from a more concentrated one.

Suppose that we want to prepare 1 L of a 0.400 *M* KMnO<sub>4</sub> solution from a solution of 1.00 *M* KMnO<sub>4</sub>. For this purpose, we need 0.400 mole of KMnO<sub>4</sub>. Because there is 1.00 mole of KMnO<sub>4</sub> in 1 L of a 1.00 *M* KMnO<sub>4</sub> solution, there is 0.400 mole of KMnO<sub>4</sub> in 0.400 L of the same solution:

$$\frac{1.00 \text{ mol}}{1 \text{ L soln}} = \frac{0.400 \text{ mol}}{0.400 \text{ L soln}}$$

Therefore, we must withdraw 400 mL from the 1.00 *M* KMnO<sub>4</sub> solution and dilute it to 1000 mL by adding water (in a 1-L volumetric flask). This method gives us 1 L of the desired solution of 0.400 *M* KMnO<sub>4</sub>.

In carrying out a dilution process, it is useful to remember that adding more solvent to a given amount of the stock solution changes (decreases) the concentration of the solution without changing the number of moles of solute present in the solution (Figure 4.16). In other words,

$$\text{moles of solute before dilution} = \text{moles of solute after dilution}$$

Because molarity is defined as moles of solute in one liter of solution, we see that the number of moles of solute is given by

$$\underbrace{\frac{\text{moles of solute}}{\text{liters of soln}}}_{M} \times \underbrace{\text{volume of soln (in liters)}}_V = \text{moles of solute}$$

or

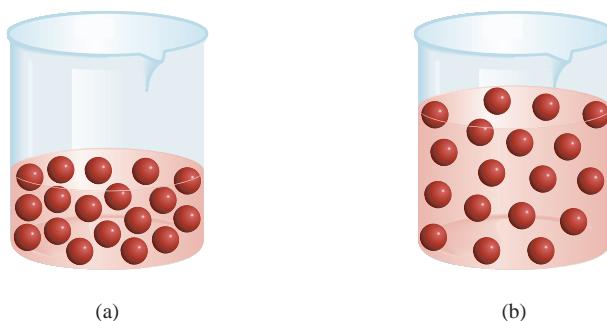
$$MV = \text{moles of solute}$$

Because all the solute comes from the original stock solution, we can conclude that

$M_i V_i$	=	$M_f V_f$	(4.3)
moles of solute before dilution		moles of solute after dilution	



Two KMnO<sub>4</sub> solutions of different concentrations.



**Figure 4.16**

The dilution of a more concentrated solution (a) to a less concentrated one (b) does not change the total number of solute particles (18).

where  $M_i$  and  $M_f$  are the initial and final concentrations of the solution in molarity and  $V_i$  and  $V_f$  are the initial and final volumes of the solution, respectively. Of course, the units of  $V_i$  and  $V_f$  must be the same (mL or L) for the calculation to work. To check the reasonableness of your results, be sure that  $M_i > M_f$  and  $V_f > V_i$ .

### Example 4.7

Describe how you would prepare  $5.00 \times 10^2$  mL of a  $1.75\text{ M}$   $\text{H}_2\text{SO}_4$  solution, starting with an  $8.61\text{ M}$  stock solution of  $\text{H}_2\text{SO}_4$ .

**Strategy** Because the concentration of the final solution is less than that of the original one, this is a dilution process. Keep in mind that in dilution, the concentration of the solution decreases but the number of moles of the solute remains the same.

**Solution** We prepare for the calculation by tabulating our data:

$$\begin{array}{ll} M_i = 8.61\text{ M} & M_f = 1.75\text{ M} \\ V_i = ? & V_f = 5.00 \times 10^2\text{ mL} \end{array}$$

Substituting in Equation (4.3),

$$\begin{aligned} (8.61\text{ M})(V_i) &= (1.75\text{ M})(5.00 \times 10^2\text{ mL}) \\ V_i &= \frac{(1.75\text{ M})(5.00 \times 10^2\text{ mL})}{8.61\text{ M}} \\ &= 102\text{ mL} \end{aligned}$$

Thus, we must dilute 102 mL of the  $8.61\text{ M}$   $\text{H}_2\text{SO}_4$  solution with sufficient water to give a final volume of  $5.00 \times 10^2$  mL in a 500-mL volumetric flask to obtain the desired concentration.

**Similar problems:** 4.65, 4.66.

**Check** The initial volume is less than the final volume, so the answer is reasonable.

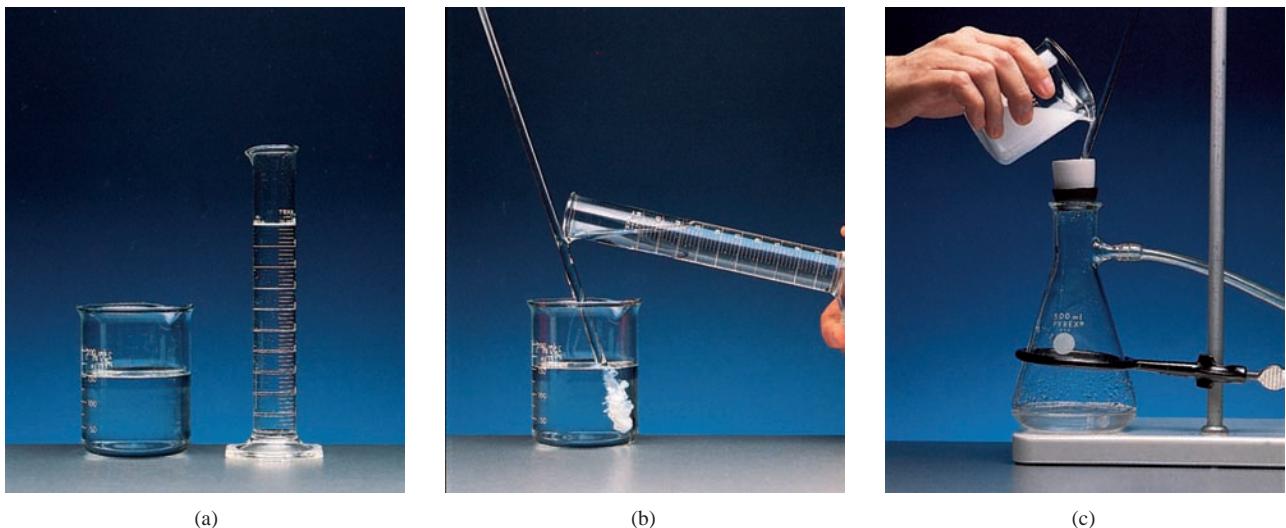
**Practice Exercise** How would you prepare  $2.00 \times 10^2$  mL of a  $0.866\text{ M}$   $\text{NaOH}$  solution, starting with a  $5.07\text{ M}$  stock solution?

## 4.6 Solution Stoichiometry

In Chapter 3 we studied stoichiometric calculations in terms of the mole method, which treats the coefficients in a balanced equation as the number of moles of reactants and products. In working with solutions of known molarity, we have to use the relationship  $MV = \text{moles of solute}$ . We will examine two types of common solution stoichiometry here: gravimetric analysis and acid-base titration.

### Gravimetric Analysis

**Gravimetric analysis** is an analytical technique based on the measurement of mass. One type of gravimetric analysis experiment involves the formation, isolation, and mass determination of a precipitate. Generally, this procedure is applied to ionic compounds. A sample substance of unknown composition is dissolved in water and allowed to react with another substance to form a precipitate. The precipitate is filtered off, dried, and weighed. Knowing the mass and chemical formula of the precipitate formed, we can calculate the mass of a particular chemical component (that is, the anion or cation) of the original sample. From the mass of the component and

**Figure 4.17**

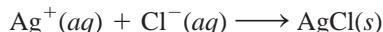
*Basic steps for gravimetric analysis. (a) A solution containing a known amount of NaCl in a beaker. (b) The precipitation of AgCl upon the addition of AgNO<sub>3</sub> solution from a measuring cylinder. In this reaction, AgNO<sub>3</sub> is the excess reagent and NaCl is the limiting reagent. (c) The solution containing the AgCl precipitate is filtered through a preweighed sintered-disk crucible, which allows the liquid (but not the precipitate) to pass through. The crucible is then removed from the apparatus, dried in an oven, and weighed again. The difference between this mass and that of the empty crucible gives the mass of the AgCl precipitate.*

the mass of the original sample, we can determine the percent composition by mass of the component in the original compound.

A reaction that is often studied in gravimetric analysis, because the reactants can be obtained in pure form, is



The net ionic equation is



The precipitate is AgCl (see Table 4.2). As an example, let's say that we are interested in knowing the purity of a sample of NaCl obtained from seawater. To do so we need to determine *experimentally* the percent by mass of Cl in NaCl. First we would accurately weigh out a sample of the NaCl and dissolve it in water. Next, we would add enough AgNO<sub>3</sub> solution to the NaCl solution to cause the precipitation of all the Cl<sup>-</sup> ions present in solution as AgCl. In this procedure, NaCl is the limiting reagent and AgNO<sub>3</sub> the excess reagent. The AgCl precipitate is separated from the solution by filtration, dried, and weighed. From the measured mass of AgCl, we can calculate the mass of Cl using the percent by mass of Cl in AgCl. Because this same amount of Cl was present in the original NaCl sample, we can calculate the percent by mass of Cl in NaCl and hence deduce its purity. Figure 4.17 shows how this procedure is performed.

Gravimetric analysis is a highly accurate technique, because the mass of a sample can be measured accurately. However, this procedure is applicable only to reactions that go to completion, or have nearly 100 percent yield. Thus, if AgCl were slightly soluble instead of being insoluble, it would not be possible to remove all the Cl<sup>-</sup> ions from the NaCl solution and the subsequent calculation would be in error.

### Example 4.8

A 0.5662-g sample of an ionic compound containing chloride ions and an unknown metal is dissolved in water and treated with an excess of  $\text{AgNO}_3$ . If 1.0882 g of  $\text{AgCl}$  precipitate forms, what is the percent by mass of Cl in the original compound?

**Strategy** We are asked to calculate the percent by mass of Cl in the unknown sample, which is

$$\% \text{ Cl} = \frac{\text{mass of Cl}}{0.5662 \text{ g sample}} \times 100\%$$

The only source of  $\text{Cl}^-$  ions is the original compound. These chloride ions eventually end up in the  $\text{AgCl}$  precipitate. Can we calculate the mass of the  $\text{Cl}^-$  ions if we know the percent by mass of Cl in  $\text{AgCl}$ ?

In general, gravimetric analysis does not establish the identity of the unknown, but it does narrow the possibilities.

**Solution** The molar masses of Cl and  $\text{AgCl}$  are 35.45 g and 143.4 g, respectively. Therefore, the percent by mass of Cl in  $\text{AgCl}$  is given by

$$\begin{aligned}\% \text{ Cl} &= \frac{35.45 \text{ g Cl}}{143.4 \text{ g AgCl}} \times 100\% \\ &= 24.72\%\end{aligned}$$

Next we calculate the mass of Cl in 1.0882 g of  $\text{AgCl}$ . To do so we convert 24.72 percent to 0.2472 and write

$$\begin{aligned}\text{mass of Cl} &= 0.2472 \times 1.0882 \text{ g} \\ &= 0.2690 \text{ g}\end{aligned}$$

Because the original compound also contained this amount of  $\text{Cl}^-$  ions, the percent by mass of Cl in the compound is

$$\begin{aligned}\% \text{ Cl} &= \frac{0.2690 \text{ g}}{0.5662 \text{ g}} \times 100\% \\ &= 47.51\%\end{aligned}$$

Similar problem: 4.72.

**Practice Exercise** A sample of 0.3220 g of an ionic compound containing the bromide ion ( $\text{Br}^-$ ) is dissolved in water and treated with an excess of  $\text{AgNO}_3$ . If the mass of the  $\text{AgBr}$  precipitate that forms is 0.6964 g, what is the percent by mass of Br in the original compound?

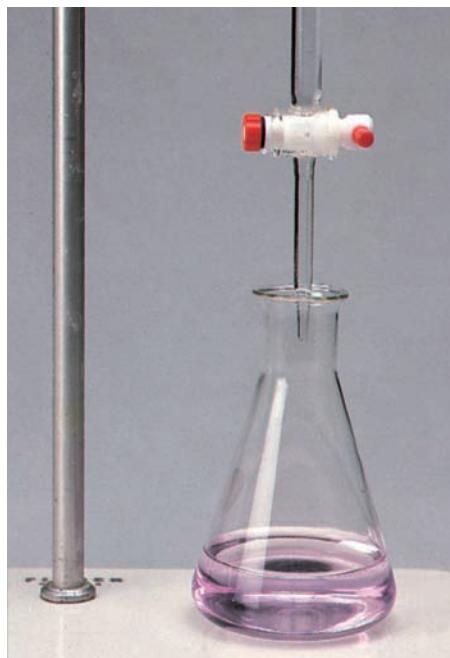
## Acid-Base Titrations

Quantitative studies of acid-base neutralization reactions are most conveniently carried out using a procedure known as **titration**. In a titration experiment, a solution of accurately known concentration, called a **standard solution**, is added gradually to another solution of unknown concentration, until the chemical reaction between the two solutions is complete. If we know the volumes of the standard and unknown solutions used in the titration, along with the concentration of the standard solution, we can calculate the concentration of the unknown solution.

Sodium hydroxide is one of the bases commonly used in the laboratory. However, because it is difficult to obtain solid sodium hydroxide in a pure form, a solution of sodium hydroxide must be *standardized* before it can be used in accurate analytical work. We can standardize the sodium hydroxide solution by titrating it against an acid solution of accurately known concentration. The acid often chosen for this task is a



(a)



(b)

**Figure 4.18**

(a) Apparatus for acid-base titration. A NaOH solution is added from the buret to a KHP solution in an Erlenmeyer flask.  
 (b) A reddish-pink color appears when the equivalence point is reached. The color here has been intensified for visual display.

monoprotic acid called potassium hydrogen phthalate (KHP), for which the molecular formula is  $\text{KHC}_8\text{H}_4\text{O}_4$ . KHP is a white, soluble solid that is commercially available in highly pure form. The reaction between KHP and sodium hydroxide is



The net ionic equation is



The procedure for the titration is shown in Figure 4.18. First, a known amount of KHP is transferred to an Erlenmeyer flask and some distilled water is added to make up a solution. Next, NaOH solution is carefully added to the KHP solution from a buret until we reach the **equivalence point**, that is, *the point at which the acid has completely reacted with or been neutralized by the base*. The equivalence point is usually signaled by a sharp change in the color of an indicator in the acid solution. In acid-base titrations, **indicators** are substances that have distinctly different colors in acidic and basic media. One commonly used indicator is phenolphthalein, which is colorless in acidic and neutral solutions but reddish pink in basic solutions. At the equivalence point, all the KHP present has been neutralized by the added NaOH and the solution is still colorless. However, if we add just one more drop of NaOH solution from the buret, the solution will immediately turn pink because the solution is now basic.



Potassium hydrogen phthalate.

### Example 4.9

In a titration experiment, a student finds that 23.48 mL of a NaOH solution are needed to neutralize 0.5468 g of KHP. What is the concentration (in molarity) of the NaOH solution?

*(Continued)*

**Strategy** We want to determine the molarity of the NaOH solution. What is the definition of molarity?

$$\text{molarity of NaOH} = \frac{\text{mol NaOH}}{\text{L soln}}$$

want to calculate

given

need to find

The volume of NaOH solution is given in the problem. Therefore, we need to find the number of moles of NaOH to solve for molarity. From the preceding equation for the reaction between KHP and NaOH shown in the text we see that 1 mole of KHP neutralizes 1 mole of NaOH. How many moles of KHP are contained in 0.5468 g of KHP?

**Solution** First, we calculate the number of moles of KHP consumed in the titration:

Recall that KHP is  $\text{KHC}_8\text{H}_4\text{O}_4$ .

$$\text{moles of KHP} = 0.5468 \text{ g KHP} \times \frac{1 \text{ mol KHP}}{204.2 \text{ g KHP}} \\ = 2.678 \times 10^{-3} \text{ mol KHP}$$

Because 1 mol KHP  $\simeq$  1 mol NaOH, there must be  $2.678 \times 10^{-3}$  mole of NaOH in 23.48 mL of NaOH solution. Finally, we calculate the number of moles of NaOH in 1 L of the solution or the molarity as follows:

$$\text{molarity of NaOH soln} = \frac{2.678 \times 10^{-3} \text{ mol NaOH}}{23.48 \text{ mL soln}} \times \frac{1000 \text{ mL soln}}{1 \text{ L soln}} \\ = 0.1141 \text{ mol NaOH/L soln} = 0.1141 M$$

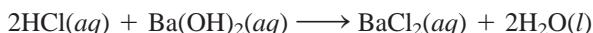
**Similar problems:** 4.77, 4.78.

**Practice Exercise** How many grams of KHP are needed to neutralize 18.64 mL of a 0.1004 M NaOH solution?

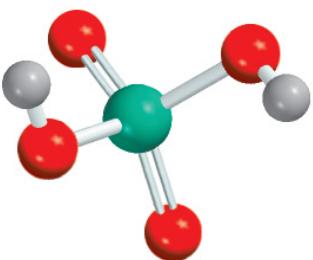
The neutralization reaction between NaOH and KHP is one of the simplest types of acid-base neutralization known. Suppose, though, that instead of KHP, we wanted to use a diprotic acid such as H<sub>2</sub>SO<sub>4</sub> for the titration. The reaction is represented by



Because  $2 \text{ mol NaOH} \approx 1 \text{ mol H}_2\text{SO}_4$ , we need twice as much NaOH to react completely with a  $\text{H}_2\text{SO}_4$  solution of the *same* molar concentration and volume as a mono-protic acid like HCl. On the other hand, we would need twice the amount of HCl to neutralize a  $\text{Ba(OH)}_2$  solution compared to a NaOH solution having the same concentration and volume because 1 mole of  $\text{Ba(OH)}_2$  yields 2 moles of  $\text{OH}^-$  ions:



In calculations involving acid-base titrations, regardless of the acid or base that takes place in the reaction, keep in mind that the total number of moles of  $\text{H}^+$  ions that have reacted at the equivalence point must be equal to the total number of moles of  $\text{OH}^-$  ions that have reacted.



### Example 4.10

How many milliliters (mL) of a  $0.610\text{ M}$  NaOH solution are needed to neutralize 20.0 mL of a  $0.245\text{ M}$   $\text{H}_2\text{SO}_4$  solution?

$\text{H}_2\text{SO}_4$  has two ionizable protons.

(Continued)

**Strategy** We want to calculate the volume of the NaOH solution. From the definition of molarity [see Equation (4.1)], we write

$$L \text{ soln} = \frac{\text{mol NaOH}}{\text{molarity}}$$

want to calculate

given

need to find

From the equation for the neutralization reaction just shown, we see that 1 mole of  $\text{H}_2\text{SO}_4$  neutralizes 2 moles of  $\text{NaOH}$ . How many moles of  $\text{H}_2\text{SO}_4$  are contained in 20.0 mL of a 0.245 M  $\text{H}_2\text{SO}_4$  solution? How many moles of  $\text{NaOH}$  would this quantity of  $\text{H}_2\text{SO}_4$  neutralize?

**Solution** First we calculate the number of moles of  $\text{H}_2\text{SO}_4$  in a 20.0 mL solution:

$$\text{moles H}_2\text{SO}_4 = \frac{0.245 \text{ mol H}_2\text{SO}_4}{1000 \text{ mL soln}} \times 20.0 \text{ mL soln}$$

$$= 4.90 \times 10^{-3} \text{ mol H}_2\text{SO}_4$$

From the stoichiometry we see that 1 mol  $\text{H}_2\text{SO}_4 \simeq 2$  mol NaOH. Therefore, the number of moles of NaOH reacted must be  $2 \times 4.90 \times 10^{-3}$  mole, or  $9.80 \times 10^{-3}$  mole. From the definition of molarity [see Equation (4.1)], we have

$$\text{liters of soln} = \frac{\text{moles of solute}}{\text{molarity}}$$

or

$$\text{volume of NaOH} = \frac{9.80 \times 10^{-3} \text{ mol NaOH}}{0.610 \text{ mol/L soln}} \\ = 0.0161 \text{ L or } 16.1 \text{ mL}$$

**Similar problem:** 4.79(b), (c).

**Practice Exercise** How many milliliters of a  $1.28\text{ M}$   $\text{H}_2\text{SO}_4$  solution are needed to neutralize 60.2 mL of a  $0.427\text{ M}$   $\text{KOH}$  solution?

## KEY EQUATIONS

$$\text{molarity } (M) = \frac{\text{moles of solute}}{\text{liters of soln}} \quad (4.1) \quad \text{Definition of molarity.}$$

$$M = \frac{n}{V} \quad (4.2) \qquad \text{Definition of molarity.}$$

$$M_i V_i = M_f V_f \quad (4.3) \qquad \text{Dilution of solution.}$$

## SUMMARY OF FACTS AND CONCEPTS

1. Aqueous solutions are electrically conducting if the solutes are electrolytes. If the solutes are nonelectrolytes, the solutions do not conduct electricity.
  2. Three major categories of chemical reactions that take place in aqueous solution are precipitation reactions, acid-base reactions, and oxidation-reduction reactions.
  3. From general rules about solubilities of ionic compounds, we can predict whether a precipitate will form in a reaction.

4. Arrhenius acids ionize in water to give  $\text{H}^+$  ions, and Arrhenius bases ionize in water to give  $\text{OH}^-$  ions. Brønsted acids donate protons, and Brønsted bases accept protons. The reaction of an acid and a base is called neutralization.
5. In redox reactions, oxidation and reduction always occur simultaneously. Oxidation is characterized by the loss of electrons, reduction by the gain of electrons. Oxidation numbers help us keep track of charge distribution and are assigned to all atoms in a compound or ion according to specific rules. Oxidation can be defined as an increase in oxidation number; reduction can be defined as a decrease in oxidation number.
6. The concentration of a solution is the amount of solute present in a given amount of solution. Molarity expresses concentration as the number of moles of solute in 1 L of solution. Adding a solvent to a solution, a process known as dilution, decreases the concentration (molarity) of the solution without changing the total number of moles of solute present in the solution.
7. Gravimetric analysis is a technique for determining the identity of a compound and/or the concentration of a solution by measuring mass. Gravimetric experiments often involve precipitation reactions.
8. In acid-base titration, a solution of known concentration (say, a base) is added gradually to a solution of unknown concentration (say, an acid) with the goal of determining the unknown concentration. The point at which the reaction in the titration is complete is called the equivalence point.

## KEY WORDS

Activity series, p. 112	Electrolyte, p. 95	Net ionic equation, p. 100	Reduction reaction, p. 107
Aqueous solution, p. 95	Equivalence point, p. 121	Neutralization reaction, p. 105	Reversible reaction, p. 97
Brønsted acid, p. 102	Gravimetric analysis, p. 118	Nonelectrolyte, p. 95	Salt, p. 105
Brønsted base, p. 102	Half-reaction, p. 106	Oxidation number, p. 107	Solubility, p. 98
Chemical equilibrium, p. 97	Hydration, p. 96	Oxidation state, p. 107	Solute, p. 95
Combination reaction, p. 109	Hydronium ion, p. 102	Oxidation reaction, p. 107	Solution, p. 95
Combustion reaction, p. 110	Indicator, p. 121	Oxidation-reduction reaction, p. 106	Solvent, p. 95
Concentration of a solution, p. 114	Ionic equation, p. 99	Oxidizing agent, p. 107	Spectator ion, p. 99
Decomposition reaction, p. 109	Metathesis reaction, p. 97	Precipitate, p. 97	Standard solution, p. 120
Dilution, p. 117	Molar concentration, p. 114	Precipitation reaction, p. 97	Titration, p. 120
Diprotic acid, p. 103	Molarity ( $M$ ), p. 114	Redox reaction, p. 106	Triprotic acid, p. 103
Displacement reaction, p. 111	Molecular equation, p. 99	Reducing agent, p. 107	
	Monoprotic acid, p. 103		

## QUESTIONS AND PROBLEMS

### Properties of Aqueous Solutions

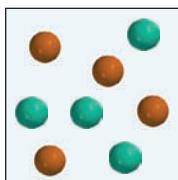
#### Review Questions

- 4.1 Define solute, solvent, and solution by describing the process of dissolving a solid in a liquid.
- 4.2 What is the difference between a nonelectrolyte and an electrolyte? Between a weak electrolyte and a strong electrolyte?
- 4.3 Describe hydration. What properties of water enable its molecules to interact with ions in solution?
- 4.4 What is the difference between the following symbols in chemical equations:  $\longrightarrow$  and  $\rightleftharpoons$ ?

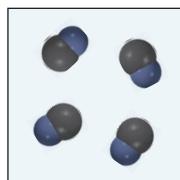
- 4.5 Water is an extremely weak electrolyte and therefore cannot conduct electricity. Why are we often cautioned not to operate electrical appliances when our hands are wet?
- 4.6 Lithium fluoride (LiF) is a strong electrolyte. What species are present in LiF(*aq*)?

#### Problems

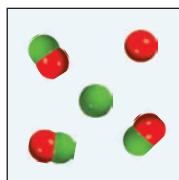
- 4.7 The aqueous solutions of three compounds are shown in the diagram. Identify each compound as a nonelectrolyte, a weak electrolyte, and a strong electrolyte.



(a)

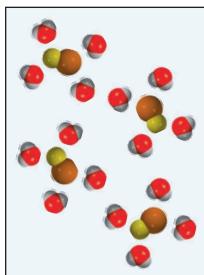


(b)



(c)

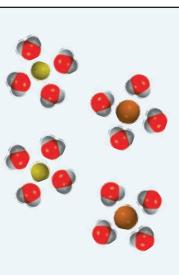
- 4.8** Which of the following diagrams best represents the hydration of NaCl when dissolved in water? The  $\text{Cl}^-$  ion is larger in size than the  $\text{Na}^+$  ion.



(a)



(b)



(c)

- 4.9** Identify each of the following substances as a strong electrolyte, weak electrolyte, or nonelectrolyte: (a)  $\text{H}_2\text{O}$ , (b) KCl, (c)  $\text{HNO}_3$ , (d)  $\text{CH}_3\text{COOH}$ , (e)  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ .

- 4.10** Identify each of the following substances as a strong electrolyte, weak electrolyte, or nonelectrolyte: (a)  $\text{Ba}(\text{NO}_3)_2$ , (b) Ne, (c)  $\text{NH}_3$ , (d) NaOH.

- 4.11** The passage of electricity through an electrolyte solution is caused by the movement of (a) electrons only, (b) cations only, (c) anions only, (d) both cations and anions.

- 4.12** Predict and explain which of the following systems are electrically conducting: (a) solid NaCl, (b) molten NaCl, (c) an aqueous solution of NaCl.

- 4.13** You are given a water-soluble compound X. Describe how you would determine whether it is an electrolyte or a nonelectrolyte. If it is an electrolyte, how would you determine whether it is strong or weak?

- 4.14** Explain why a solution of HCl in benzene does not conduct electricity but in water it does.

## Precipitation Reactions

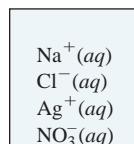
### Review Questions

- 4.15** What is the difference between an ionic equation and a molecular equation?

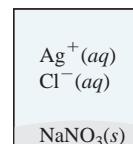
- 4.16** What is the advantage of writing net ionic equations?

### Problems

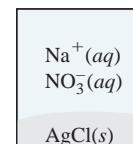
- 4.17** Two aqueous solutions of  $\text{AgNO}_3$  and  $\text{NaCl}$  are mixed. Which of the following diagrams best represents the mixture?



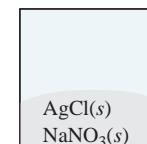
(a)



(b)

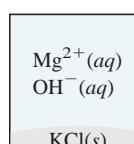


(c)

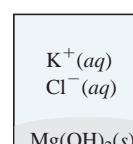


(d)

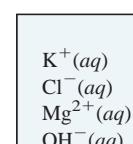
- 4.18** Two aqueous solutions of KOH and  $\text{MgCl}_2$  are mixed. Which of the following diagrams best represents the mixture?



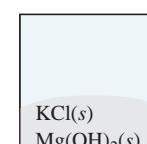
(a)



(b)



(c)

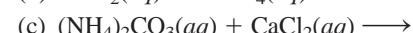
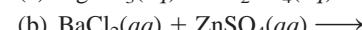


(d)

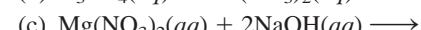
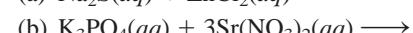
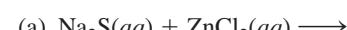
- 4.19** Characterize the following compounds as soluble or insoluble in water: (a)  $\text{Ca}_3(\text{PO}_4)_2$ , (b)  $\text{Mn}(\text{OH})_2$ , (c)  $\text{AgClO}_3$ , (d)  $\text{K}_2\text{S}$ .

- 4.20** Characterize the following compounds as soluble or insoluble in water: (a)  $\text{CaCO}_3$ , (b)  $\text{ZnSO}_4$ , (c)  $\text{Hg}(\text{NO}_3)_2$ , (d)  $\text{HgSO}_4$ , (e)  $\text{NH}_4\text{ClO}_4$ .

- 4.21** Write ionic and net ionic equations for the following reactions:



- 4.22** Write ionic and net ionic equations for the following reactions:



- 4.23** Which of the following processes will likely result in a precipitation reaction? (a) Mixing a  $\text{NaNO}_3$  solution with a  $\text{CuSO}_4$  solution. (b) Mixing a  $\text{BaCl}_2$  solution with a  $\text{K}_2\text{SO}_4$  solution. Write a net ionic equation for the precipitation reaction.

- 4.24** With reference to Table 4.2, suggest one method by which you might separate (a)  $\text{K}^+$  from  $\text{Ag}^+$ , (b)  $\text{Ba}^{2+}$  from  $\text{Pb}^{2+}$ , (c)  $\text{NH}_4^+$  from  $\text{Ca}^{2+}$ , (d)  $\text{Ba}^{2+}$  from  $\text{Cu}^{2+}$ . All cations are assumed to be in aqueous solution, and the common anion is the nitrate ion.

## Acid-Base Reactions

### Review Questions

- 4.25 List the general properties of acids and bases.
- 4.26 Give Arrhenius's and Brønsted's definitions of an acid and a base. Why are Brønsted's definitions more useful in describing acid-base properties?
- 4.27 Give an example of a monoprotic acid, a diprotic acid, and a triprotic acid.
- 4.28 What are the characteristics of an acid-base neutralization reaction?
- 4.29 What factors qualify a compound as a salt? Specify which of the following compounds are salts: CH<sub>4</sub>, NaF, NaOH, CaO, BaSO<sub>4</sub>, HNO<sub>3</sub>, NH<sub>3</sub>, KBr?
- 4.30 Identify the following as a weak or strong acid or base: (a) NH<sub>3</sub>, (b) H<sub>3</sub>PO<sub>4</sub>, (c) LiOH, (d) HCOOH (formic acid), (e) H<sub>2</sub>SO<sub>4</sub>, (f) HF, (g) Ba(OH)<sub>2</sub>.

### Problems

- 4.31 Identify each of the following species as a Brønsted acid, base, or both: (a) HI, (b) CH<sub>3</sub>COO<sup>-</sup>, (c) H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, (d) HSO<sub>4</sub><sup>-</sup>.
- 4.32 Identify each of the following species as a Brønsted acid, base, or both: (a) PO<sub>4</sub><sup>3-</sup>, (b) ClO<sub>2</sub><sup>-</sup>, (c) NH<sub>4</sub><sup>+</sup>, (d) HCO<sub>3</sub><sup>-</sup>.
- 4.33 Balance the following equations and write the corresponding ionic and net ionic equations (if appropriate):  
 (a) HBr(aq) + NH<sub>3</sub>(aq) →  
 (b) Ba(OH)<sub>2</sub>(aq) + H<sub>3</sub>PO<sub>4</sub>(aq) →  
 (c) HClO<sub>4</sub>(aq) + Mg(OH)<sub>2</sub>(s) →
- 4.34 Balance the following equations and write the corresponding ionic and net ionic equations (if appropriate):  
 (a) CH<sub>3</sub>COOH(aq) + KOH(aq) →  
 (b) H<sub>2</sub>CO<sub>3</sub>(aq) + NaOH(aq) →  
 (c) HNO<sub>3</sub>(aq) + Ba(OH)<sub>2</sub>(aq) →

## Oxidation-Reduction Reactions

### Review Questions

- 4.35 Define the following terms: half-reaction, oxidation reaction, reduction reaction, reducing agent, oxidizing agent, redox reaction.
- 4.36 What is an oxidation number? How is it used to identify redox reactions? Explain why, except for ionic compounds, oxidation number does not have any physical significance.
- 4.37 (a) Without referring to Figure 4.10, give the oxidation numbers of the alkali and alkaline earth metals in their compounds. (b) Give the highest oxidation numbers that the Groups 3A–7A elements can have.
- 4.38 Is it possible to have a reaction in which oxidation occurs and reduction does not? Explain.

### Problems

- 4.39 For the complete redox reactions given here, (i) break down each reaction into its half-reactions; (ii) identify the oxidizing agent; (iii) identify the reducing agent.  
 (a) 2Sr + O<sub>2</sub> → 2SrO  
 (b) 2Li + H<sub>2</sub> → 2LiH  
 (c) 2Cs + Br<sub>2</sub> → 2CsBr  
 (d) 3Mg + N<sub>2</sub> → Mg<sub>3</sub>N<sub>2</sub>
- 4.40 For the complete redox reactions given here, write the half-reactions and identify the oxidizing and reducing agents:  
 (a) 4Fe + 3O<sub>2</sub> → 2Fe<sub>2</sub>O<sub>3</sub>  
 (b) Cl<sub>2</sub> + 2NaBr → 2NaCl + Br<sub>2</sub>  
 (c) Si + 2F<sub>2</sub> → SiF<sub>4</sub>  
 (d) H<sub>2</sub> + Cl<sub>2</sub> → 2HCl
- 4.41 Arrange the following species in order of increasing oxidation number of the sulfur atom: (a) H<sub>2</sub>S, (b) S<sub>8</sub>, (c) H<sub>2</sub>SO<sub>4</sub>, (d) S<sup>2-</sup>, (e) HS<sup>-</sup>, (f) SO<sub>2</sub>, (g) SO<sub>3</sub>.
- 4.42 Phosphorus forms many oxoacids. Indicate the oxidation number of phosphorus in each of the following acids: (a) HPO<sub>3</sub>, (b) H<sub>3</sub>PO<sub>2</sub>, (c) H<sub>3</sub>PO<sub>3</sub>, (d) H<sub>3</sub>PO<sub>4</sub>, (e) H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, (f) H<sub>5</sub>P<sub>3</sub>O<sub>10</sub>.
- 4.43 Give the oxidation number of the underlined atoms in the following molecules and ions: (a) ClF, (b) IF<sub>7</sub>, (c) CH<sub>4</sub>, (d) C<sub>2</sub>H<sub>2</sub>, (e) C<sub>2</sub>H<sub>4</sub>, (f) K<sub>2</sub>CrO<sub>4</sub>, (g) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, (h) KMnO<sub>4</sub>, (i) NaHCO<sub>3</sub>, (j) Li<sub>2</sub>, (k) NaIO<sub>3</sub>, (l) KO<sub>2</sub>, (m) PF<sub>6</sub><sup>-</sup>, (n) KAuCl<sub>4</sub>.
- 4.44 Give the oxidation number for the following species: H<sub>2</sub>, Se<sub>8</sub>, P<sub>4</sub>, O, U, As<sub>4</sub>, B<sub>12</sub>.
- 4.45 Give oxidation numbers for the underlined atoms in the following molecules and ions: (a) Cs<sub>2</sub>O, (b) CaI<sub>2</sub>, (c) Al<sub>2</sub>O<sub>3</sub>, (d) H<sub>3</sub>AsO<sub>3</sub>, (e) TiO<sub>2</sub>, (f) MoO<sub>4</sub><sup>2-</sup>, (g) PtCl<sub>6</sub><sup>2-</sup>, (h) PtCl<sub>6</sub><sup>4-</sup>, (i) SnF<sub>2</sub>, (j) ClF<sub>3</sub>, (k) SbF<sub>6</sub><sup>-</sup>.
- 4.46 Give the oxidation numbers of the underlined atoms in the following molecules and ions: (a) Mg<sub>3</sub>N<sub>2</sub>, (b) CsO<sub>2</sub>, (c) CaC<sub>2</sub>, (d) CO<sub>3</sub><sup>2-</sup>, (e) C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, (f) ZnO<sub>2</sub><sup>2-</sup>, (g) NaBH<sub>4</sub>, (h) WO<sub>4</sub><sup>2-</sup>.
- 4.47 Nitric acid is a strong oxidizing agent. State which of the following species is *least* likely to be produced when nitric acid reacts with a strong reducing agent such as zinc metal, and explain why: N<sub>2</sub>O, NO, NO<sub>2</sub>, N<sub>2</sub>O<sub>4</sub>, N<sub>2</sub>O<sub>5</sub>, NH<sub>4</sub><sup>+</sup>.
- 4.48 Which of the following metals can react with water?  
 (a) Au, (b) Li, (c) Hg, (d) Ca, (e) Pt.
- 4.49 On the basis of oxidation number considerations, one of the following oxides would not react with molecular oxygen: NO, N<sub>2</sub>O, SO<sub>2</sub>, SO<sub>3</sub>, P<sub>4</sub>O<sub>6</sub>. Which one is it? Why?
- 4.50 Predict the outcome of the reactions represented by the following equations by using the activity series, and balance the equations.

- (a)  $\text{Cu}(s) + \text{HCl}(aq) \longrightarrow$   
 (b)  $\text{I}_2(s) + \text{NaBr}(aq) \longrightarrow$   
 (c)  $\text{Mg}(s) + \text{CuSO}_4(aq) \longrightarrow$   
 (d)  $\text{Cl}_2(g) + \text{KBr}(aq) \longrightarrow$

## Concentration of Solutions

### Review Questions

- 4.51 Write the equation for calculating molarity. Why is molarity a convenient concentration unit in chemistry?
- 4.52 Describe the steps involved in preparing a solution of known molar concentration using a volumetric flask.

### Problems

- 4.53 Calculate the mass of KI in grams required to prepare  $5.00 \times 10^2$  mL of a  $2.80\text{ M}$  solution.
- 4.54 Describe how you would prepare 250 mL of a  $0.707\text{ M}$   $\text{NaNO}_3$  solution.
- 4.55 How many moles of  $\text{MgCl}_2$  are present in 60.0 mL of  $0.100\text{ M}$   $\text{MgCl}_2$  solution?
- 4.56 How many grams of KOH are present in 35.0 mL of a  $5.50\text{ M}$  solution?
- 4.57 Calculate the molarity of each of the following solutions: (a) 29.0 g of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) in 545 mL of solution, (b) 15.4 g of sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) in 74.0 mL of solution, (c) 9.00 g of sodium chloride ( $\text{NaCl}$ ) in 86.4 mL of solution.
- 4.58 Calculate the molarity of each of the following solutions: (a) 6.57 g of methanol ( $\text{CH}_3\text{OH}$ ) in  $1.50 \times 10^2$  mL of solution, (b) 10.4 g of calcium chloride ( $\text{CaCl}_2$ ) in  $2.20 \times 10^2$  mL of solution, (c) 7.82 g of naphthalene ( $\text{C}_{10}\text{H}_8$ ) in 85.2 mL of benzene solution.
- 4.59 Calculate the volume in mL of a solution required to provide the following: (a) 2.14 g of sodium chloride from a  $0.270\text{ M}$  solution, (b) 4.30 g of ethanol from a  $1.50\text{ M}$  solution, (c) 0.85 g of acetic acid ( $\text{CH}_3\text{COOH}$ ) from a  $0.30\text{ M}$  solution.
- 4.60 Determine how many grams of each of the following solutes would be needed to make  $2.50 \times 10^2$  mL of a  $0.100\text{ M}$  solution: (a) cesium iodide ( $\text{CsI}$ ), (b) sulfuric acid ( $\text{H}_2\text{SO}_4$ ), (c) sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), (d) potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), (e) potassium permanganate ( $\text{KMnO}_4$ ).

## Dilution of Solutions

### Review Questions

- 4.61 Describe the basic steps involved in diluting a solution of known concentration.
- 4.62 Write the equation that enables us to calculate the concentration of a diluted solution. Give units for all the terms.

### Problems

- 4.63 Describe how to prepare 1.00 L of  $0.646\text{ M}$  HCl solution, starting with a  $2.00\text{ M}$  HCl solution.
- 4.64 Water is added to 25.0 mL of a  $0.866\text{ M}$   $\text{KNO}_3$  solution until the volume of the solution is exactly 500 mL. What is the concentration of the final solution?
- 4.65 How would you prepare 60.0 mL of  $0.200\text{ M}$   $\text{HNO}_3$  from a stock solution of  $4.00\text{ M}$   $\text{HNO}_3$ ?
- 4.66 You have 505 mL of a  $0.125\text{ M}$  HCl solution and you want to dilute it to exactly  $0.100\text{ M}$ . How much water should you add?
- 4.67 A 35.2-mL,  $1.66\text{ M}$   $\text{KMnO}_4$  solution is mixed with 16.7 mL of  $0.892\text{ M}$   $\text{KMnO}_4$  solution. Calculate the concentration of the final solution.
- 4.68 A 46.2-mL,  $0.568\text{ M}$  calcium nitrate [ $\text{Ca}(\text{NO}_3)_2$ ] solution is mixed with 80.5 mL of  $1.396\text{ M}$  calcium nitrate solution. Calculate the concentration of the final solution.

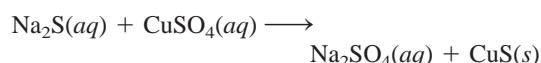
## Gravimetric Analysis

### Review Questions

- 4.69 Describe the basic steps involved in gravimetric analysis. How does this procedure help us determine the identity of a compound or the purity of a compound if its formula is known?
- 4.70 Distilled water must be used in the gravimetric analysis of chlorides. Why?

### Problems

- 4.71 If 30.0 mL of  $0.150\text{ M}$   $\text{CaCl}_2$  is added to 15.0 mL of  $0.100\text{ M}$   $\text{AgNO}_3$ , what is the mass in grams of  $\text{AgCl}$  precipitate?
- 4.72 A sample of 0.6760 g of an unknown compound containing barium ions ( $\text{Ba}^{2+}$ ) is dissolved in water and treated with an excess of  $\text{Na}_2\text{SO}_4$ . If the mass of the  $\text{BaSO}_4$  precipitate formed is 0.4105 g, what is the percent by mass of Ba in the original unknown compound?
- 4.73 How many grams of  $\text{NaCl}$  are required to precipitate most of the  $\text{Ag}^+$  ions from  $2.50 \times 10^2$  mL of  $0.0113\text{ M}$   $\text{AgNO}_3$  solution? Write the net ionic equation for the reaction.
- 4.74 The concentration of  $\text{Cu}^{2+}$  ions in the water (which also contains sulfate ions) discharged from a certain industrial plant is determined by adding excess sodium sulfide ( $\text{Na}_2\text{S}$ ) solution to 0.800 L of the water. The molecular equation is



Write the net ionic equation and calculate the molar concentration of  $\text{Cu}^{2+}$  in the water sample if 0.0177 g of solid CuS is formed.

## Acid-Base Titrations

### Review Questions

- 4.75 Describe the basic steps involved in an acid-base titration. Why is this technique of great practical value?
- 4.76 How does an acid-base indicator work?

### Problems

4.77 A quantity of 18.68 mL of a KOH solution is needed to neutralize 0.4218 g of KHP. What is the concentration (in molarity) of the KOH solution?

4.78 Calculate the concentration (in molarity) of a NaOH solution if 25.0 mL of the solution are needed to neutralize 17.4 mL of a 0.312 M HCl solution.

4.79 Calculate the volume in mL of a 1.420 M NaOH solution required to titrate the following solutions:

- 25.00 mL of a 2.430 M HCl solution
- 25.00 mL of a 4.500 M  $\text{H}_2\text{SO}_4$  solution
- 25.00 mL of a 1.500 M  $\text{H}_3\text{PO}_4$  solution

4.80 What volume of a 0.500 M HCl solution is needed to neutralize each of the following:

- 10.0 mL of a 0.300 M NaOH solution
- 10.0 mL of a 0.200 M  $\text{Ba}(\text{OH})_2$  solution

### Additional Problems

4.81 Classify these reactions according to the types discussed in the chapter:

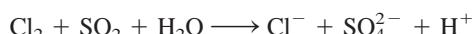
- $\text{Cl}_2 + 2\text{OH}^- \longrightarrow \text{Cl}^- + \text{ClO}^- + \text{H}_2\text{O}$
- $\text{Ca}^{2+} + \text{CO}_3^{2-} \longrightarrow \text{CaCO}_3$
- $\text{NH}_3 + \text{H}^+ \longrightarrow \text{NH}_4^+$
- $2\text{CCl}_4 + \text{CrO}_4^{2-} \longrightarrow 2\text{COCl}_2 + \text{CrO}_2\text{Cl}_2 + 2\text{Cl}^-$
- $\text{Ca} + \text{F}_2 \longrightarrow \text{CaF}_2$
- $2\text{Li} + \text{H}_2 \longrightarrow 2\text{LiH}$
- $\text{Ba}(\text{NO}_3)_2 + \text{Na}_2\text{SO}_4 \longrightarrow 2\text{NaNO}_3 + \text{BaSO}_4$
- $\text{CuO} + \text{H}_2 \longrightarrow \text{Cu} + \text{H}_2\text{O}$
- $\text{Zn} + 2\text{HCl} \longrightarrow \text{ZnCl}_2 + \text{H}_2$
- $2\text{FeCl}_2 + \text{Cl}_2 \longrightarrow 2\text{FeCl}_3$

4.82 Using the apparatus shown in Figure 4.1, a student found that the lightbulb was brightly lit when the electrodes were immersed in a sulfuric acid solution. However, after the addition of a certain amount of barium hydroxide  $[\text{Ba}(\text{OH})_2]$  solution, the light began to dim even though  $\text{Ba}(\text{OH})_2$  is also a strong electrolyte. Explain.

4.83 Someone gave you a colorless liquid. Describe three chemical tests you would perform on the liquid to show that it is water.

4.84 You are given two colorless solutions, one containing NaCl and the other sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ). Suggest a chemical and a physical test that would distinguish between these two solutions.

4.85 Chlorine ( $\text{Cl}_2$ ) is used to purify drinking water. Too much chlorine is harmful to humans. The excess chlorine is often removed by treatment with sulfur dioxide ( $\text{SO}_2$ ). Balance the following equation that represents this procedure:



4.86 Before aluminum was obtained by electrolytic reduction from its ore ( $\text{Al}_2\text{O}_3$ ), the metal was produced by chemical reduction of  $\text{AlCl}_3$ . Which metals would you use to reduce  $\text{Al}^{3+}$  to Al?

4.87 Oxygen ( $\text{O}_2$ ) and carbon dioxide ( $\text{CO}_2$ ) are colorless and odorless gases. Suggest two chemical tests that would enable you to distinguish between them.

4.88 Based on oxidation number, explain why carbon monoxide (CO) is flammable but carbon dioxide ( $\text{CO}_2$ ) is not.

4.89 Which of these aqueous solutions would you expect to be the best conductor of electricity at 25°C? Explain your answer.

- 0.20 M NaCl
- 0.60 M  $\text{CH}_3\text{COOH}$
- 0.25 M HCl
- 0.20 M  $\text{Mg}(\text{NO}_3)_2$

4.90 A  $5.00 \times 10^{-2}$ -mL sample of 2.00 M HCl solution is treated with 4.47 g of magnesium. Calculate the concentration of the acid solution after all the metal has reacted. Assume that the volume remains unchanged.

4.91 Calculate the volume (in liters) of a 0.156 M  $\text{CuSO}_4$  solution that would react with 7.89 g of zinc.

4.92 Sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) can be obtained in very pure form and can be used to standardize acid solutions. What is the molarity of an HCl solution if 28.3 mL of the solution is required to react with 0.256 g of  $\text{Na}_2\text{CO}_3$ ?

4.93 A 3.664-g sample of a monoprotic acid was dissolved in water and required 20.27 mL of a 0.1578 M NaOH solution for neutralization. Calculate the molar mass of the acid.

4.94 Acetic acid ( $\text{CH}_3\text{COOH}$ ) is an important ingredient of vinegar. A sample of 50.0 mL of a commercial vinegar is titrated against a 1.00 M NaOH solution. What is the concentration (in M) of acetic acid present in the vinegar if 5.75 mL of the base were required for the titration?

4.95 Calculate the mass of precipitate formed when 2.27 L of 0.0820 M  $\text{Ba}(\text{OH})_2$  are mixed with 3.06 L of 0.0664 M  $\text{Na}_2\text{SO}_4$ .

- 4.96** Milk of magnesia is an aqueous suspension of magnesium hydroxide  $\text{Mg}(\text{OH})_2$  used to treat acid indigestion. Calculate the volume of a  $0.035\text{ M}$  HCl solution (a typical acid concentration in an upset stomach) needed to react with two spoonfuls of milk of magnesia [approximately 10.0 mL at  $0.080\text{ g Mg(OH)}_2/\text{mL}$ ].
- 4.97** A 1.00-g sample of a metal X (that is known to form  $\text{X}^{2+}$  ions) was added to a 0.100 L of  $0.500\text{ M}$   $\text{H}_2\text{SO}_4$ . After all the metal had reacted, the remaining acid required  $0.0334\text{ L}$  of  $0.500\text{ M}$  NaOH solution for neutralization. Calculate the molar mass of the metal and identify the element.
- 4.98** A 60.0-mL  $0.513\text{ M}$  glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) solution is mixed with 120.0 mL of  $2.33\text{ M}$  glucose solution. What is the concentration of the final solution? Assume the volumes are additive.
- 4.99** You are given a soluble compound of unknown molecular formula. (a) Describe three tests that would show that the compound is an acid. (b) Once you have established that the compound is an acid, describe how you would determine its molar mass using an NaOH solution of known concentration. (Assume the acid is monoprotic.) (c) How would you find out whether the acid is weak or strong? You are provided with a sample of NaCl and an apparatus like that shown in Figure 4.1 for comparison.
- 4.100** Someone spilled concentrated sulfuric acid on the floor of a chemistry laboratory. To neutralize the acid, would it be preferable to pour concentrated sodium hydroxide solution or spray solid sodium bicarbonate over the acid? Explain your choice and the chemical basis for the action.
- 4.101** These are common household compounds: table salt ( $\text{NaCl}$ ), table sugar (sucrose), vinegar (contains acetic acid), baking soda ( $\text{NaHCO}_3$ ), washing soda ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ), boric acid ( $\text{H}_3\text{BO}_3$ , used in eyewash), epsom salt ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), sodium hydroxide (used in drain openers), ammonia, milk of magnesia  $\text{Mg}(\text{OH})_2$ , and calcium carbonate. Based on what you have learned in this chapter, describe test(s) that would enable you to identify each of these compounds.
- 4.102** A 0.8870-g sample of a mixture of  $\text{NaCl}$  and  $\text{KCl}$  is dissolved in water, and the solution is then treated with an excess of  $\text{AgNO}_3$  to yield 1.913 g of  $\text{AgCl}$ . Calculate the percent by mass of each compound in the mixture.
- 4.103** Phosphoric acid ( $\text{H}_3\text{PO}_4$ ) is an important industrial chemical used in fertilizers, detergents, and in the food industry. It is produced by two different methods. In the *electric furnace method* elemental phosphorus ( $\text{P}_4$ ) is burned in air to form  $\text{P}_4\text{O}_{10}$ , which is then reacted with water to give  $\text{H}_3\text{PO}_4$ . In the *wet process* the mineral phosphate rock  $[\text{Ca}_5(\text{PO}_4)_3\text{F}]$  is reacted with sulfuric acid to give  $\text{H}_3\text{PO}_4$  (and HF and  $\text{CaSO}_4$ ). Write equations for these processes and classify each step as precipitation, acid-base, or redox reaction.
- 4.104** Give a chemical explanation for each of these: (a) When calcium metal is added to a sulfuric acid solution, hydrogen gas is generated. After a few minutes, the reaction slows down and eventually stops even though none of the reactants is used up. Explain. (b) In the activity series aluminum is above hydrogen, yet the metal appears to be unreactive toward steam and hydrochloric acid. Why? (c) Sodium and potassium lie above copper in the activity series. Explain why  $\text{Cu}^{2+}$  ions in a  $\text{CuSO}_4$  solution are not converted to metallic copper upon the addition of these metals. (d) A metal M reacts slowly with steam. There is no visible change when it is placed in a pale green iron(II) sulfate solution. Where should we place M in the activity series?
- 4.105** A number of metals are involved in redox reactions in biological systems in which the oxidation state of the metals changes. Which of these metals are most likely to take part in such reactions: Na, K, Mg, Ca, Mn, Fe, Co, Cu, Zn? Explain.
- 4.106** The recommended procedure for preparing a very dilute solution is not to weigh out a very small mass or measure a very small volume of a stock solution. Instead, it is done by a series of dilutions. A sample of  $0.8214\text{ g}$  of  $\text{KMnO}_4$  was dissolved in water and made up to the volume in a 500-mL volumetric flask. A 2.000-mL sample of this solution was transferred to a 1000-mL volumetric flask and diluted to the mark with water. Next, 10.00 mL of the diluted solution were transferred to a 250-mL flask and diluted to the mark with water. (a) Calculate the concentration (in molarity) of the final solution. (b) Calculate the mass of  $\text{KMnO}_4$  needed to directly prepare the final solution.
- 4.107** A 325-mL sample of solution contains  $25.3\text{ g}$  of  $\text{CaCl}_2$ . (a) Calculate the molar concentration of  $\text{Cl}^-$  in this solution. (b) How many grams of  $\text{Cl}^-$  are in  $0.100\text{ L}$  of this solution?
- 4.108** Acetylsalicylic acid ( $\text{C}_9\text{H}_8\text{O}_4$ ) is a monoprotic acid commonly known as “aspirin.” A typical aspirin tablet, however, contains only a small amount of the acid. In an experiment to determine its composition, an aspirin tablet was crushed and dissolved in water. It took  $12.25\text{ mL}$  of  $0.1466\text{ M}$  NaOH to neutralize the solution. Calculate the number of grains of aspirin in the tablet. (One grain =  $0.0648\text{ g}$ .)
- 4.109** This “cycle of copper” experiment is performed in some general chemistry laboratories. The series of reactions starts with copper and ends with metallic copper. The steps are: (1) A piece of copper wire of known mass is allowed to react with concentrated

nitric acid [the products are copper(II) nitrate, nitrogen dioxide, and water]. (2) The copper(II) nitrate is treated with a sodium hydroxide solution to form copper(II) hydroxide precipitate. (3) On heating, copper(II) hydroxide decomposes to yield copper(II) oxide. (4) The copper(II) oxide is reacted with concentrated sulfuric acid to yield copper(II) sulfate. (5) Copper(II) sulfate is treated with an excess of zinc metal to form metallic copper. (6) The remaining zinc metal is removed by treatment with hydrochloric acid, and metallic copper is filtered, dried, and weighed. (a) Write a balanced equation for each step and classify the reactions. (b) Assuming that a student started with 65.6 g of copper, calculate the theoretical yield at each step. (c) Considering the nature of the steps, comment on why it is possible to recover most of the copper used at the start.

- 4.110** Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) is one of the most important nitrogen-containing fertilizers. Its purity can be analyzed by titrating a solution of  $\text{NH}_4\text{NO}_3$  with

a standard NaOH solution. In one experiment a 0.2041-g sample of industrially prepared  $\text{NH}_4\text{NO}_3$  required 24.42 mL of 0.1023 M NaOH for neutralization. (a) Write a net ionic equation for the reaction. (b) What is the percent purity of the sample?

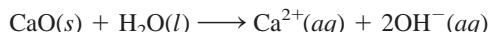
- 4.111** Hydrogen halides (HF, HCl, HBr, HI) are highly reactive compounds that have many industrial and laboratory uses. (a) In the laboratory, HF and HCl can be generated by reacting  $\text{CaF}_2$  and  $\text{NaCl}$  with concentrated sulfuric acid. Write appropriate equations for the reactions. (*Hint:* These are not redox reactions.) (b) Why is it that HBr and HI cannot be prepared similarly, that is, by reacting  $\text{NaBr}$  and  $\text{NaI}$  with concentrated sulfuric acid? (*Hint:*  $\text{H}_2\text{SO}_4$  is a stronger oxidizing agent than both  $\text{Br}_2$  and  $\text{I}_2$ .) (c) HBr can be prepared by reacting phosphorus tribromide ( $\text{PBr}_3$ ) with water. Write an equation for this reaction.
- 4.112** Referring to Figure 4.14, explain why one must first dissolve the solid completely before making up the solution to the correct volume.

## SPECIAL PROBLEMS

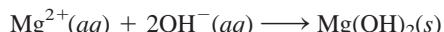
- 4.113** Magnesium is a valuable, lightweight metal. It is used as a structural metal and in alloys, in batteries, and in chemical synthesis. Although magnesium is plentiful in Earth's crust, it is cheaper to "mine" the metal from seawater. Magnesium forms the second most abundant cation in the sea (after sodium); there are about 1.3 g of magnesium in 1 kg of seawater. The method of obtaining magnesium from seawater employs all three types of reactions discussed in this chapter: precipitation, acid-base, and redox reactions. In the first stage in the recovery of magnesium, limestone ( $\text{CaCO}_3$ ) is heated at high temperatures to produce quicklime, or calcium oxide ( $\text{CaO}$ ):



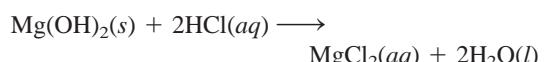
When calcium oxide is treated with seawater, it forms calcium hydroxide [ $\text{Ca}(\text{OH})_2$ ], which is slightly soluble and ionizes to give  $\text{Ca}^{2+}$  and  $\text{OH}^-$  ions:



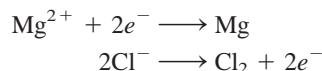
The surplus hydroxide ions cause the much less soluble magnesium hydroxide to precipitate:



The solid magnesium hydroxide is filtered and reacted with hydrochloric acid to form magnesium chloride ( $\text{MgCl}_2$ ):

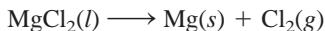


After the water is evaporated, the solid magnesium chloride is melted in a steel cell. The molten magnesium chloride contains both  $\text{Mg}^{2+}$  and  $\text{Cl}^-$  ions. In a process called electrolysis, an electric current is passed through the cell to reduce the  $\text{Mg}^{2+}$  ions and oxidize the  $\text{Cl}^-$  ions. The half-reactions are



Magnesium hydroxide was precipitated from processed seawater in settling ponds. The Dow Chemical Company once operated.

The overall reaction is



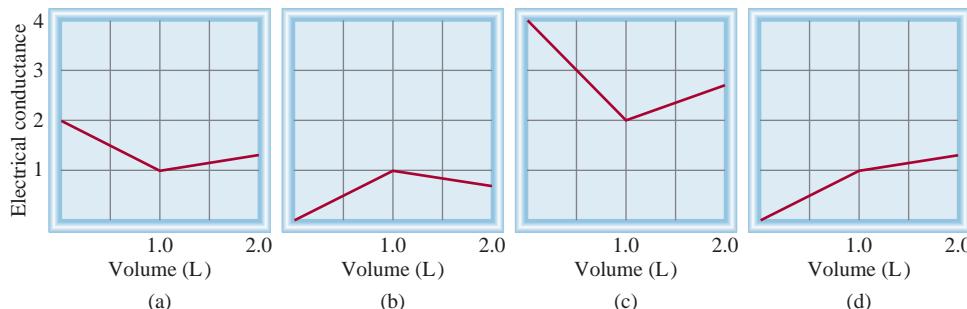
This is how magnesium metal is produced. The chlorine gas generated can be converted to hydrochloric acid and recycled through the process.

- (a) Identify the precipitation, acid-base, and redox processes.
  - (b) Instead of calcium oxide, why don't we simply add sodium hydroxide to precipitate magnesium hydroxide?
  - (c) Sometimes a mineral called dolomite (a combination of  $\text{CaCO}_3$  and  $\text{MgCO}_3$ ) is substituted for limestone ( $\text{CaCO}_3$ ) to bring about the precipitation of magnesium hydroxide. What is the advantage of using dolomite?
  - (d) What are the advantages of mining magnesium from the ocean rather than from Earth's crust?
- 4.114** A 5.012-g sample of an iron chloride hydrate was dried in an oven. The mass of the anhydrous compound was 3.195 g. The compound was dissolved in water and reacted with an excess of  $\text{AgNO}_3$ . The precipitate of  $\text{AgCl}$  formed weighed 7.225 g. What is the formula of the original compound?

- 4.115** A 22.02-mL solution containing 1.615 g  $\text{Mg}(\text{NO}_3)_2$  is mixed with a 28.64-mL solution containing 1.073 g NaOH. Calculate the concentrations of the ions remaining in solution after the reaction is complete. Assume volumes are additive.

**4.116** Because acid-base and precipitation reactions discussed in this chapter all involve ionic species, their progress can be monitored by measuring the electrical conductance of the solution. Match the following reactions with the diagrams shown here. The electrical conductance is shown in arbitrary units.

- (1) A 1.0 M KOH solution is added to 1.0 L of 1.0 M  $\text{CH}_3\text{COOH}$ .
- (2) A 1.0 M NaOH solution is added to 1.0 L of 1.0 M HCl.
- (3) A 1.0 M  $\text{BaCl}_2$  solution is added to 1.0 L of 1.0 M  $\text{K}_2\text{SO}_4$ .
- (4) A 1.0 M NaCl solution is added to 1.0 L of 1.0 M  $\text{AgNO}_3$ .
- (5) A 1.0 M  $\text{CH}_3\text{COOH}$  solution is added to 1.0 L of 1.0 M  $\text{NH}_3$ .



## ANSWERS TO PRACTICE EXERCISES

- 4.1** (a) Insoluble, (b) insoluble, (c) soluble. **4.2**  $\text{Al}^{3+}(aq) + 3\text{OH}^-(aq) \longrightarrow \text{Al}(\text{OH})_3(s)$ . **4.3** (a) Brønsted base, (b) Brønsted acid, (c) Brønsted acid and Brønsted base.  
**4.4** (a) P: +3, F: -1; (b) Mn: +7, O: -2. **4.5** 0.452 M.

- 4.6** 494 mL. **4.7** Dilute 34.2 mL of the stock solution to 200 mL. **4.8** 92.02%. **4.9** 0.3822 g.  
**4.10** 10.1 mL.

# 5



A tornado is a violently rotating column of air extending from a thunderstorm to the ground.

## Gases

### CHAPTER OUTLINE

- 5.1 Substances That Exist as Gases 133
- 5.2 Pressure of a Gas 134
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- 5.3 The Gas Laws 136
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  - Density and Molar Mass of a Gaseous Substance •
  - Gas Stoichiometry
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  - Application to the Gas Laws • Distribution of Molecular Speeds •
  - Root-Mean-Square Speed • Gas Diffusion and Effusion
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### ESSENTIAL CONCEPTS

**Properties of Gases** Gases assume the volume and shape of their containers; they are easily compressible; they mix evenly and completely; and they have much lower densities than liquids and solids.

**Gas Pressures** Pressure is one of the most readily measurable properties of a gas. A barometer measures atmospheric pressure and a manometer measures the pressure of a gas in the laboratory.

**The Gas Laws** Over the years, a number of laws have been developed to explain the physical behavior of gases. These laws show the relationships among the pressure, temperature, volume, and amount of a gas.

**The Ideal Gas Equation** The molecules of an ideal gas possess no volume and exert no forces on one another. At low pressures and high temperatures, most gases can be assumed to behave ideally; their physical behavior is described by the ideal gas equation.

**Kinetic Molecular Theory of Gases** Macroscopic properties like pressure and temperature of a gas can be related to the kinetic motion of molecules. The kinetic molecular theory of gases assumes that the molecules are ideal, the number of molecules is very large, and that their motions are totally random. Both gas diffusion and gas effusion demonstrate random molecular motion and are governed by the same mathematical laws.

**Nonideal Behavior of Gases** To account for the behavior of real gases, the ideal gas equation is modified to include the finite volume of molecules and the attractive forces among them.

### Interactive



### Activity Summary

1. Animation: The Gas Laws (5.3)
2. Interactivity: Boyle's Law (5.3)
3. Interactivity: Volume in Gas Laws (5.3)
4. Interactivity: Primary Gas Laws (5.4)
5. Interactivity: Dalton's Law (5.5)
6. Animation: Collecting a Gas over Water (5.5)
7. Animation: Diffusion of Gases (5.6)

## 5.1 Substances That Exist as Gases

We live at the bottom of an ocean of air whose composition by volume is roughly 78 percent N<sub>2</sub>, 21 percent O<sub>2</sub>, and 1 percent other gases, including CO<sub>2</sub>. In the 1990s, the chemistry of this vital mixture of gases became a source of great interest because of the detrimental effects of environmental pollution. Here we will focus generally on the behavior of substances that exist as gases under normal atmospheric conditions, which are defined as 25°C and 1 atmosphere (atm) pressure (see Section 5.2).

Only 11 elements are gases under normal atmospheric conditions. Table 5.1 lists these, along with a number of gaseous compounds. Note that the elements hydrogen, nitrogen, oxygen, fluorine, and chlorine exist as gaseous diatomic molecules. Another form of oxygen, ozone (O<sub>3</sub>), is also a gas at room temperature. All the elements in Group 8A, the noble gases, are monatomic gases: He, Ne, Ar, Kr, Xe, and Rn.

Of the gases listed in Table 5.1, only O<sub>2</sub> is essential for our survival. Hydrogen cyanide (HCN) is a deadly poison. Carbon monoxide (CO), hydrogen sulfide (H<sub>2</sub>S), nitrogen dioxide (NO<sub>2</sub>), O<sub>3</sub>, and sulfur dioxide (SO<sub>2</sub>) are somewhat less toxic. The gases He and Ne are chemically inert; that is, they do not react with any other substance. Most gases are colorless. Exceptions are F<sub>2</sub>, Cl<sub>2</sub>, and NO<sub>2</sub>. The dark-brown color of NO<sub>2</sub> is sometimes visible in polluted air. All gases have the following physical characteristics:

- Gases assume the volume and shape of their containers.
- Gases are the most compressible of the states of matter.
- Gases will mix evenly and completely when confined to the same container.
- Gases have much lower densities than liquids and solids.

1A	2A							8A
H								He
		N	O	F	Ne			
				Cl	Ar			
					Kr			
					Xe			
					Rn			

Elements that exist as gases at 25°C and 1 atm. The noble gases (the Group 8A elements) are monatomic species; the other elements exist as diatomic molecules. Ozone (O<sub>3</sub>) is also a gas.



NO<sub>2</sub> gas.

**TABLE 5.1** Some Substances Found as Gases at 1 Atm and 25°C

Elements	Compounds
H <sub>2</sub> (molecular hydrogen)	HF (hydrogen fluoride)
N <sub>2</sub> (molecular nitrogen)	HCl (hydrogen chloride)
O <sub>2</sub> (molecular oxygen)	HBr (hydrogen bromide)
O <sub>3</sub> (ozone)	HI (hydrogen iodide)
F <sub>2</sub> (molecular fluorine)	CO (carbon monoxide)
Cl <sub>2</sub> (molecular chlorine)	CO <sub>2</sub> (carbon dioxide)
He (helium)	NH <sub>3</sub> (ammonia)
Ne (neon)	NO (nitric oxide)
Ar (argon)	NO <sub>2</sub> (nitrogen dioxide)
Kr (krypton)	N <sub>2</sub> O (nitrous oxide)
Xe (xenon)	SO <sub>2</sub> (sulfur dioxide)
Rn (radon)	H <sub>2</sub> S (hydrogen sulfide)
	HCN (hydrogen cyanide)*

A gas is a substance that is normally in the gaseous state at ordinary temperatures and pressures; a vapor is the gaseous form of any substance that is a liquid or a solid at normal temperatures and pressures. Thus, at 25°C and 1 atm pressure, we speak of water vapor and oxygen gas.

\* The boiling point of HCN is 26°C, but it is close enough to qualify as a gas at ordinary atmospheric conditions.

## 5.2 Pressure of a Gas

Gases exert pressure on any surface with which they come in contact, because gas molecules are constantly in motion. We humans have adapted so well physiologically to the pressure of the air around us that we are usually unaware of it, perhaps as fish are not conscious of the water's pressure on them.

It is easy to demonstrate atmospheric pressure. One everyday example is the ability to drink a liquid through a straw. Sucking air out of the straw reduces the pressure inside the straw. The greater atmospheric pressure on the liquid pushes it up into the straw to replace the air that has been sucked out.

### SI Units of Pressure

Pressure is one of the most readily measurable properties of a gas. To understand how we measure the pressure of a gas, it is helpful to know how the units of measurement are derived. We begin with velocity and acceleration.

*Velocity* is defined as the change in distance with elapsed time; that is,

$$\text{velocity} = \frac{\text{distance moved}}{\text{elapsed time}}$$

The SI unit for velocity is m/s, although we also use cm/s.

*Acceleration* is the change in velocity with time, or

$$\text{acceleration} = \frac{\text{change in velocity}}{\text{elapsed time}}$$

Acceleration is measured in m/s<sup>2</sup> (or cm/s<sup>2</sup>).

The second law of motion, formulated by Sir Isaac Newton in the late seventeenth century, defines another term, from which the units of pressure are derived, namely, *force*. According to this law,

$$\text{force} = \text{mass} \times \text{acceleration}$$

1 N is roughly equivalent to the force exerted by Earth's gravity on an apple.

In this context, the *SI unit of force* is the **newton (N)**, where

$$1 \text{ N} = 1 \text{ kg m/s}^2$$

Finally, we define **pressure** as *force applied per unit area*:

$$\text{pressure} = \frac{\text{force}}{\text{area}}$$

The SI unit of pressure is the **pascal (Pa)**, defined as *one newton per square meter*:

$$1 \text{ Pa} = 1 \text{ N/m}^2$$

### Atmospheric Pressure

The atoms and molecules of the gases in the atmosphere, like those of all other matter, are subject to Earth's gravitational pull. As a consequence, the atmosphere is much denser near the surface of Earth than at high altitudes. (The air outside the pressurized cabin of an airplane at 9 km is too thin to breathe.) In fact, the density of air

decreases very rapidly with increasing distance from Earth. Measurements show that about 50 percent of the atmosphere lies within 6.4 km of Earth's surface, 90 percent within 16 km, and 99 percent within 32 km. Not surprisingly, the denser the air is, the greater the pressure it exerts. The force experienced by any area exposed to Earth's atmosphere is equal to *the weight of the column of air above it*. **Atmospheric pressure** is the pressure exerted by Earth's atmosphere (Figure 5.1). The actual value of atmospheric pressure depends on location, temperature, and weather conditions.

Does atmospheric pressure only act downward, as you might infer from its definition? Imagine what would happen, then, if you were to hold a piece of paper tight with both hands above your head. You might expect the paper to bend due to the pressure of air acting on it, but this does not happen. The reason is that air, like water, is a fluid. The pressure exerted on an object in a fluid comes from all directions—downward and upward, as well as from the left and from the right. At the molecular level, air pressure results from collisions between the air molecules and any surface with which they come in contact. The magnitude of pressure depends on how often and how strongly the molecules impact the surface. It turns out that there are just as many molecules hitting the paper from the top as there are from underneath, so the paper stays flat.

How is atmospheric pressure measured? The **barometer** is probably the most familiar *instrument for measuring atmospheric pressure*. A simple barometer consists of a long glass tube, closed at one end and filled with mercury. If the tube is carefully inverted in a dish of mercury so that no air enters the tube, some mercury will flow out of the tube into the dish, creating a vacuum at the top (Figure 5.2). The weight of the mercury remaining in the tube is supported by atmospheric pressure acting on the surface of the mercury in the dish. **Standard atmospheric pressure (1 atm)** is equal to *the pressure that supports a column of mercury exactly 760 mm (or 76 cm) high at 0°C at sea level*. In other words, the standard atmosphere equals a pressure of 760 mmHg, where mmHg represents the pressure exerted by a column of mercury 1 mm high. The mmHg unit is also called the *torr*, after the Italian scientist Evangelista Torricelli, who invented the barometer. Thus,

$$1 \text{ torr} = 1 \text{ mmHg}$$

and

$$\begin{aligned} 1 \text{ atm} &= 760 \text{ mmHg (exactly)} \\ &= 760 \text{ torr} \end{aligned}$$

The relation between atmospheres and pascals (see Appendix 1) is

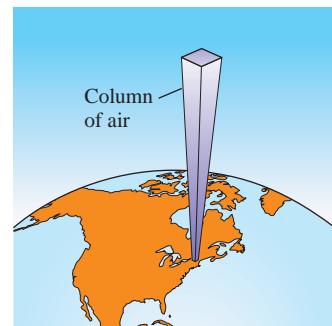
$$\begin{aligned} 1 \text{ atm} &= 101,325 \text{ Pa} \\ &= 1.01325 \times 10^5 \text{ Pa} \end{aligned}$$

and because  $1000 \text{ Pa} = 1 \text{ kPa}$  (kilopascal)

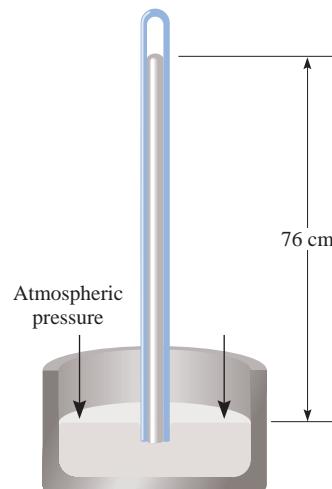
$$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$$

### Example 5.1

The pressure outside a jet plane flying at high altitude falls considerably below standard atmospheric pressure. Therefore, the air inside the cabin must be pressurized to protect the passengers. What is the pressure in atmospheres in the cabin if the barometer reading is 688 mmHg?



**Figure 5.1**  
A column of air extending from sea level to the upper atmosphere.

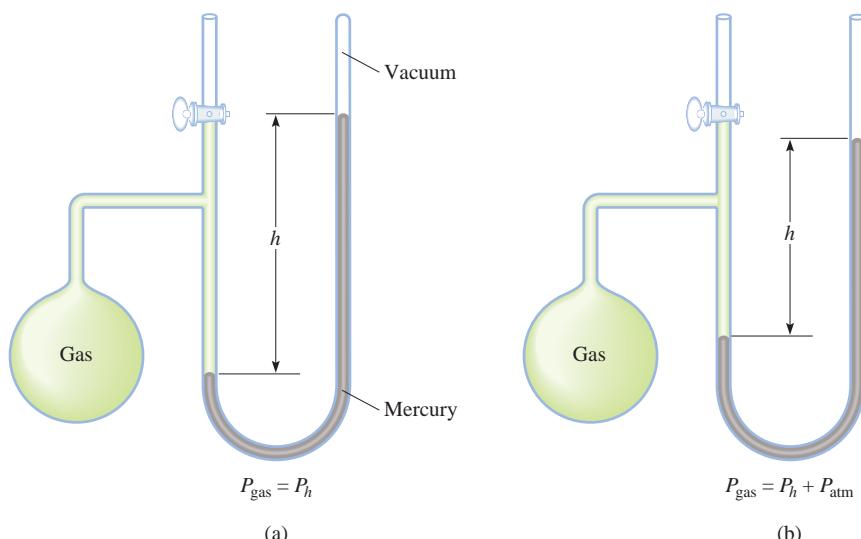


**Figure 5.2**  
A barometer for measuring atmospheric pressure. Above the mercury in the tube is a vacuum. The column of mercury is supported by the atmospheric pressure.

(Continued)

**Figure 5.3**

*Two types of manometers used to measure gas pressures.*  
*(a) Gas pressure is less than atmospheric pressure. (b) Gas pressure is greater than atmospheric pressure.*



**Strategy** Because  $1 \text{ atm} = 760 \text{ mmHg}$ , the following conversion factor is needed to obtain the pressure in atmospheres

$$\frac{1 \text{ atm}}{760 \text{ mmHg}}$$

**Solution** The pressure in the cabin is given by

$$\begin{aligned} \text{pressure} &= 688 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \\ &= 0.905 \text{ atm} \end{aligned}$$

**Similar problem:** 5.14.

**Practice Exercise** Convert 749 mmHg to atmospheres.

A **manometer** is a device used to measure the pressure of gases other than the atmosphere. The principle of operation of a manometer is similar to that of a barometer. There are two types of manometers, shown in Figure 5.3. The *closed-tube manometer* is normally used to measure pressures below atmospheric pressure [Figure 5.3(a)], whereas the *open-tube manometer* is better suited for measuring pressures equal to or greater than atmospheric pressure [Figure 5.3(b)].

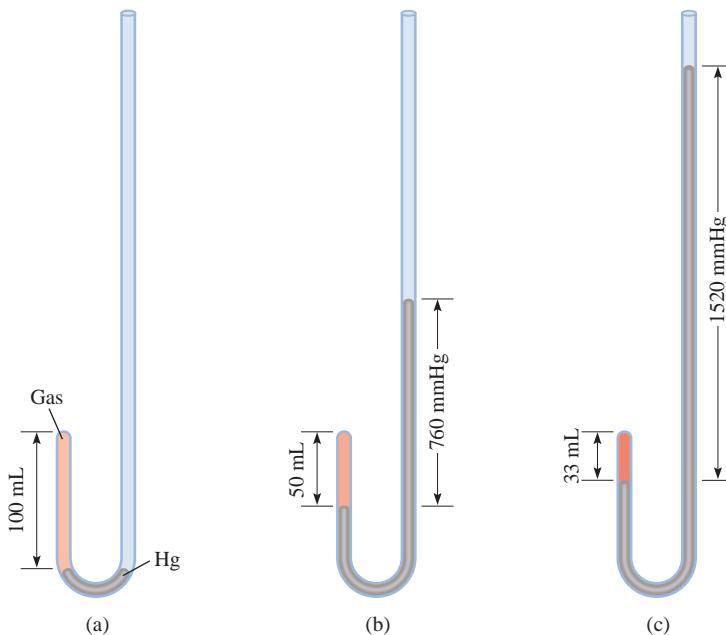
Nearly all barometers and most manometers use mercury as the working fluid, despite the fact that it is a toxic substance with a harmful vapor. The reason is that mercury has a very high density (13.6 g/mL) compared with most other liquids. Because the height of the liquid in a column is inversely proportional to the liquid's density, this property enables the construction of manageable small barometers and manometers.

## 5.3 The Gas Laws



**Animation:**  
The Gas Laws  
ARIS, Animations

The gas laws we will study in this chapter are the product of countless experiments on the physical properties of gases that were carried out over several centuries. Each of these generalizations regarding the macroscopic behavior of gaseous substances represents a milestone in the history of science. Together they have played a major role in the development of many ideas in chemistry.

**Figure 5.4**

Apparatus for studying the relationship between pressure and volume of a gas. (a) The levels of mercury are equal and the pressure of the gas is equal to the atmospheric pressure (760 mmHg). The gas volume is 100 mL. (b) Doubling the pressure by adding more mercury reduces the gas volume to 50 mL. (c) Tripling the pressure decreases the gas volume to one-third of the original volume. The temperature and amount of gas are kept constant.

## The Pressure-Volume Relationship: Boyle's Law

In the seventeenth century, the British chemist Robert Boyle studied the behavior of gases systematically and quantitatively. In one series of studies, Boyle investigated the pressure-volume relationship of a gas sample using an apparatus like that shown in Figure 5.4. In Figure 5.4(a) the pressure exerted on the gas by the mercury added to the tube is equal to atmospheric pressure. In Figure 5.4(b) an increase in pressure due to the addition of more mercury results in a decrease in the volume of the gas and in unequal levels of mercury in the tube. Boyle noticed that when temperature is held constant, the volume ( $V$ ) of a given amount of a gas decreases as the total applied pressure ( $P$ )—atmospheric pressure plus the pressure due to the added mercury—is increased. This relationship between pressure and volume is evident in Figure 5.4. Conversely, if the applied pressure is decreased, the gas volume becomes larger.

The mathematical expression showing an inverse relationship between pressure and volume is

$$P \propto \frac{1}{V}$$

where the symbol  $\propto$  means *proportional to*. To change  $\propto$  to an equals sign, we must write

$$P = k_1 \times \frac{1}{V} \quad (5.1a)$$

where  $k_1$  is a constant called the *proportionality constant*. Equation (5.1a) is an expression of **Boyle's law**, which states that *the pressure of a fixed amount of gas maintained at constant temperature is inversely proportional to the volume of the gas*. We can rearrange Equation (5.1a) and obtain

$$PV = k_1 \quad (5.1b)$$

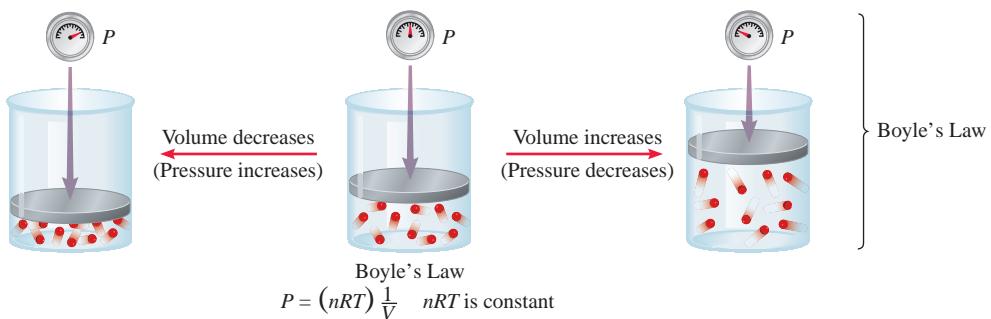
This form of Boyle's law says that the product of the pressure and volume of a gas at constant temperature and amount of gas is a constant. Figure 5.5 is a schematic

**The pressure applied to a gas is equal to the gas pressure.**

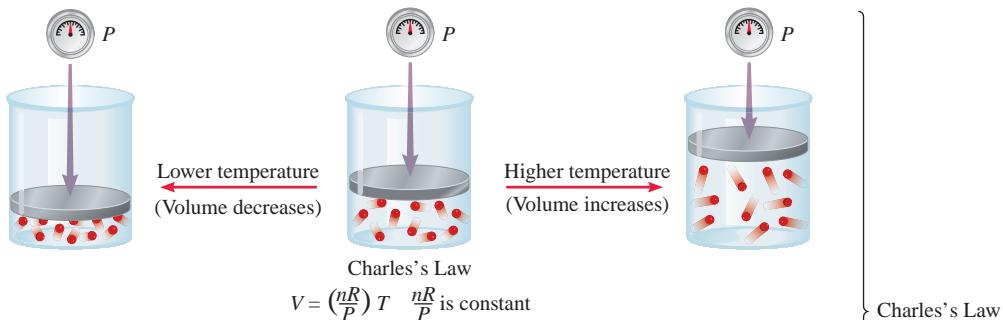


**Interactivity:**  
Boyle's Law  
ARIS, Interactives

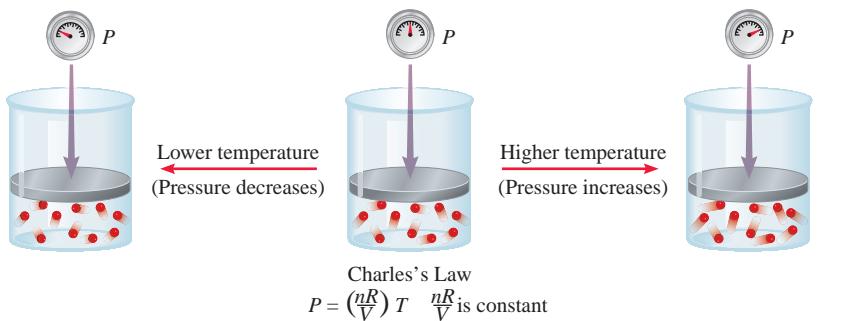
Increasing or decreasing the volume of a gas at a constant temperature



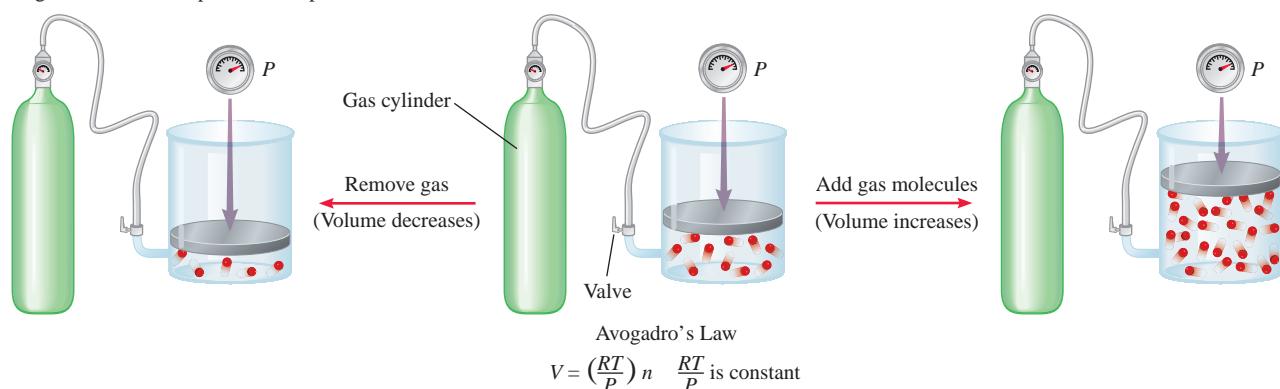
Heating or cooling a gas at constant pressure



Heating or cooling a gas at constant volume

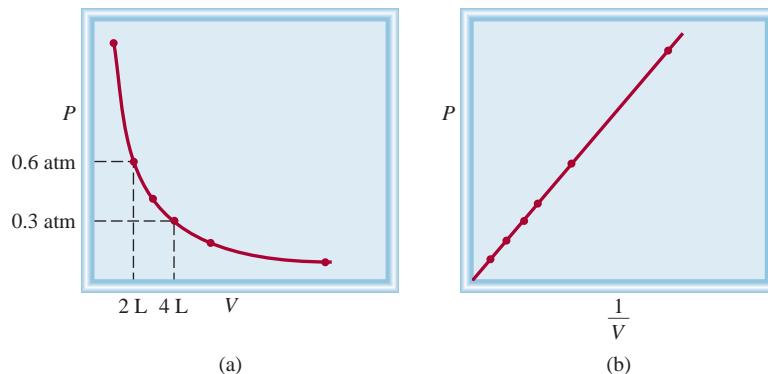


Dependence of volume on amount of gas at constant temperature and pressure



**Figure 5.5**

Schematic illustrations of Boyle's law, Charles's law, and Avogadro's law.



**Figure 5.6**  
Graphs showing variation of the volume of a gas with the pressure exerted on the gas, at constant temperature. (a)  $P$  versus  $V$ . Note that the volume of the gas doubles as the pressure is halved. (b)  $P$  versus  $1/V$ .

representation of Boyle's law. The quantity  $n$  is the number of moles of the gas and  $R$  is a constant to be defined in Section 5.4. Thus, the proportionality constant  $k_1$  in Equations (5.1) is equal to  $nRT$ .

The concept of one quantity being proportional to another and the use of a proportionality constant can be clarified through the following analogy. The daily income of a movie theater depends on both the price of the tickets (in dollars per ticket) and the number of tickets sold. Assuming that the theater charges one price for all tickets, we write

$$\text{income} = (\text{dollar/ticket}) \times \text{number of tickets sold}$$

Because the number of tickets sold varies from day to day, the income on a given day is said to be proportional to the number of tickets sold:

$$\begin{aligned}\text{income} &\propto \text{number of tickets sold} \\ &= C \times \text{number of tickets sold}\end{aligned}$$

where  $C$ , the proportionality constant, is the price per ticket.

Figure 5.6 shows two conventional ways of expressing Boyle's findings graphically. Figure 5.6(a) is a graph of the equation  $PV = k_1$ ; Figure 5.6(b) is a graph of the equivalent equation  $P = k_1 \times 1/V$ . Note that the latter is a linear equation of the form  $y = mx + b$ , where  $m = k_1$  and  $b = 0$ .

Although the individual values of pressure and volume can vary greatly for a given sample of gas, as long as the temperature is held constant and the amount of the gas does not change,  $P$  times  $V$  is always equal to the same constant. Therefore, for a given sample of gas under two different sets of conditions at constant temperature, we have

$$P_1V_1 = k_1 = P_2V_2$$

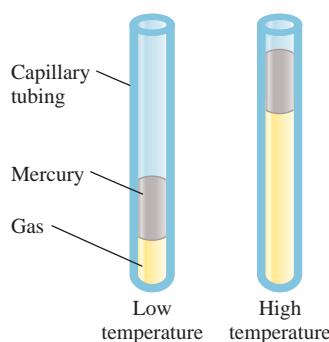
or

$$P_1V_1 = P_2V_2 \quad (5.2)$$

where  $V_1$  and  $V_2$  are the volumes at pressures  $P_1$  and  $P_2$ , respectively.

### The Temperature-Volume Relationship: Charles's and Gay-Lussac's Law

Boyle's law depends on the temperature of the system remaining constant. But suppose the temperature changes: How does a change in temperature affect the volume and pressure of a gas? Let us first look at the effect of temperature on the volume of

**Figure 5.7**

*Variation of the volume of a gas sample with temperature, at constant pressure. The pressure exerted on the gas is the sum of the atmospheric pressure and the pressure due to the weight of the mercury.*

**Under special experimental conditions, scientists have succeeded in approaching absolute zero to within a small fraction of a kelvin.**

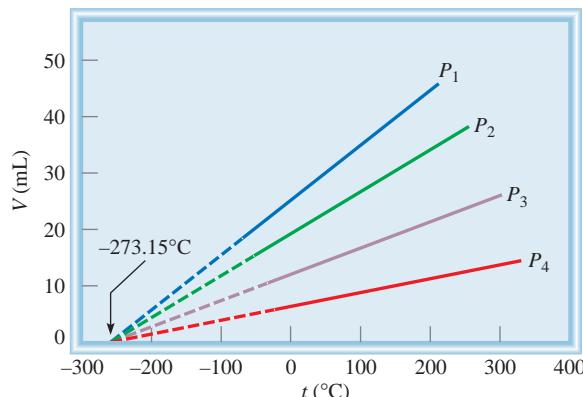
a gas. The earliest investigators of this relationship were French scientists, Jacques Charles and Joseph Gay-Lussac. Their studies showed that, at constant pressure, the volume of a gas sample expands when heated and contracts when cooled (Figure 5.7). The quantitative relations involved in changes in gas temperature and volume turn out to be remarkably consistent. For example, we observe an interesting phenomenon when we study the temperature-volume relationship at various pressures. At any given pressure, the plot of volume versus temperature yields a straight line. By extending the line to zero volume, we find the intercept on the temperature axis to be  $-273.15^{\circ}\text{C}$ . At any other pressure, we obtain a different straight line for the volume-temperature plot, but we get the *same* zero-volume temperature intercept at  $-273.15^{\circ}\text{C}$ . (Figure 5.8). (In practice, we can measure the volume of a gas over only a limited temperature range, because all gases condense at low temperatures to form liquids.)

In 1848 the Scottish physicist Lord Kelvin realized the significance of this phenomenon. He identified  $-273.15^{\circ}\text{C}$ . as *absolute zero, theoretically the lowest attainable temperature*. Then he set up an *absolute temperature scale*, now called the *Kelvin temperature scale*, with *absolute zero as the starting point*. On the Kelvin scale, one kelvin (K) is equal in magnitude to one degree Celsius. The only difference between the absolute temperature scale and the Celsius scale is that the zero position is shifted. Important points on the two scales match up as follows:

	Kelvin Scale	Celsius Scale
Absolute zero	0 K	$-273.15^{\circ}\text{C}$ .
Freezing point of water	273.15 K	$0^{\circ}\text{C}$
Boiling point of water	373.15 K	$100^{\circ}\text{C}$

The conversion between  $^{\circ}\text{C}$  and K is given in Section 1.5:

$$\text{? K} = (\text{? } ^{\circ}\text{C} + 273.15^{\circ}\text{C}) \frac{1 \text{ K}}{1^{\circ}\text{C}}$$

**Figure 5.8**

*Variation of the volume of a gas sample with temperature, at constant pressure. Each line represents the variation at a certain pressure. The pressures increase from  $P_1$  to  $P_4$ . All gases ultimately condense (become liquids) if they are cooled to sufficiently low temperatures; the solid portions of the lines represent the temperature region above the condensation point. When these lines are extrapolated, or extended (the dashed portions), they all intersect at the point representing zero volume and a temperature of  $-273.15^{\circ}\text{C}$ .*

In most calculations we will use 273 instead of 273.15 as the term relating K and °C. By convention, we use  $T$  to denote absolute (kelvin) temperature and  $t$  to indicate temperature on the Celsius scale.

The dependence of the volume of a gas on temperature is given by

$$\begin{aligned}V &\propto T \\V &= k_2 T\end{aligned}$$

or

$$\frac{V}{T} = k_2 \quad (5.3)$$

where  $k_2$  is the proportionality constant. Equation (5.3) is known as **Charles's and Gay-Lussac's law**, or simply **Charles's law**, which states that *the volume of a fixed amount of gas maintained at constant pressure is directly proportional to the absolute temperature of the gas*. Charles's law is also illustrated in Figure 5.5. We see that the proportionality constant  $k_2$  in Equation (5.3) is equal to  $nR/P$ .

Just as we did for pressure-volume relationships at constant temperature, we can compare two sets of volume-temperature conditions for a given sample of gas at constant pressure. From Equation (5.3) we can write

$$\frac{V_1}{T_1} = k_2 = \frac{V_2}{T_2}$$

or

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (5.4)$$

**Temperature must be in kelvins in gas law calculations.**

where  $V_1$  and  $V_2$  are the volumes of the gas at temperatures  $T_1$  and  $T_2$  (both in kelvins), respectively.

Another form of Charles's law shows that at constant amount of gas and volume, the pressure of a gas is proportional to temperature

$$\begin{aligned}P &\propto T \\P &= k_3 T\end{aligned}$$

or

$$\frac{P}{T} = k_3 \quad (5.5)$$

From Figure 5.5 we see that  $k_3 = nR/V$ . Starting with Equation (5.5), we have

$$\frac{P_1}{T_1} = k_3 = \frac{P_2}{T_2}$$

or

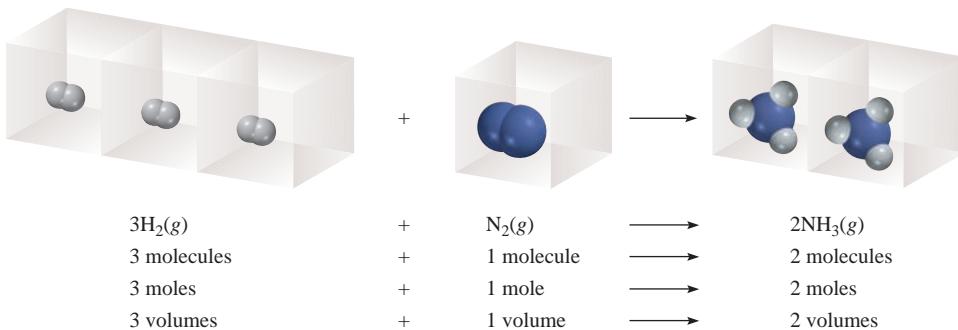
$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad (5.6)$$

where  $P_1$  and  $P_2$  are the pressures of the gas at temperatures  $T_1$  and  $T_2$ , respectively.

## The Volume-Amount Relationship: Avogadro's Law

The work of the Italian scientist Amedeo Avogadro complemented the studies of Boyle, Charles, and Gay-Lussac. In 1811 he published a hypothesis stating that at the same

**Avogadro's name first appeared in Section 3.2.**

**Figure 5.9**

Volume relationship of gases in a chemical reaction. The ratio of the volumes of molecular hydrogen to molecular nitrogen is 3:1, and that of ammonia (the product) to molecular hydrogen and molecular nitrogen combined (the reactants) is 2:4, or 1:2.

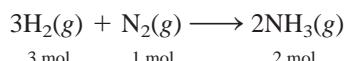
temperature and pressure, equal volumes of different gases contain the same number of molecules (or atoms if the gas is monatomic). It follows that the volume of any given gas must be proportional to the number of moles of molecules present; that is,

$$V \propto n$$

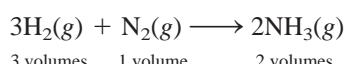
$$V = k_4 n \quad (5.7)$$

where  $n$  represents the number of moles and  $k_4$  is the proportionality constant. Equation (5.7) is the mathematical expression of *Avogadro's law*, which states that *at constant pressure and temperature, the volume of a gas is directly proportional to the number of moles of the gas present*. From Figure 5.5 we see that  $k_4 = RT/P$ .

According to Avogadro's law we see that when two gases react with each other, their reacting volumes have a simple ratio to each other. If the product is a gas, its volume is related to the volume of the reactants by a simple ratio (a fact demonstrated earlier by Gay-Lussac). For example, consider the synthesis of ammonia from molecular hydrogen and molecular nitrogen:



Because, at the same temperature and pressure, the volumes of gases are directly proportional to the number of moles of the gases present, we can now write



The volume ratio of molecular hydrogen to molecular nitrogen is 3:1, and that of ammonia (the product) to molecular hydrogen and molecular nitrogen combined (the reactants) is 2:4, or 1:2 (Figure 5.9).

## 5.4 The Ideal Gas Equation

Let us summarize the gas laws we have discussed so far:

$$\text{Boyle's law: } V \propto \frac{1}{P} \quad (\text{at constant } n \text{ and } T)$$

$$\text{Charles's law: } V \propto T \quad (\text{at constant } n \text{ and } P)$$

$$\text{Avogadro's law: } V \propto n \quad (\text{at constant } P \text{ and } T)$$



**Interactivity:**  
Volume in Gas Laws  
ARIS, Interactives



**Interactivity:**  
Primary Gas Laws  
ARIS, Interactives

We can combine all three expressions to form a single master equation for the behavior of gases:

$$V \propto \frac{nT}{P}$$

$$V = R \frac{nT}{P}$$

or

$$PV = nRT \quad (5.8)$$

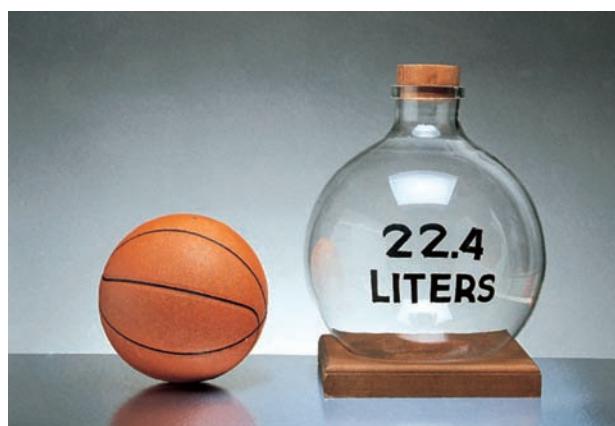
where  $R$ , the proportionality constant, is called the **gas constant**. Equation (5.8), which is called the **ideal gas equation**, describes the relationship among the four variables  $P$ ,  $V$ ,  $T$ , and  $n$ . An **ideal gas** is a hypothetical gas whose pressure-volume-temperature behavior can be completely accounted for by the ideal gas equation. The molecules of an ideal gas do not attract or repel one another, and their volume is negligible compared with the volume of the container. Although there is no such thing in nature as an ideal gas, discrepancies in the behavior of real gases over reasonable temperature and pressure ranges do not significantly affect calculations. Thus, we can safely use the ideal gas equation to solve many gas problems.

Before we can apply the ideal gas equation to a real system, we must evaluate the gas constant  $R$ . At 0°C (273.15 K) and 1 atm pressure, many real gases behave like an ideal gas. Experiments show that under these conditions, 1 mole of an ideal gas occupies 22.414 L, which is somewhat greater than the volume of a basketball, as shown in Figure 5.10. The conditions 0°C and 1 atm are called **standard temperature and pressure**, often abbreviated **STP**. From Equation (5.8) we can write

$$\begin{aligned} R &= \frac{PV}{nT} \\ &= \frac{(1 \text{ atm})(22.414 \text{ L})}{(1 \text{ mol})(273.15 \text{ K})} \\ &= 0.082057 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \\ &= 0.082057 \text{ L} \cdot \text{atm/K} \cdot \text{mol} \end{aligned}$$

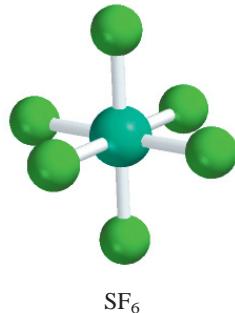
Keep in mind that the ideal gas equation, unlike the gas laws discussed in Section 5.3, applies to systems that do not undergo changes in pressure, volume, temperature, and amount of a gas.

The gas constant can be expressed in different units (see Appendix 2).



**Figure 5.10**  
A comparison of the molar volume at STP (which is approximately 22.4 L) with a basketball.

The dots between L and atm and between K and mol remind us that both L and atm are in the numerator and both K and mol are in the denominator. For most calculations, we will round off the value of  $R$  to three significant figures (0.0821 L · atm/K · mol) and use 22.4 L for the molar volume of a gas at STP.



### Example 5.2

Sulfur hexafluoride ( $\text{SF}_6$ ) is a colorless, odorless, very unreactive gas. Calculate the pressure (in atm) exerted by 1.82 moles of the gas in a steel vessel of volume 5.43 L at 45°C.

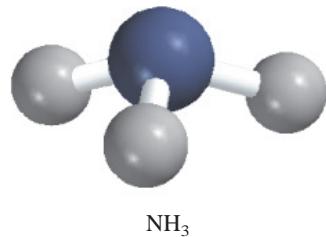
**Strategy** The problem gives the amount of the gas and its volume and temperature. Is the gas undergoing a change in any of its properties? What equation should we use to solve for the pressure? What temperature unit should we use?

**Solution** Because no changes in gas properties occur, we can use the ideal gas equation to calculate the pressure. Rearranging Equation (5.8), we write

$$\begin{aligned} P &= \frac{nRT}{V} \\ &= \frac{(1.82 \text{ mol})(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(45 + 273) \text{ K}}{5.43 \text{ L}} \\ &= 8.75 \text{ atm} \end{aligned}$$

Similar problems: 5.32, 5.33.

**Practice Exercise** Calculate the volume (in liters) occupied by 2.12 moles of nitric oxide (NO) at 6.54 atm and 76°C.



### Example 5.3

Calculate the volume (in liters) occupied by 7.40 g of  $\text{NH}_3$  at STP.

**Strategy** What is the volume of one mole of an ideal gas at STP? How many moles are there in 7.40 g of  $\text{NH}_3$ ?

**Solution** Recognizing that 1 mole of an ideal gas occupies 22.4 L at STP and using the molar mass of  $\text{NH}_3$  (17.03 g), we write the sequence of conversions as



so the volume of  $\text{NH}_3$  is given by

$$\begin{aligned} V &= 7.40 \text{ g } \text{NH}_3 \times \frac{1 \text{ mol } \text{NH}_3}{17.03 \text{ g } \text{NH}_3} \times \frac{22.4 \text{ L}}{1 \text{ mol } \text{NH}_3} \\ &= 9.73 \text{ L} \end{aligned}$$

It is often true in chemistry, particularly in gas-law calculations, that a problem can be solved in more than one way. Here the problem can also be solved by first converting 7.40 g of  $\text{NH}_3$  to the number of moles of  $\text{NH}_3$ , and then applying the ideal gas equation ( $V = nRT/P$ ). Try it.

**Check** Because 7.40 g of  $\text{NH}_3$  is smaller than its molar mass, its volume at STP should be smaller than 22.4 L. Therefore, the answer is reasonable.

**Practice Exercise** What is the volume (in liters) occupied by 49.8 g of HCl at STP?

Similar problems: 5.41, 5.43.

The ideal gas equation is useful for problems that do not involve changes in  $P$ ,  $V$ ,  $T$ , and  $n$  for a gas sample. At times, however, we need to deal with changes in pressure, volume, and temperature, or even in the amount of a gas. When conditions change, we must employ a modified form of the ideal gas equation that takes into account the initial and final conditions. We derive the modified equation as follows. From Equation (5.8),

$$R = \frac{P_1 V_1}{n_1 T_1} \text{ (before change)} \quad \text{and} \quad R = \frac{P_2 V_2}{n_2 T_2} \text{ (after change)}$$

Therefore,

$$\frac{P_1 V_1}{n_1 T_1} = R = \frac{P_2 V_2}{n_2 T_2} \quad (5.9)$$

The subscripts 1 and 2 denote the initial and final states of the gas. All of the gas laws discussed so far can be derived from Equation (5.9).

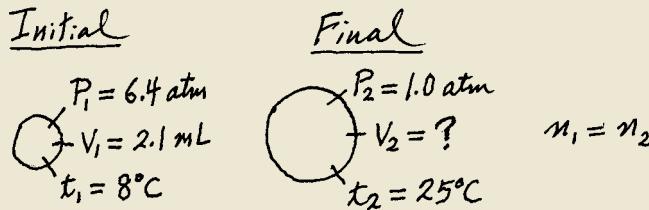
If  $n_1 = n_2$ , as is usually the case because the amount of gas normally does not change, the equation then becomes

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad (5.10)$$

### Example 5.4

A small bubble rises from the bottom of a lake, where the temperature and pressure are  $8^\circ\text{C}$  and 6.4 atm, to the water's surface, where the temperature is  $25^\circ\text{C}$  and the pressure is 1.0 atm. Calculate the final volume (in mL) of the bubble if its initial volume was 2.1 mL.

**Strategy** In solving this kind of problem, where a lot of information is given, it is sometimes helpful to make a sketch of the situation, as shown here:



What temperature unit should be used in the calculation?

**Solution** According to Equation (5.9)

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

We assume that the amount of air in the bubble remains constant, that is,  $n_1 = n_2$  so that

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

(Continued)

We can use any appropriate units for volume (or pressure) as long as we use the same units on both sides of the equation.

which is Equation (5.10). The given information is summarized:

Initial Conditions	Final Conditions
$P_1 = 6.4 \text{ atm}$	$P_2 = 1.0 \text{ atm}$
$V_1 = 2.1 \text{ mL}$	$V_2 = ?$
$T_1 = (8 + 273) \text{ K} = 281 \text{ K}$	$T_2 = (25 + 273) \text{ K} = 298 \text{ K}$

Rearranging Equation (5.10) gives

$$\begin{aligned} V_2 &= V_1 \times \frac{P_1}{P_2} \times \frac{T_2}{T_1} \\ &= 2.1 \text{ mL} \times \frac{6.4 \text{ atm}}{1.0 \text{ atm}} \times \frac{298 \text{ K}}{281 \text{ K}} \\ &= 14 \text{ mL} \end{aligned}$$

**Check** We see that the final volume involves multiplying the initial volume by a ratio of pressures ( $P_1/P_2$ ) and a ratio of temperatures ( $T_2/T_1$ ). Recall that volume is inversely proportional to pressure, and volume is directly proportional to temperature. Because the pressure decreases and temperature increases as the bubble rises, we expect the bubble's volume to increase. In fact, here the change in pressure plays a greater role in the volume change.

Similar problems: 5.35, 5.39.

**Practice Exercise** A gas initially at 4.0 L, 1.2 atm, and 66°C undergoes a change so that its final volume and temperature are 1.7 L and 42°C. What is its final pressure? Assume the number of moles remains unchanged.

## Density and Molar Mass of a Gaseous Substance

The ideal gas equation can be applied to determine the density or molar mass of a gaseous substance. Rearranging Equation (5.8), we write

$$\frac{n}{V} = \frac{P}{RT}$$

The number of moles of the gas,  $n$ , is given by

$$n = \frac{m}{\mathcal{M}}$$

in which  $m$  is the mass of the gas in grams and  $\mathcal{M}$  is its molar mass. Therefore,

$$\frac{m}{\mathcal{M}V} = \frac{P}{RT}$$

Because density,  $d$ , is mass per unit volume, we can write

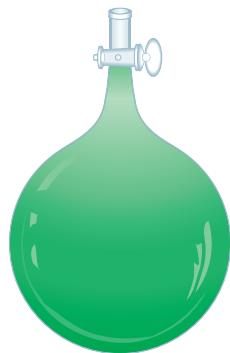
$$d = \frac{m}{V} = \frac{P\mathcal{M}}{RT} \quad (5.11)$$

Equation (5.11) enables us to calculate the density of a gas (given in units of grams per liter). More often, the density of a gas can be measured, so this equation can be

rearranged for us to calculate the molar mass of a gaseous substance:

$$\mathcal{M} = \frac{dRT}{P} \quad (5.12)$$

In a typical experiment, a bulb of known volume is filled with the gaseous substance under study. The temperature and pressure of the gas sample are recorded, and the total mass of the bulb plus gas sample is determined (Figure 5.11). The bulb is then evacuated (emptied) and weighed again. The difference in mass is the mass of the gas. The density of the gas is equal to its mass divided by the volume of the bulb. Then we can calculate the molar mass of the substance using Equation (5.12).



**Figure 5.11**

An apparatus for measuring the density of a gas. A bulb of known volume is filled with the gas under study at a certain temperature and pressure. First the bulb is weighed, and then it is emptied (evacuated) and weighed again. The difference in masses gives the mass of the gas. Knowing the volume of the bulb, we can calculate the density of the gas.

### Example 5.5

A chemist has synthesized a greenish-yellow gaseous compound of chlorine and oxygen and finds that its density is 7.71 g/L at 36°C and 2.88 atm. Calculate the molar mass of the compound and determine its molecular formula.

**Strategy** Because Equations (5.11) and (5.12) are rearrangements of each other, we can calculate the molar mass of a gas if we know its density, temperature, and pressure. The molecular formula of the compound must be consistent with its molar mass. What temperature unit should we use?

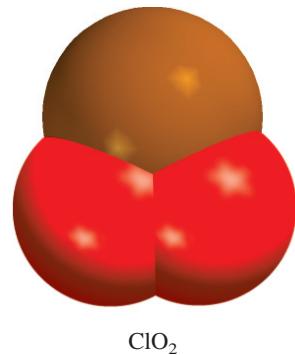
**Solution** From Equation (5.12)

$$\begin{aligned}\mathcal{M} &= \frac{dRT}{P} \\ &= \frac{(7.71 \text{ g/L})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(36 + 273) \text{ K}}{2.88 \text{ atm}} \\ &= 67.9 \text{ g/mol}\end{aligned}$$

We can determine the molecular formula of the compound by trial and error, using only the knowledge of the molar masses of chlorine (35.45 g) and oxygen (16.00 g). We know that a compound containing one Cl atom and one O atom would have a molar mass of 51.45 g, which is too low, while the molar mass of a compound made up of two Cl atoms and one O atom is 86.90 g, which is too high. Thus, the compound must contain one Cl atom and two O atoms and have the formula  $\text{ClO}_2$ , which has a molar mass of 67.45 g.

**Practice Exercise** The density of a gaseous organic compound is 3.38 g/L at 40°C and 1.97 atm. What is its molar mass?

Note that we can determine the molar mass of a compound without knowing its molecular formula.

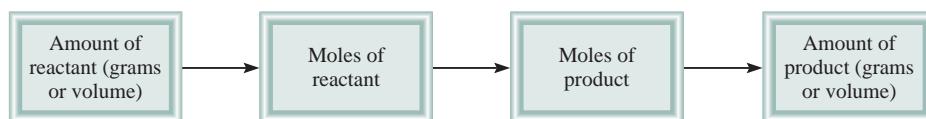


Similar problems: 5.47, 5.49.

## Gas Stoichiometry

In Chapter 3 we used relationships between amounts (in moles) and masses (in grams) of reactants and products to solve stoichiometry problems. When the reactants and/or products are gases, we can also use the relationships between amounts (moles,  $n$ ) and volume ( $V$ ) to solve such problems (Figure 5.12).

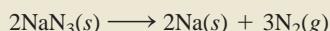
**Figure 5.12**  
Stoichiometric calculations involving gases.



An air bag can protect the driver in an automobile collision.

### Example 5.6

Sodium azide ( $\text{NaN}_3$ ) is used in some automobile air bags. The impact of a collision triggers the decomposition of  $\text{NaN}_3$  as follows:



The nitrogen gas produced quickly inflates the bag between the driver and the windshield and dashboard. Calculate the volume of  $\text{N}_2$  generated at  $80^\circ\text{C}$  and 823 mmHg by the decomposition of 60.0 g of  $\text{NaN}_3$ .

**Strategy** From the balanced equation we see that  $2 \text{ mol } \text{NaN}_3 \approx 3 \text{ mol } \text{N}_2$  so the conversion factor between  $\text{NaN}_3$  and  $\text{N}_2$  is

$$\frac{3 \text{ mol } \text{N}_2}{2 \text{ mol } \text{NaN}_3}$$

Because the mass of  $\text{NaN}_3$  is given, we can calculate the number of moles of  $\text{NaN}_3$  and hence the number of moles of  $\text{N}_2$  produced. Finally, we can calculate the volume of  $\text{N}_2$  using the ideal gas equation.

**Solution** The sequence of conversions is as follows:



First we calculate the number of moles of  $\text{N}_2$  produced by 60.0 g of  $\text{NaN}_3$ :

$$\begin{aligned} \text{moles of } \text{N}_2 &= 60.0 \text{ g } \cancel{\text{NaN}_3} \times \frac{1 \text{ mol } \cancel{\text{NaN}_3}}{65.02 \text{ g } \cancel{\text{NaN}_3}} \times \frac{3 \text{ mol } \text{N}_2}{2 \text{ mol } \cancel{\text{NaN}_3}} \\ &= 1.38 \text{ mol } \text{N}_2 \end{aligned}$$

The volume of 1.38 moles of  $\text{N}_2$  can be obtained by using the ideal gas equation:

$$\begin{aligned} V &= \frac{nRT}{P} = \frac{(1.38 \text{ mol})(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(80 + 273 \text{ K})}{(823/760) \text{ atm}} \\ &= 36.9 \text{ L} \end{aligned}$$

**Similar problems:** 5.51, 5.52.

**Practice Exercise** The equation for the metabolic breakdown of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) is the same as the equation for the combustion of glucose in air:



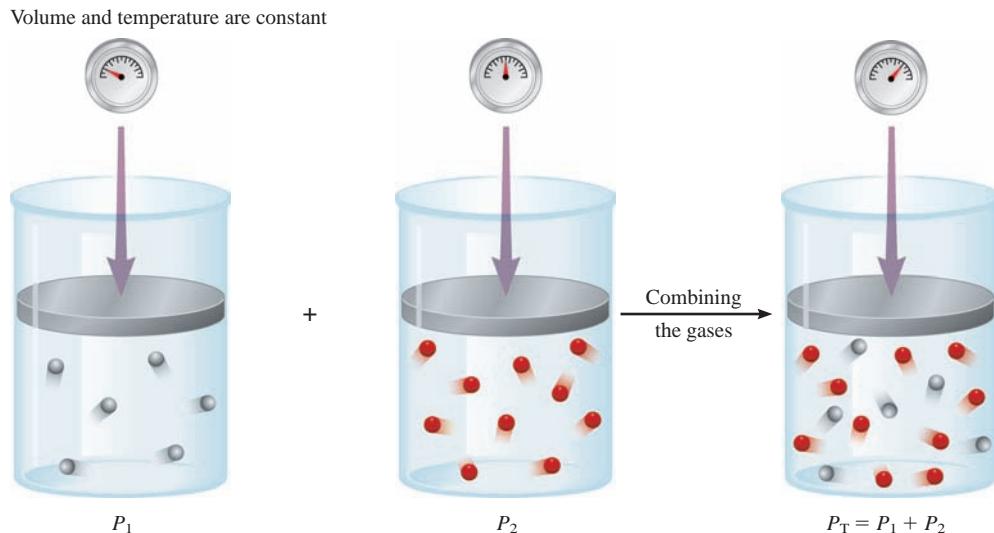
Calculate the volume of  $\text{CO}_2$  produced at  $37^\circ\text{C}$  and 1.00 atm when 5.60 g of glucose is used up in the reaction.

## 5.5 Dalton's Law of Partial Pressures

Thus far we have concentrated on the behavior of pure gaseous substances, but experimental studies very often involve mixtures of gases. For example, for a study of air pollution, we may be interested in the pressure-volume-temperature relationship of a



**Interactivity:**  
Dalton's Law  
ARIS, Interactives

**Figure 5.13**

Schematic illustration of Dalton's law of partial pressures.

sample of air, which contains several gases. In this case, and all cases involving mixtures of gases, the total gas pressure is related to **partial pressures**, that is, *the pressures of individual gas components in the mixture*. In 1801 Dalton formulated a law, now known as **Dalton's law of partial pressures**, which states that *the total pressure of a mixture of gases is just the sum of the pressures that each gas would exert if it were present alone*. Figure 5.13 illustrates Dalton's law.

Consider a case in which two gases, A and B, are in a container of volume V. The pressure exerted by gas A, according to the ideal gas equation, is

$$P_A = \frac{n_A RT}{V}$$

where  $n_A$  is the number of moles of A present. Similarly, the pressure exerted by gas B is

$$P_B = \frac{n_B RT}{V}$$

In a mixture of gases A and B, the total pressure  $P_T$  is the result of the collisions of both types of molecules, A and B, with the walls of the container. Thus, according to Dalton's law,

$$\begin{aligned} P_T &= P_A + P_B \\ &= \frac{n_A RT}{V} + \frac{n_B RT}{V} \\ &= \frac{RT}{V} (n_A + n_B) \\ &= \frac{nRT}{V} \end{aligned}$$

As mentioned earlier, gas pressure results from the impact of gas molecules against the walls of the container.

where  $n$ , the total number of moles of gases present, is given by  $n = n_A + n_B$ , and  $P_A$  and  $P_B$  are the partial pressures of gases A and B, respectively. For a mixture of gases, then,  $P_T$  depends only on the total number of moles of gas present, not on the nature of the gas molecules.

In general, the total pressure of a mixture of gases is given by

$$P_T = P_1 + P_2 + P_3 + \dots$$

where  $P_1, P_2, P_3, \dots$  are the partial pressures of components 1, 2, 3,  $\dots$ . To see how each partial pressure is related to the total pressure, consider again the case of a mixture of two gases A and B. Dividing  $P_A$  by  $P_T$ , we obtain

$$\begin{aligned} \frac{P_A}{P_T} &= \frac{n_A RT/V}{(n_A + n_B)RT/V} \\ &= \frac{n_A}{n_A + n_B} \\ &= X_A \end{aligned}$$

where  $X_A$  is called the mole fraction of A. The **mole fraction** is a dimensionless quantity that expresses the ratio of the number of moles of one component to the number of moles of all components present. In general, the mole fraction of component  $i$  in a mixture is given by

$$X_i = \frac{n_i}{n_T} \quad (5.13)$$

where  $n_i$  and  $n_T$  are the number of moles of component  $i$  and the total number of moles present, respectively. The mole fraction is always smaller than 1. We can now express the partial pressure of A as

$$P_A = X_A P_T$$

Similarly,

$$P_B = X_B P_T$$

Note that the sum of the mole fractions for a mixture of gases must be unity. If only two components are present, then

$$X_A + X_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1$$

If a system contains more than two gases, then the partial pressure of the  $i$ th component is related to the total pressure by

$$P_i = X_i P_T \quad (5.14)$$

How are partial pressures determined? A manometer can measure only the total pressure of a gaseous mixture. To obtain the partial pressures, we need to know the mole fractions of the components, which would involve elaborate chemical analyses. The most direct method of measuring partial pressures is using a mass spectrometer. The relative intensities of the peaks in a mass spectrum are directly proportional to the amounts, and hence to the mole fractions, of the gases present.

### Example 5.7

A mixture of gases contains 4.46 moles of neon (Ne), 0.74 mole of argon (Ar), and 2.15 moles of xenon (Xe). Calculate the partial pressures of the gases if the total pressure is 2.00 atm at a certain temperature.

**Strategy** What is the relationship between the partial pressure of a gas and the total gas pressure? How do we calculate the mole fraction of a gas?

**Solution** According to Equation (5.14), the partial pressure of Ne ( $P_{\text{Ne}}$ ) is equal to the product of its mole fraction ( $X_{\text{Ne}}$ ) and the total pressure ( $P_T$ )

$$P_{\text{Ne}} = X_{\text{Ne}} P_T$$

↑ need to find  
want to calculate      ↓ given

Using Equation (5.13), we calculate the mole fraction of Ne as follows:

$$X_{\text{Ne}} = \frac{n_{\text{Ne}}}{n_{\text{Ne}} + n_{\text{Ar}} + n_{\text{Xe}}} = \frac{4.46 \text{ mol}}{4.46 \text{ mol} + 0.74 \text{ mol} + 2.15 \text{ mol}} \\ = 0.607$$

Therefore,

$$P_{\text{Ne}} = X_{\text{Ne}} P_T \\ = 0.607 \times 2.00 \text{ atm} \\ = 1.21 \text{ atm}$$

Similarly,

$$P_{\text{Ar}} = X_{\text{Ar}} P_T \\ = 0.10 \times 2.00 \text{ atm} \\ = 0.20 \text{ atm}$$

and

$$P_{\text{Xe}} = X_{\text{Xe}} P_T \\ = 0.293 \times 2.00 \text{ atm} \\ = 0.586 \text{ atm}$$

**Check** Make sure that the sum of the partial pressures is equal to the given total pressure; that is,  $(1.21 + 0.20 + 0.586) \text{ atm} = 2.00 \text{ atm}$ .

Similar problems: 5.57, 5.58.

**Practice Exercise** A sample of natural gas contains 8.24 moles of methane ( $\text{CH}_4$ ), 0.421 mole of ethane ( $\text{C}_2\text{H}_6$ ), and 0.116 mole of propane ( $\text{C}_3\text{H}_8$ ). If the total pressure of the gases is 1.37 atm, what are the partial pressures of the gases?

Dalton's law of partial pressures is useful for calculating volumes of gases collected over water. For example, when potassium chlorate ( $\text{KClO}_3$ ) is heated, it decomposes to KCl and  $\text{O}_2$ :



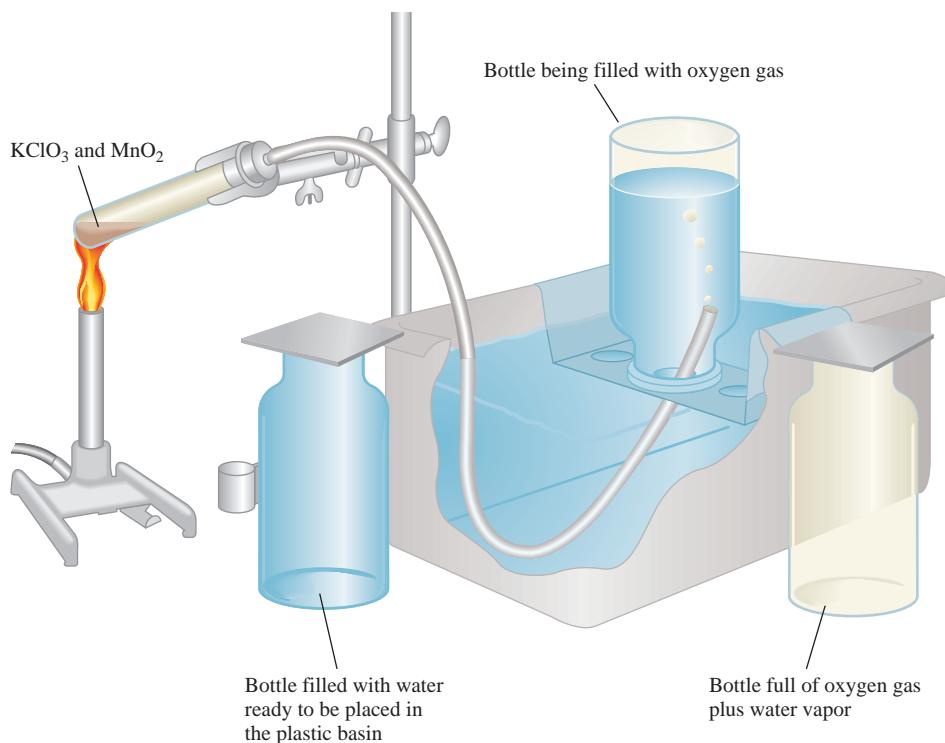
The oxygen gas can be collected over water, as shown in Figure 5.14. Initially, the inverted bottle is completely filled with water. As oxygen gas is generated, the gas



**Animation:**  
Collecting a Gas over Water  
ARIS, Animations

**Figure 5.14**

An apparatus for collecting gas over water. The oxygen generated by heating potassium chlorate ( $KClO_3$ ) in the presence of a small amount of manganese dioxide ( $MnO_2$ ), which speeds up the reaction, is bubbled through water and collected in a bottle as shown. Water originally present in the bottle is pushed into the trough by the oxygen gas.

**TABLE 5.2**

**Pressure of Water Vapor at Various Temperatures**

Temperature (°C)	Water Vapor Pressure (mmHg)
0	4.58
5	6.54
10	9.21
15	12.79
20	17.54
25	23.76
30	31.82
35	42.18
40	55.32
45	71.88
50	92.51
55	118.04
60	149.38
65	187.54
70	233.7
75	289.1
80	355.1
85	433.6
90	525.76
95	633.90
100	760.00

bubbles rise to the top and displace water from the bottle. This method of collecting a gas is based on the assumptions that the gas does not react with water and that it is not appreciably soluble in it. These assumptions are valid for oxygen gas, but not for gases such as  $NH_3$ , which dissolves readily in water. The oxygen gas collected in this way is not pure, however, because water vapor is also present in the bottle. The total gas pressure is equal to the sum of the pressures exerted by the oxygen gas and the water vapor:

$$P_T = P_{O_2} + P_{H_2O}$$

Consequently, we must allow for the pressure caused by the presence of water vapor when we calculate the amount of  $O_2$  generated. Table 5.2 shows the pressure of water vapor at various temperatures.

### Example 5.8

Oxygen gas generated by the decomposition of potassium chlorate is collected as shown in Figure 5.14. The volume of oxygen collected at 24°C and atmospheric pressure of 762 mmHg is 128 mL. Calculate the mass (in grams) of oxygen gas obtained. The pressure of the water vapor at 24°C is 22.4 mmHg.

**Strategy** To solve for the mass of  $O_2$  generated, we must first calculate the partial pressure of  $O_2$  in the mixture. What gas law do we need? How do we convert pressure of  $O_2$  gas to mass of  $O_2$  in grams?

**Solution** From Dalton's law of partial pressures we know that

$$P_T = P_{O_2} + P_{H_2O}$$

(Continued)

Therefore,

$$\begin{aligned} P_{\text{O}_2} &= P_{\text{T}} - P_{\text{H}_2\text{O}} \\ &= 762 \text{ mmHg} - 22.4 \text{ mmHg} \\ &= 740 \text{ mmHg} \end{aligned}$$

From the ideal gas equation we write

$$PV = nRT = \frac{m}{M}RT$$

where  $m$  and  $M$  are the mass of  $\text{O}_2$  collected and the molar mass of  $\text{O}_2$ , respectively.

Rearranging the equation we obtain

$$\begin{aligned} m &= \frac{PV\cdot M}{RT} = \frac{(740/760) \text{ atm} (0.128 \text{ L}) (32.00 \text{ g/mol})}{(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(273 + 24) \text{ K}} \\ &= 0.164 \text{ g} \end{aligned}$$

**Similar problems:** 5.61, 5.62.

**Practice Exercise** Hydrogen gas generated when calcium metal reacts with water is collected as shown in Figure 5.14. The volume of gas collected at  $30^\circ\text{C}$  and pressure of 988 mmHg is 641 mL. What is the mass (in grams) of the hydrogen gas obtained? The pressure of water vapor at  $30^\circ\text{C}$  is 31.82 mmHg.

## 5.6 The Kinetic Molecular Theory of Gases

The gas laws help us to predict the behavior of gases, but they do not explain what happens at the molecular level to cause the changes we observe in the macroscopic world. For example, why does a gas expand on heating?

In the nineteenth century, a number of physicists, notably the Austrian physicist Ludwig Boltzmann and the Scottish physicist James Clerk Maxwell, found that the physical properties of gases can be explained in terms of the motion of individual molecules. This molecular movement is a form of *energy*, which we define as the capacity to do work or to produce change. In mechanics, *work* is defined as force times distance. Because energy can be measured as work, we can write

$$\begin{aligned} \text{energy} &= \text{work done} \\ &= \text{force} \times \text{distance} \end{aligned}$$

The **joule (J)** is the SI unit of energy

$$\begin{aligned} 1 \text{ J} &= 1 \text{ kg m}^2/\text{s}^2 \\ &= 1 \text{ N m} \end{aligned}$$

Alternatively, energy can be expressed in kilojoules (kJ):

$$1 \text{ kJ} = 1000 \text{ J}$$

As we will see in Chapter 6, there are many different kinds of energy. **Kinetic energy (KE)** is the type of energy expended by a moving object, or *energy of motion*.

The findings of Maxwell, Boltzmann, and others resulted in a number of generalizations about gas behavior that have since been known as the **kinetic molecular**

**theory of gases**, or simply the *kinetic theory of gases*. Central to the kinetic theory are these assumptions:

1. A gas is composed of molecules that are separated from each other by distances far greater than their own dimensions. The molecules can be considered to be “points”; that is, they possess mass but have negligible volume.
2. Gas molecules are in constant motion in random directions, and they frequently collide with one another. Collisions among molecules are perfectly elastic. In other words, energy can be transferred from one molecule to another as a result of a collision. Nevertheless, the total energy of all the molecules in a system remains the same.
3. Gas molecules exert neither attractive nor repulsive forces on one another.
4. The average kinetic energy of the molecules is proportional to the temperature of the gas in kelvins. Any two gases at the same temperature will have the same average kinetic energy. The average kinetic energy of a molecule is given by

$$\overline{\text{KE}} = \frac{1}{2}mu\overline{u^2}$$

where  $m$  is the mass of the molecule and  $u$  is its speed. The horizontal bar denotes an average value. The quantity  $\overline{u^2}$  is called mean square speed; it is the average of the square of the speeds of all the molecules:

$$\overline{u^2} = \frac{u_1^2 + u_2^2 + \cdots + u_N^2}{N}$$

where  $N$  is the number of molecules.

Assumption 4 enables us to write

$$\begin{aligned}\overline{\text{KE}} &\propto T \\ \frac{1}{2}mu\overline{u^2} &\propto T \\ \frac{1}{2}mu\overline{u^2} &= CT\end{aligned}\tag{5.15}$$

where  $C$  is the proportionality constant and  $T$  is the absolute temperature.

According to the kinetic molecular theory, gas pressure is the result of collisions between molecules and the walls of their container. It depends on the frequency of collision per unit area and on how “hard” the molecules strike the wall. The theory also provides a molecular interpretation of temperature. According to Equation (5.15), the absolute temperature of a gas is a measure of the average kinetic energy of the molecules. In other words, the absolute temperature is a measure of the random motion of the molecules—the higher the temperature, the more energetic the molecules. Because it is related to the temperature of the gas sample, random molecular motion is sometimes referred to as *thermal motion*.

## Application to the Gas Laws

Although the kinetic theory of gases is based on a rather simple model, the mathematical details involved are very complex. However, on a qualitative basis, it is possible to use the theory to account for the general properties of substances in the gaseous state. The following examples illustrate the range of its utility:

- **Compressibility of Gases.** Because molecules in the gas phase are separated by large distances (assumption 1), gases can be compressed easily to occupy less volume.

- **Boyle's Law.** The pressure exerted by a gas results from the impact of its molecules on the walls of the container. The collision rate, or the number of molecular collisions with the walls per second, is proportional to the number density (that is, number of molecules per unit volume) of the gas. Decreasing the volume of a given amount of gas increases its number density and hence its collision rate. For this reason, the pressure of a gas is inversely proportional to the volume it occupies; as volume decreases, pressure increases and vice versa.
- **Charles's Law.** Because the average kinetic energy of gas molecules is proportional to the sample's absolute temperature (assumption 4), raising the temperature increases the average kinetic energy. Consequently, molecules will collide with the walls of the container more frequently and with greater impact if the gas is heated, and thus the pressure increases. The volume of gas will expand until the gas pressure is balanced by the constant external pressure (see Figure 5.7).
- **Avogadro's Law.** We have shown that the pressure of a gas is directly proportional to both the density and the temperature of the gas. Because the mass of the gas is directly proportional to the number of moles ( $n$ ) of the gas, we can represent density by  $n/V$ . Therefore,

$$P \propto \frac{n}{V} T$$

For two gases, 1 and 2, we write

$$\begin{aligned} P_1 &\propto \frac{n_1 T_1}{V_1} = C \frac{n_1 T_1}{V_1} \\ P_2 &\propto \frac{n_2 T_2}{V_2} = C \frac{n_2 T_2}{V_2} \end{aligned}$$

where  $C$  is the proportionality constant. Thus, for two gases under the same conditions of pressure, volume, and temperature (that is, when  $P_1 = P_2$ ,  $T_1 = T_2$ , and  $V_1 = V_2$ ), it follows that  $n_1 = n_2$ , which is a mathematical expression of Avogadro's law.

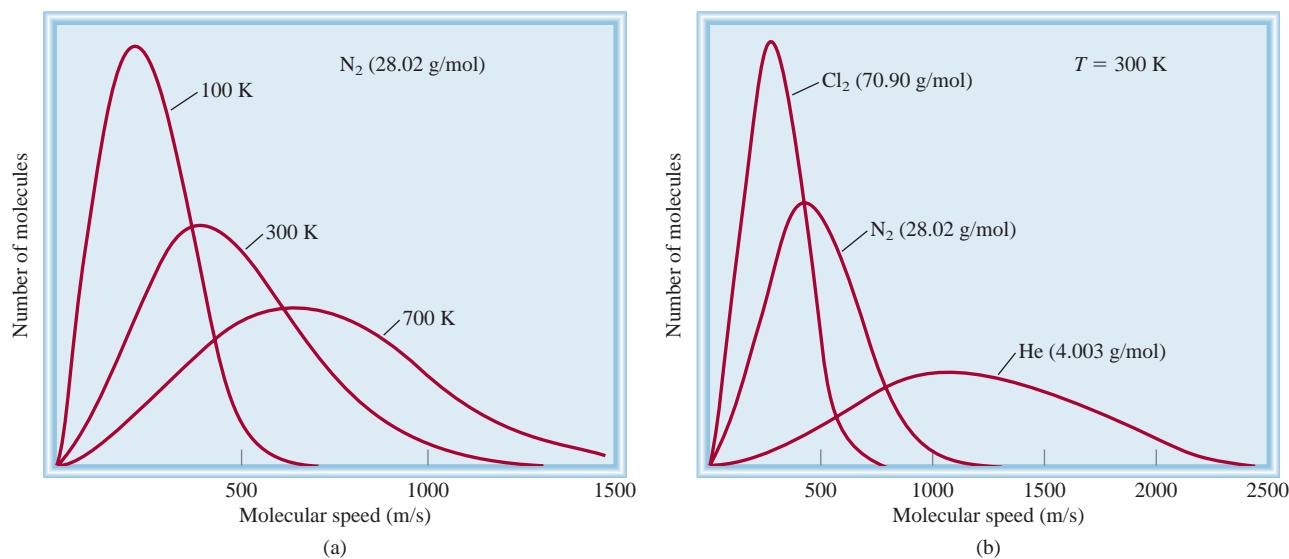
- **Dalton's Law of Partial Pressures.** If molecules do not attract or repel one another (assumption 3), then the pressure exerted by one type of molecule is unaffected by the presence of another gas. Consequently, the total pressure is given by the sum of individual gas pressures.

**Another way of stating Avogadro's law is that at the same pressure and temperature, equal volumes of gases, whether they are the same or different gases, contain equal numbers of molecules.**

## Distribution of Molecular Speeds

The kinetic theory of gases enables us to investigate molecular motion in more detail. Suppose we have a large number of gas molecules, say, 1 mole, in a container. As long as we hold the temperature constant, the average kinetic energy and the mean-square speed will remain unchanged as time passes. As you might expect, the motion of the molecules is totally random and unpredictable. At a given instant, how many molecules are moving at a particular speed? To answer this question Maxwell analyzed the behavior of gas molecules at different temperatures.

Figure 5.15(a) shows typical *Maxwell speed distribution curves* for nitrogen gas at three different temperatures. At a given temperature, the distribution curve tells us the number of molecules moving at a certain speed. The peak of each curve represents the *most probable speed*, that is, the speed of the largest number of molecules. Note that the most probable speed increases as temperature increases (the peak shifts

**Figure 5.15**

(a) The speed distribution of speeds for nitrogen gas at three different temperatures. At the higher temperatures, more molecules are moving at faster speeds. (b) The distribution of speeds for three gases at 300 K. At a given temperature, the lighter molecules are moving faster, on the average.

toward the right). Furthermore, the curve also begins to flatten out with increasing temperature, indicating that larger numbers of molecules are moving at greater speed. Figure 5.15(b) shows the speed distributions of three gases at the same temperature. The difference in the curves can be explained by noting that lighter molecules move faster, on average, than heavier ones.

### Root-Mean-Square Speed

How fast does a molecule move, on the average, at any temperature  $T$ ? One way to estimate molecular speed is to calculate the **root-mean-square (rms) speed ( $u_{\text{rms}}$ )**, which is *an average molecular speed*. One of the results of the kinetic theory of gases is that the total kinetic energy of a mole of any gas equals  $\frac{3}{2}RT$ . Earlier we saw that the average kinetic energy of one molecule is  $\frac{1}{2}mu^2$  and so we can write

$$N_A \left( \frac{1}{2}mu^2 \right) = \frac{3}{2}RT$$

Recall that  $m$  is the mass of a single molecule.

where  $N_A$  is Avogadro's number. Because  $N_A m = M$ , where  $M$  is the molar mass, this equation can be rearranged to give

$$\overline{u^2} = \frac{3RT}{M}$$

Taking the square root of both sides gives

$$\sqrt{\overline{u^2}} = u_{\text{rms}} = \sqrt{\frac{3RT}{M}} \quad (5.16)$$

Equation (5.16) shows that the root-mean-square speed of a gas increases with the square root of its temperature (in kelvins). Because  $M$  appears in the denominator, it

follows that the heavier the gas, the more slowly its molecules move. If we substitute  $8.314 \text{ J/K} \cdot \text{mol}$  for  $R$  (see Appendix 1) and convert the molar mass to kg/mol, then  $u_{\text{rms}}$  will be calculated in meters per second (m/s).

### Example 5.9

Calculate the root-mean-square speeds of helium atoms and nitrogen molecules in m/s at 25°C.

**Strategy** To calculate the root-mean-square speed we need Equation (5.16). What units should we use for  $R$  and  $\mathcal{M}$  so that  $u_{\text{rms}}$  will be expressed in m/s?

**Solution** To calculate  $u_{\text{rms}}$ , the units of  $R$  should be  $8.314 \text{ J/K} \cdot \text{mol}$  and, because  $1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2$ , the molar mass must be in kg/mol. The molar mass of He is 4.003 g/mol, or  $4.003 \times 10^{-3}$  kg/mol. From Equation (5.16),

$$\begin{aligned} u_{\text{rms}} &= \sqrt{\frac{3RT}{\mathcal{M}}} \\ &= \sqrt{\frac{3(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})}{4.003 \times 10^{-3} \text{ kg/mol}}} \\ &= \sqrt{1.86 \times 10^6 \text{ J/kg}} \end{aligned}$$

Using the conversion factor  $1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2$  we get

$$\begin{aligned} u_{\text{rms}} &= \sqrt{1.86 \times 10^6 \text{ kg m}^2/\text{kg} \cdot \text{s}^2} \\ &= \sqrt{1.86 \times 10^6 \text{ m}^2/\text{s}^2} \\ &= 1.36 \times 10^3 \text{ m/s} \end{aligned}$$

The procedure is the same for N<sub>2</sub>, the molar mass of which is 28.02 g/mol, or  $2.802 \times 10^{-2}$  kg/mol so that we write

$$\begin{aligned} u_{\text{rms}} &= \sqrt{\frac{3(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})}{2.802 \times 10^{-2} \text{ kg/mol}}} \\ &= \sqrt{2.65 \times 10^5 \text{ m}^2/\text{s}^2} \\ &= 515 \text{ m/s} \end{aligned}$$

**Check** Because He is a lighter gas, we expect it to move faster, on average, than N<sub>2</sub>. A quick way to check the answers is to note that the ratio of the two  $u_{\text{rms}}$  values ( $1.36 \times 10^3/515 \approx 2.6$ ) should be equal to the square root of the ratios of the molar masses of N<sub>2</sub> to He, that is,  $\sqrt{28/4} \approx 2.6$ .

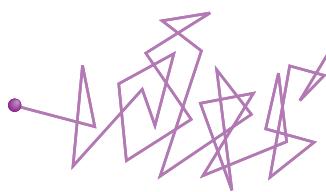
**Practice Exercise** Calculate the root-mean-square speed of molecular chlorine in m/s at 20°C.

The calculation in Example 5.9 has an interesting relationship to the composition of Earth's atmosphere. Unlike Jupiter, Earth does not have appreciable amounts of hydrogen or helium in its atmosphere. Why is this the case? A smaller planet than Jupiter, Earth has a weaker gravitational attraction for these lighter molecules. A fairly straightforward calculation shows that to escape Earth's gravitational field, a molecule must possess an escape velocity equal to or greater than  $1.1 \times 10^4 \text{ m/s}$ . Because the average speed of helium is considerably greater than that of molecular nitrogen or molecular oxygen, more helium atoms escape from Earth's atmosphere into outer space. Consequently, only a trace amount of helium is present in our atmosphere. On

Similar problems: 5.71, 5.72.



Jupiter. The interior of this massive planet consists mainly of hydrogen.

**Figure 5.16**

The path traveled by a single gas molecule. Each change in direction represents a collision with another molecule.

Diffusion always proceeds from a region of higher concentration to one where the concentration is lower.



**Animation:**  
Diffusion of Gases  
ARIS, Animations

the other hand, Jupiter, with a mass about 320 times greater than that of Earth, retains both heavy and light gases in its atmosphere.

## Gas Diffusion and Effusion

### Gas Diffusion

A direct demonstration of random motion is provided by **diffusion**, the gradual mixing of molecules of one gas with molecules of another by virtue of their kinetic properties. Despite the fact that molecular speeds are very great, the diffusion process takes a relatively long time to complete. For example, when a bottle of concentrated ammonia solution is opened at one end of a lab bench, it takes some time before a person at the other end of the bench can smell it. The reason is that a molecule experiences numerous collisions while moving from one end of the bench to the other, as shown in Figure 5.16. Thus, diffusion of gases always happens gradually, and not instantly as molecular speeds seem to suggest. Furthermore, because the root-mean-square speed of a light gas is greater than that of a heavier gas (see Example 5.9), a lighter gas will diffuse through a certain space more quickly than will a heavier gas. Figure 5.17 illustrates gaseous diffusion.

In 1832 the Scottish chemist Thomas Graham found that *under the same conditions of temperature and pressure, rates of diffusion for gases are inversely proportional to the square roots of their molar masses*. This statement, now known as **Graham's law of diffusion**, is expressed mathematically as

$$\frac{r_1}{r_2} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}} \quad (5.17)$$

where  $r_1$  and  $r_2$  are the diffusion rates of gases 1 and 2, and  $\mathcal{M}_1$  and  $\mathcal{M}_2$  are their molar masses, respectively.

### Gas Effusion

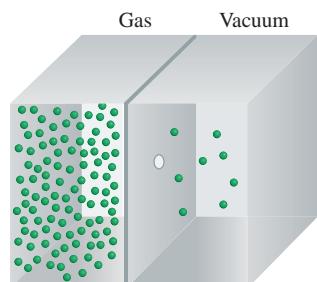
Whereas diffusion is a process by which one gas gradually mixes with another, **effusion** is the process by which a gas under pressure escapes from one compartment of a container to another by passing through a small opening. Figure 5.18 shows the

**Figure 5.17**

A demonstration of gas diffusion.  $\text{NH}_3$  gas (from a bottle containing aqueous ammonia) combines with  $\text{HCl}$  gas (from a bottle containing hydrochloric acid) to form solid  $\text{NH}_4\text{Cl}$ . Because  $\text{NH}_3$  is lighter and therefore diffuses faster, solid  $\text{NH}_4\text{Cl}$  first appears nearer the  $\text{HCl}$  bottle (on the right).



effusion of a gas into a vacuum. Although effusion differs from diffusion in nature, the rate of effusion of a gas has the same form as Graham's law of diffusion [see Equation (5.17)]. A helium-filled rubber balloon deflates faster than an air-filled one because the rate of effusion through the pores of the rubber is faster for the lighter helium atoms than for the air molecules. Industrially, gas effusion is used to separate uranium isotopes in the forms of gaseous  $^{235}\text{UF}_6$  and  $^{238}\text{UF}_6$ . By subjecting the gases to many stages of effusion, scientists were able to obtain highly enriched  $^{235}\text{U}$  isotope, which was used in the construction of atomic bombs during World War II.



### Example 5.10

A flammable gas made up only of carbon and hydrogen is found to effuse through a porous barrier in 1.50 min. Under the same conditions of temperature and pressure, it takes an equal volume of bromine vapor 4.73 min to effuse through the same barrier. Calculate the molar mass of the unknown gas, and suggest what this gas might be.

**Strategy** The rate of diffusion is the number of molecules passing through a porous barrier in a given time. The longer the time it takes, the slower is the rate. Therefore, the rate is *inversely proportional to the time* required for diffusion, Equation (5.17) can now be written as  $r_1/r_2 = t_2/t_1 = \sqrt{\mathcal{M}_2/\mathcal{M}_1}$ , where  $t_1$  and  $t_2$  are the times for effusion for gases 1 and 2, respectively.

**Solution** From the molar mass of  $\text{Br}_2$ , we write

$$\frac{1.50 \text{ min}}{4.73 \text{ min}} = \sqrt{\frac{\mathcal{M}}{159.8 \text{ g/mol}}}$$

where  $\mathcal{M}$  is the molar mass of the unknown gas. Solving for  $\mathcal{M}$ , we obtain

$$\begin{aligned} \mathcal{M} &= \left( \frac{1.50 \text{ min}}{4.73 \text{ min}} \right)^2 \times 159.8 \text{ g/mol} \\ &= 16.1 \text{ g/mol} \end{aligned}$$

Because the molar mass of carbon is 12.01 g and that of hydrogen is 1.008 g, the gas is methane ( $\text{CH}_4$ ).

**Practice Exercise** It takes 192 s for an unknown gas to effuse through a porous wall and 84 s for the same volume of  $\text{N}_2$  gas to effuse at the same temperature and pressure. What is the molar mass of the unknown gas?

**Figure 5.18**

*Gas effusion.* Gas molecules move from a high-pressure region (left) to a low-pressure one through a pinhole.

Similar problems: 5.108, 5.109.

## 5.7 Deviation from Ideal Behavior

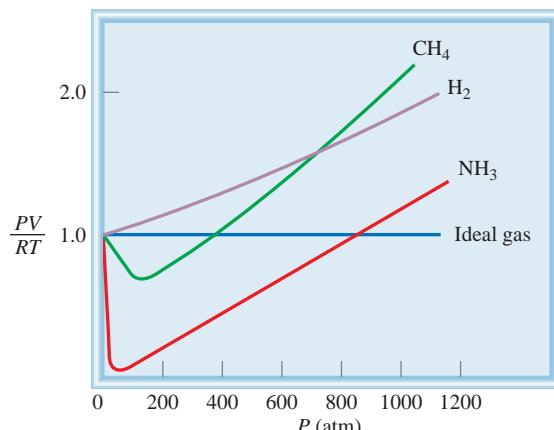
The gas laws and the kinetic molecular theory assume that molecules in the gaseous state do not exert any force, either attractive or repulsive, on one another. The other assumption is that the volume of the molecules is negligibly small compared with that of the container. A gas that satisfies these two conditions is said to exhibit *ideal behavior*.

Although we can assume that real gases behave like an ideal gas, we cannot expect them to do so under all conditions. For example, without intermolecular forces, gases could not condense to form liquids. The important question is: Under what conditions will gases most likely exhibit nonideal behavior?

Figure 5.19 shows  $PV/RT$  plotted against  $P$  for three real gases and an ideal gas at a given temperature. This graph provides a test of ideal gas behavior. According to the ideal gas equation (for 1 mole of gas),  $PV/RT$  equals 1, regardless of the actual gas

**Figure 5.19**

Plot of  $PV/RT$  versus  $P$  of 1 mole of a gas at  $0^\circ\text{C}$ . For 1 mole of an ideal gas,  $PV/RT$  is equal to 1, no matter what the pressure of the gas is. For real gases, we observe various deviations from ideality at high pressures. At very low pressures, all gases exhibit ideal behavior; that is, their  $PV/RT$  values all converge to 1 as  $P$  approaches zero.



pressure. (When  $n = 1$ ,  $PV = nRT$  becomes  $PV = RT$ , or  $PV/RT = 1$ .) For real gases, this is true only at moderately low pressures ( $\leq 5$  atm); significant deviations occur as pressure increases. Attractive forces operate among molecules at relatively short distances. At atmospheric pressure, the molecules in a gas are far apart and the attractive forces are negligible. At high pressures, the density of the gas increases; the molecules are much closer to one another. Intermolecular forces can then be significant enough to affect the motion of the molecules, and the gas will not behave ideally.

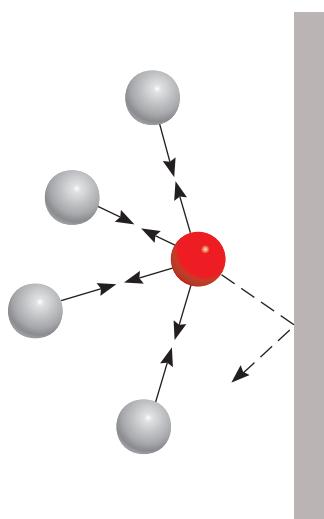
Another way to observe the nonideal behavior of gases is to lower the temperature. Cooling a gas decreases the molecules' average kinetic energy, which in a sense deprives molecules of the drive they need to break from their mutual attraction.

To study real gases accurately, then, we need to modify the ideal gas equation, taking into account intermolecular forces and finite molecular volumes. Such an analysis was first made by the Dutch physicist J. D. van der Waals in 1873. Besides being mathematically simple, van der Waals's treatment provides us with an interpretation of real gas behavior at the molecular level.

Consider the approach of a particular molecule toward the wall of a container (Figure 5.20). The intermolecular attractions exerted by its neighbors tend to soften the impact made by this molecule against the wall. The overall effect is a lower gas pressure than we would expect for an ideal gas. Van der Waals suggested that the pressure exerted by an ideal gas,  $P_{\text{ideal}}$ , is related to the experimentally measured; that is, observed pressure,  $P_{\text{obs}}$ , by the equation

$$P_{\text{ideal}} = P_{\text{real}} + \frac{an^2}{V^2}$$

↑                      ↑  
observed      correction  
pressure      term

**Figure 5.20**

Effect of intermolecular forces on the pressure exerted by a gas. The speed of a molecule that is moving toward the container wall (red sphere) is reduced by the attractive forces exerted by its neighbors (gray spheres). Consequently, the impact this molecule makes with the wall is not as great as it would be if no intermolecular forces were present. In general, the measured gas pressure is lower than the pressure the gas would exert if it behaved ideally.

where  $a$  is a constant and  $n$  and  $V$  are the number of moles and volume of the gas, respectively. The correction term for pressure ( $an^2/V^2$ ) can be understood as follows. The intermolecular interaction that gives rise to nonideal behavior depends on how frequently any two molecules approach each other closely. The number of such "encounters" increases with the square of the number of molecules per unit volume,  $(n/V)^2$ , because the presence of each of the two molecules in a particular region is proportional to  $n/V$ . The quantity  $P_{\text{ideal}}$  is the pressure we would measure if there were no intermolecular attractions, and so  $a$  is just a proportionality constant.

Another correction concerns the volume occupied by the gas molecules. In the ideal gas equation,  $V$  represents the volume of the container. However, each molecule

does occupy a finite, although small, intrinsic volume, so the effective volume of the gas becomes  $(V - nb)$ , where  $n$  is the number of moles of the gas and  $b$  is a constant. The term  $nb$  represents the volume occupied by  $n$  moles of the gas.

Having taken into account the corrections for pressure and volume, we can rewrite the ideal gas equation as follows:

$$\underbrace{\left( P + \frac{an^2}{V^2} \right)}_{\text{corrected pressure}} \underbrace{(V - nb)}_{\text{corrected volume}} = nRT \quad (5.18)$$

Equation (5.18), relating  $P$ ,  $V$ ,  $T$ , and  $n$  for a nonideal gas, is known as the *van der Waals equation*. The van der Waals constants  $a$  and  $b$  are selected to give the best possible agreement between Equation (5.18) and observed behavior of a particular gas.

Table 5.3 lists the values of  $a$  and  $b$  for a number of gases. The value of  $a$  indicates how strongly molecules of a given type of gas attract one another. We see that helium atoms have the weakest attraction for one another, because helium has the smallest  $a$  value. There is also a rough correlation between molecular size and  $b$ . Generally, the larger the molecule (or atom), the greater  $b$  is, but the relationship between  $b$  and molecular (or atomic) size is not a simple one.

**TABLE 5.3**
**van der Waals  
Constants of Some  
Common Gases**

Gas	$\frac{a}{\text{atm} \cdot \text{L}^2}$	$\frac{b}{\text{mol}}$
He	0.034	0.0237
Ne	0.211	0.0171
Ar	1.34	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0266
H <sub>2</sub>	0.244	0.0266
N <sub>2</sub>	1.39	0.0391
O <sub>2</sub>	1.36	0.0318
Cl <sub>2</sub>	6.49	0.0562
CO <sub>2</sub>	3.59	0.0427
CH <sub>4</sub>	2.25	0.0428
CCl <sub>4</sub>	20.4	0.138
NH <sub>3</sub>	4.17	0.0371
H <sub>2</sub> O	5.46	0.0305

### Example 5.11

Given that 3.50 moles of NH<sub>3</sub> occupy 5.20 L at 47°C, calculate the pressure of the gas (in atm) using (a) the ideal gas equation and (b) the van der Waals equation.

**Strategy** To calculate the pressure of NH<sub>3</sub> using the ideal gas equation, we proceed as in Example 5.2. What corrections are made to the pressure and volume terms in the van der Waals equation?

**Solution** (a) We have the following data:

$$\begin{aligned} V &= 5.20 \text{ L} \\ T &= (47 + 273) \text{ K} = 320 \text{ K} \\ n &= 3.50 \text{ mol} \\ R &= 0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol} \end{aligned}$$

Substituting these values in the ideal gas equation, we write

$$\begin{aligned} P &= \frac{nRT}{V} \\ &= \frac{(3.50 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(320 \text{ K})}{5.20 \text{ L}} \\ &= 17.7 \text{ atm} \end{aligned}$$

(b) We need Equation (5.18). It is convenient to first calculate the correction terms in Equation (5.18) separately. From Table 5.3, we have

$$a = 4.17 \text{ atm} \cdot \text{L}^2/\text{mol}^2$$

$$b = 0.0371 \text{ L/mol}$$

(Continued)

so that the correction terms for pressure and volume are

$$\frac{an^2}{V^2} = \frac{(4.17 \text{ atm} \cdot \text{L}^2/\text{mol}^2)(3.50 \text{ mol})^2}{(5.20 \text{ L})^2} = 1.89 \text{ atm}$$

$$nb = (3.50 \text{ mol})(0.0371 \text{ L/mol}) = 0.130 \text{ L}$$

Finally, substituting these values in the van der Waals equation, we have

$$(P + 1.89 \text{ atm})(5.20 \text{ L} - 0.130 \text{ L}) = (3.50 \text{ mol})(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(320 \text{ K})$$

$$P = 16.2 \text{ atm}$$

**Check** Based on your understanding of nonideal gas behavior, is it reasonable that the pressure calculated using the van der Waals equation should be smaller than that using the ideal gas equation? Why?

**Similar problems:** 5.79, 5.80.

**Practice Exercise** Using the data shown in Table 5.3, calculate the pressure exerted by 4.37 moles of molecular chlorine confined in a volume of 2.45 L at 38°C. Compare the pressure with that calculated using the ideal gas equation.

## KEY EQUATIONS

$P_1V_1 = P_2V_2$	(5.2)	Boyle's law. For calculating pressure or volume changes.
$\frac{V_1}{T_1} = \frac{V_2}{T_2}$	(5.4)	Charles's law. For calculating temperature or volume changes.
$\frac{P_1}{T_1} = \frac{P_2}{T_2}$	(5.6)	Charles's law. For calculating temperature or pressure changes.
$V = k_4n$	(5.7)	Avogadro's law. Constant $P$ and $T$ .
$PV = nRT$	(5.8)	Ideal gas equation.
$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$	(5.9)	Combined ideal gas equations for initial and final states.
$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$	(5.10)	For calculating changes in pressure, temperature, or volume when $n$ is constant.
$d = \frac{PM}{RT}$	(5.11)	For calculating density or molar mass.
$X_i = \frac{n_i}{n_T}$	(5.13)	Definition of mole fraction.
$P_i = X_iP_T$	(5.14)	Dalton's law of partial pressures. For calculating partial pressures.
$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$	(5.16)	For calculating the root-mean-square speed of gas molecules.
$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$	(5.17)	Graham's law of diffusion and effusion.
$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$	(5.18)	van der Waals equation. For calculating the pressure of a nonideal gas.

## SUMMARY OF FACTS AND CONCEPTS

- Under atmospheric conditions, a number of elemental substances are gases: H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, O<sub>3</sub>, F<sub>2</sub>, Cl<sub>2</sub>, and the Group 8A elements (the noble gases).
- Gases exert pressure because their molecules move freely and collide with any surface in their paths. Gas pressure units include millimeters of mercury (mmHg), torr, pascals, and atmospheres. One atmosphere equals 760 mmHg, or 760 torr.
- The pressure-volume relationships of ideal gases are governed by Boyle's law: Volume is inversely proportional to pressure (at constant  $T$  and  $n$ ). The temperature-volume relationships of ideal gases are described by Charles's and Gay-Lussac's law: Volume is directly proportional to temperature (at constant  $P$  and  $n$ ). Absolute zero ( $-273.15^{\circ}\text{C}$ ) is the lowest theoretically attainable temperature. On the Kelvin temperature scale, 0 K is absolute zero. In all gas law calculations, temperature must be expressed in kelvins. The amount-volume relationships of ideal gases are described by Avogadro's law: Equal volumes of gases contain equal numbers of molecules (at the same  $T$  and  $P$ ).
- The ideal gas equation,  $PV = nRT$ , combines the laws of Boyle, Charles, and Avogadro. This equation describes the behavior of an ideal gas.
- Dalton's law of partial pressures states that in a mixture of gases each gas exerts the same pressure as it would if it were alone and occupied the same volume.
- The kinetic molecular theory, a mathematical way of describing the behavior of gas molecules, is based on the following assumptions: Gas molecules are separated by distances far greater than their own dimensions, they possess mass but have negligible volume, they are in constant motion, and they frequently collide with one another. The molecules neither attract nor repel one another. A Maxwell speed distribution curve shows how many gas molecules are moving at various speeds at a given temperature. As temperature increases, more molecules move at greater speeds.
- In diffusion, two gases gradually mix with each other. In effusion, gas molecules move through a small opening under pressure. Both processes are governed by the same mathematical laws.
- The van der Waals equation is a modification of the ideal gas equation that takes into account the nonideal behavior of real gases. It corrects for two facts: Real gas molecules do exert forces on each other and they do have volume. The van der Waals constants are determined experimentally for each gas.

## KEY WORDS

Absolute temperature scale, p. 140	Dalton's law of partial pressures, p. 149	Kelvin temperature scale, p. 140	Pressure, p. 134
Absolute zero, p. 140	Diffusion, p. 158	Kinetic energy (KE), p. 153	Root-mean-square (rms) speed ( $u_{\text{rms}}$ ), p. 156
Atmospheric pressure, p. 135	Effusion, p. 158	Kinetic molecular theory of gases, p. 153	Standard atmospheric pressure (1 atm), p. 135
Avogadro's law, p. 142	Gas constant ( $R$ ), p. 143	Manometer, p. 136	Standard temperature and pressure (STP), p. 143
Barometer, p. 135	Graham's law of diffusion, p. 158	Mole fraction, p. 150	van der Waals equation, p. 161
Boyle's law, p. 137	Ideal gas, p. 143	Newton (N), p. 134	
Charles's and Gay-Lussac's law, p. 141	Ideal gas equation, p. 143	Partial pressure, p. 149	
Charles's law, p. 141	Joule (J), p. 153	Pascal (Pa), p. 134	

## QUESTIONS AND PROBLEMS

### Substances That Exist as Gases

#### Review Questions

- 5.1 Name five elements and five compounds that exist as gases at room temperature.
- 5.2 List the physical characteristics of gases.

### Pressure of a Gas

#### Review Questions

- 5.3 Define pressure and give the common units for pressure.

- 5.4 Describe how a barometer and a manometer are used to measure gas pressure.
- 5.5 Why is mercury a more suitable substance to use in a barometer than water?
- 5.6 Explain why the height of mercury in a barometer is independent of the cross-sectional area of the tube. Would the barometer still work if the tubing were tilted at an angle, say  $15^\circ$  (see Figure 5.2)?
- 5.7 Would it be easier to drink water with a straw on top of Mt. Everest or at the foot? Explain.
- 5.8 Is the atmospheric pressure in a mine that is 500 m below sea level greater or less than 1 atm?
- 5.9 What is the difference between a gas and a vapor? At  $25^\circ\text{C}$ , which of the following substances in the gas phase should be properly called a gas and which should be called a vapor: molecular nitrogen ( $\text{N}_2$ ), mercury?
- 5.10 If the maximum distance that water may be brought up a well by a suction pump is 34 ft (10.3 m), how is it possible to obtain water and oil from hundreds of feet below the surface of Earth?
- 5.11 Why is it that if the barometer reading falls in one part of the world, it must rise somewhere else?
- 5.12 Why do astronauts have to wear protective suits when they are on the surface of the moon?

### Problems

- 5.13 Convert 562 mmHg to atm.
- 5.14** The atmospheric pressure at the summit of Mt. McKinley is 606 mmHg on a certain day. What is the pressure in atm and in kPa?

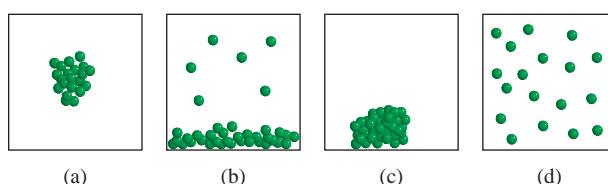
## The Gas Laws

### Review Questions

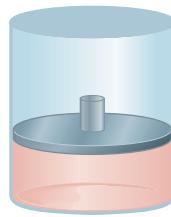
- 5.15 State the following gas laws in words and also in the form of an equation: Boyle's law, Charles's law, Avogadro's law. In each case, indicate the conditions under which the law is applicable, and give the units for each quantity in the equation.
- 5.16 Explain why a helium weather balloon expands as it rises in the air. Assume that the temperature remains constant.

### Problems

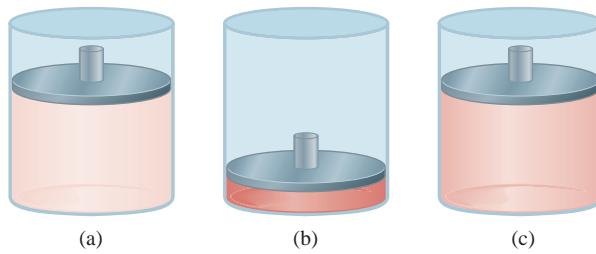
- 5.17 A gaseous sample of a substance is cooled at constant pressure. Which of the following diagrams best represents the situation if the final temperature is (a) above the boiling point of the substance and (b) below the boiling point but above the freezing point of the substance?



- 5.18** Consider the following gaseous sample in a cylinder fitted with a movable piston. Initially there are  $n$  moles of the gas at temperature  $T$ , pressure  $P$ , and volume  $V$ .



Choose the cylinder shown next that correctly represents the gas after each of the following changes.  
 (1) The pressure on the piston is tripled at constant  $n$  and  $T$ .  
 (2) The temperature is doubled at constant  $n$  and  $P$ .  
 (3)  $n$  moles of another gas are added at constant  $T$  and  $P$ .  
 (4)  $T$  is halved and pressure on the piston is reduced to a quarter of its original value.



- 5.19 A gas occupying a volume of 725 mL at a pressure of 0.970 atm is allowed to expand at constant temperature until its pressure reaches 0.541 atm. What is its final volume?
- 5.20** At  $46^\circ\text{C}$  a sample of ammonia gas exerts a pressure of 5.3 atm. What is the pressure when the volume of the gas is reduced to one-tenth (0.10) of the original value at the same temperature?
- 5.21 The volume of a gas is 5.80 L, measured at 1.00 atm. What is the pressure of the gas in mmHg if the volume is changed to 9.65 L? (The temperature remains constant.)
- 5.22** A sample of air occupies 3.8 L when the pressure is 1.2 atm. (a) What volume does it occupy at 6.6 atm? (b) What pressure is required in order to compress it to 0.075 L? (The temperature is kept constant.)

- 5.23 A 36.4-L volume of methane gas is heated from 25°C to 88°C at constant pressure. What is the final volume of the gas?
- 5.24** Under constant-pressure conditions a sample of hydrogen gas initially at 88°C and 9.6 L is cooled until its final volume is 3.4 L. What is its final temperature?
- 5.25 Ammonia burns in oxygen gas to form nitric oxide (NO) and water vapor. How many volumes of NO are obtained from one volume of ammonia at the same temperature and pressure?
- 5.26** Molecular chlorine and molecular fluorine combine to form a gaseous product. Under the same conditions of temperature and pressure it is found that one volume of Cl<sub>2</sub> reacts with three volumes of F<sub>2</sub> to yield two volumes of the product. What is the formula of the product?

## The Ideal Gas Equation

### Review Questions

- 5.27 List the characteristics of an ideal gas.
- 5.28 Write the ideal gas equation and also state it in words. Give the units for each term in the equation.
- 5.29 What are standard temperature and pressure (STP)? What is the significance of STP in relation to the volume of 1 mole of an ideal gas?
- 5.30 Why is the density of a gas much lower than that of a liquid or solid under atmospheric conditions? What units are normally used to express the density of gases?

### Problems

- 5.31 A sample of nitrogen gas kept in a container of volume 2.3 L and at a temperature of 32°C exerts a pressure of 4.7 atm. Calculate the number of moles of gas present.
- 5.32** Given that 6.9 moles of carbon monoxide gas are present in a container of volume 30.4 L, what is the pressure of the gas (in atm) if the temperature is 62°C?
- 5.33 What volume will 5.6 moles of sulfur hexafluoride (SF<sub>6</sub>) gas occupy if the temperature and pressure of the gas are 128°C and 9.4 atm?
- 5.34** A certain amount of gas at 25°C and at a pressure of 0.800 atm is contained in a glass vessel. Suppose that the vessel can withstand a pressure of 2.00 atm. How high can you raise the temperature of the gas without bursting the vessel?
- 5.35 A gas-filled balloon having a volume of 2.50 L at 1.2 atm and 25°C is allowed to rise to the stratosphere (about 30 km above the surface of Earth), where the temperature and pressure are -23°C and  $3.00 \times 10^{-3}$  atm, respectively. Calculate the final volume of the balloon.
- 5.36** The temperature of 2.5 L of a gas initially at STP is increased to 250°C at constant volume. Calculate the final pressure of the gas in atm.

- 5.37 The pressure of 6.0 L of an ideal gas in a flexible container is decreased to one-third of its original pressure, and its absolute temperature is decreased by one-half. What is the final volume of the gas?
- 5.38** A gas evolved during the fermentation of glucose (wine making) has a volume of 0.78 L when measured at 20.1°C and 1.00 atm. What was the volume of this gas at the fermentation temperature of 36.5°C and 1.00 atm pressure?
- 5.39 An ideal gas originally at 0.85 atm and 66°C was allowed to expand until its final volume, pressure, and temperature were 94 mL, 0.60 atm, and 45°C, respectively. What was its initial volume?
- 5.40** The volume of a gas at STP is 488 mL. Calculate its volume at 22.5 atm and 150°C.
- 5.41 A gas at 772 mmHg and 35.0°C occupies a volume of 6.85 L. Calculate its volume at STP.
- 5.42** Dry ice is solid carbon dioxide. A 0.050-g sample of dry ice is placed in an evacuated 4.6-L vessel at 30°C. Calculate the pressure inside the vessel after all the dry ice has been converted to CO<sub>2</sub> gas.
- 5.43 A volume of 0.280 L of a gas at STP weighs 0.400 g. Calculate the molar mass of the gas.
- 5.44** A quantity of gas weighing 7.10 g at 741 torr and 44°C occupies a volume of 5.40 L. What is its molar mass?
- 5.45 The ozone molecules present in the stratosphere absorb much of the harmful radiation from the sun. Typically, the temperature and pressure of ozone in the stratosphere are 250 K and  $1.0 \times 10^{-3}$  atm, respectively. How many ozone molecules are present in 1.0 L of air under these conditions?
- 5.46** Assuming that air contains 78 percent N<sub>2</sub>, 21 percent O<sub>2</sub>, and 1 percent Ar, all by volume, how many molecules of each type of gas are present in 1.0 L of air at STP?
- 5.47 A 2.10-L vessel contains 4.65 g of a gas at 1.00 atm and 27.0°C. (a) Calculate the density of the gas in grams per liter. (b) What is the molar mass of the gas?
- 5.48** Calculate the density of hydrogen bromide (HBr) gas in grams per liter at 733 mmHg and 46°C.
- 5.49 A certain anesthetic contains 64.9 percent C, 13.5 percent H, and 21.6 percent O by mass. At 120°C and 750 mmHg, 1.00 L of the gaseous compound weighs 2.30 g. What is the molecular formula of the compound?
- 5.50** A compound has the empirical formula SF<sub>4</sub>. At 20°C, 0.100 g of the gaseous compound occupies a volume of 22.1 mL and exerts a pressure of 1.02 atm. What is its molecular formula?
- 5.51 Dissolving 3.00 g of an impure sample of calcium carbonate in hydrochloric acid produced 0.656 L of carbon dioxide (measured at 20.0°C and 792 mmHg).

Calculate the percent by mass of calcium carbonate in the sample. State any assumptions.

- 5.52** Calculate the mass in grams of hydrogen chloride produced when 5.6 L of molecular hydrogen measured at STP react with an excess of molecular chlorine gas.
- 5.53** A quantity of 0.225 g of a metal M (molar mass = 27.0 g/mol) liberated 0.303 L of molecular hydrogen (measured at 17°C and 741 mmHg) from an excess of hydrochloric acid. Deduce from these data the corresponding equation and write formulas for the oxide and sulfate of M.
- 5.54** A compound of P and F was analyzed as follows: Heating 0.2324 g of the compound in a 378-cm<sup>3</sup> container turned all of it to gas, which had a pressure of 97.3 mmHg at 77°C. Then the gas was mixed with calcium chloride solution, which turned all of the F to 0.2631 g of CaF<sub>2</sub>. Determine the molecular formula of the compound.

## Dalton's Law of Partial Pressures

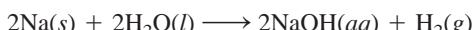
### Review Questions

- 5.55** Define Dalton's law of partial pressures and mole fraction. Does mole fraction have units?
- 5.56** A sample of air contains only nitrogen and oxygen gases whose partial pressures are 0.80 atm and 0.20 atm, respectively. Calculate the total pressure and the mole fractions of the gases.

### Problems

- 5.57** A mixture of gases contains CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>8</sub>. If the total pressure is 1.50 atm and the numbers of moles of the gases present are 0.31 mole for CH<sub>4</sub>, 0.25 mole for C<sub>2</sub>H<sub>6</sub>, and 0.29 mole for C<sub>3</sub>H<sub>8</sub>, calculate the partial pressures of the gases.
- 5.58** A 2.5-L flask at 15°C contains a mixture of three gases, N<sub>2</sub>, He, and Ne, at partial pressures of 0.32 atm for N<sub>2</sub>, 0.15 atm for He, and 0.42 atm for Ne. (a) Calculate the total pressure of the mixture. (b) Calculate the volume in liters at STP occupied by He and Ne if the N<sub>2</sub> is removed selectively.
- 5.59** Dry air near sea level has the following composition by volume: N<sub>2</sub>, 78.08 percent; O<sub>2</sub>, 20.94 percent; Ar, 0.93 percent; CO<sub>2</sub>, 0.05 percent. The atmospheric pressure is 1.00 atm. Calculate (a) the partial pressure of each gas in atm and (b) the concentration of each gas in moles per liter at 0°C. (*Hint:* Because volume is proportional to the number of moles present, mole fractions of gases can be expressed as ratios of volumes at the same temperature and pressure.)
- 5.60** A mixture of helium and neon gases is collected over water at 28.0°C and 745 mmHg. If the partial pressure of helium is 368 mmHg, what is the partial pressure of neon? (Vapor pressure of water at 28°C = 28.3 mmHg.)

- 5.61** A piece of sodium metal undergoes complete reaction with water as follows:



The hydrogen gas generated is collected over water at 25.0°C. The volume of the gas is 246 mL measured at 1.00 atm. Calculate the number of grams of sodium used in the reaction. (Vapor pressure of water at 25°C = 0.0313 atm.)

- 5.62** A sample of zinc metal is allowed to react completely with an excess of hydrochloric acid:



The hydrogen gas produced is collected over water at 25.0°C using an arrangement similar to that shown in Figure 5.14. The volume of the gas is 7.80 L, and the atmospheric pressure is 0.980 atm. Calculate the amount of zinc metal in grams consumed in the reaction. (Vapor pressure of water at 25°C = 23.8 mmHg.)

- 5.63** Helium is mixed with oxygen gas for deep sea divers. Calculate the percent by volume of oxygen gas in the mixture if the diver has to submerge to a depth where the total pressure is 4.2 atm. The partial pressure of oxygen is maintained at 0.20 atm at this depth.

- 5.64** A sample of ammonia (NH<sub>3</sub>) gas is completely decomposed to nitrogen and hydrogen gases over heated iron wool. If the total pressure is 866 mmHg, calculate the partial pressures of N<sub>2</sub> and H<sub>2</sub>.

## Kinetic Molecular Theory of Gases

### Review Questions

- 5.65** What are the basic assumptions of the kinetic molecular theory of gases?
- 5.66** What is thermal motion?
- 5.67** What does the Maxwell speed distribution curve tell us? Does Maxwell's theory work for a sample of 200 molecules? Explain.
- 5.68** Write the expression for the root-mean-square speed for a gas at temperature *T*. Define each term in the equation and show the units that are used in the calculations.
- 5.69** Which of the following two statements is correct? (a) Heat is produced by the collision of gas molecules against one another. (b) When a gas is heated, the molecules collide with one another more often.
- 5.70** As we know, UF<sub>6</sub> is a much heavier gas than helium. Yet at a given temperature, the average kinetic energies of the samples of the two gases are the same. Explain.

### Problems

- 5.71** Compare the root-mean-square speeds of O<sub>2</sub> and UF<sub>6</sub> at 65°C.

- 5.72** The temperature in the stratosphere is  $-23^{\circ}\text{C}$ . Calculate the root-mean-square speeds of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{O}_3$  molecules in this region.
- 5.73** The average distance traveled by a molecule between successive collisions is called *mean free path*. For a given amount of a gas, how does the mean free path of a gas depend on (a) density, (b) temperature at constant volume, (c) pressure at constant temperature, (d) volume at constant temperature, and (e) size of the atoms?
- 5.74** At a certain temperature the speeds of six gaseous molecules in a container are 2.0 m/s, 2.2 m/s, 2.6 m/s, 2.7 m/s, 3.3 m/s, and 3.5 m/s. Calculate the root-mean-square speed and the average speed of the molecules. These two average values are close to each other, but the root-mean-square value is always the larger of the two. Why?

## Deviation from Ideal Behavior

### Review Questions

- 5.75** Give two pieces of evidence to show that gases do not behave ideally under all conditions.
- 5.76** Under what set of conditions would a gas be expected to behave most ideally? (a) High temperature and low pressure, (b) high temperature and high pressure, (c) low temperature and high pressure, (d) low temperature and low pressure.
- 5.77** Write the van der Waals equation for a real gas. Explain clearly the meaning of the corrective terms for pressure and volume.
- 5.78** The temperature of a real gas that is allowed to expand into a vacuum usually drops. Explain.

### Problems

- 5.79** Using the data shown in Table 5.3, calculate the pressure exerted by 2.50 moles of  $\text{CO}_2$  confined in a volume of 5.00 L at 450 K. Compare the pressure with that calculated using the ideal gas equation.
- 5.80** At  $27^{\circ}\text{C}$ , 10.0 moles of a gas in a 1.50-L container exert a pressure of 130 atm. Is this an ideal gas?

## Additional Problems

- 5.81** Discuss the following phenomena in terms of the gas laws: (a) the pressure in an automobile tire increasing on a hot day, (b) the “popping” of a paper bag, (c) the expansion of a weather balloon as it rises in the air, (d) the loud noise heard when a lightbulb shatters.
- 5.82** Nitroglycerin, an explosive, decomposes according to the equation

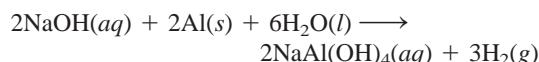


Calculate the total volume of gases produced when collected at 1.2 atm and  $25^{\circ}\text{C}$  from  $2.6 \times 10^2$  g of

- nitroglycerin. What are the partial pressures of the gases under these conditions?
- 5.83** The empirical formula of a compound is CH. At  $200^{\circ}\text{C}$ , 0.145 g of this compound occupies 97.2 mL at a pressure of 0.74 atm. What is the molecular formula of the compound?
- 5.84** When ammonium nitrite ( $\text{NH}_4\text{NO}_2$ ) is heated, it decomposes to give nitrogen gas. This property is used to inflate some tennis balls. (a) Write a balanced equation for the reaction. (b) Calculate the quantity (in grams) of  $\text{NH}_4\text{NO}_2$  needed to inflate a tennis ball to a volume of 86.2 mL at 1.20 atm and  $22^{\circ}\text{C}$ .
- 5.85** The percent by mass of bicarbonate ( $\text{HCO}_3^-$ ) in a certain Alka-Seltzer product is 32.5 percent. Calculate the volume of  $\text{CO}_2$  generated (in milliliters) at  $37^{\circ}\text{C}$  and 1.00 atm when a person ingests a 3.29-g tablet. (Hint: The reaction is between  $\text{HCO}_3^-$  and HCl acid in the stomach.)
- 5.86** The boiling point of liquid nitrogen is  $-196^{\circ}\text{C}$ . On the basis of this information alone, do you think nitrogen is an ideal gas?
- 5.87** In the metallurgical process of refining nickel, the metal is first combined with carbon monoxide to form tetracarbonylnickel, which is a gas at  $43^{\circ}\text{C}$ :
- $$\text{Ni}(s) + 4\text{CO}(g) \longrightarrow \text{Ni}(\text{CO})_4(g)$$
- This reaction separates nickel from other solid impurities. (a) Starting with 86.4 g of Ni, calculate the pressure of  $\text{Ni}(\text{CO})_4$  in a container of volume 4.00 L. (Assume the above reaction goes to completion.) (b) On further heating the sample above  $43^{\circ}\text{C}$ , it is observed that the pressure of the gas increases much more rapidly than predicted based on the ideal gas equation. Explain.
- 5.88** The partial pressure of carbon dioxide varies with seasons. Would you expect the partial pressure in the Northern Hemisphere to be higher in the summer or winter? Explain.
- 5.89** A healthy adult exhales about  $5.0 \times 10^2$  mL of a gaseous mixture with each breath. Calculate the number of molecules present in this volume at  $37^{\circ}\text{C}$  and 1.1 atm. List the major components of this gaseous mixture.
- 5.90** Sodium bicarbonate ( $\text{NaHCO}_3$ ) is called baking soda because when heated, it releases carbon dioxide gas, which is responsible for the rising of cookies, doughnuts, and bread. (a) Calculate the volume (in liters) of  $\text{CO}_2$  produced by heating 5.0 g of  $\text{NaHCO}_3$  at  $180^{\circ}\text{C}$  and 1.3 atm. (b) Ammonium bicarbonate ( $\text{NH}_4\text{HCO}_3$ ) has also been used for the same purpose. Suggest one advantage and one disadvantage of using  $\text{NH}_4\text{HCO}_3$  instead of  $\text{NaHCO}_3$  for baking.
- 5.91** A barometer having a cross-sectional area of  $1.00 \text{ cm}^2$  at sea level measures a pressure of 76.0 cm of

mercury. The pressure exerted by this column of mercury is equal to the pressure exerted by all the air on 1 cm<sup>2</sup> of Earth's surface. Given that the density of mercury is 13.6 g/mL, and the average radius of Earth is 6371 km, calculate the total mass of Earth's atmosphere in kilograms. (*Hint:* The surface area of a sphere is  $4\pi r^2$ , in which  $r$  is the radius of the sphere.)

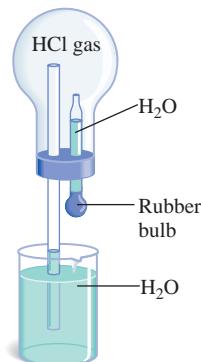
- 5.92** Some commercial drain cleaners contain two components: sodium hydroxide and aluminum powder. When the mixture is poured down a clogged drain, the following reaction occurs:



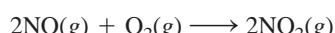
The heat generated in this reaction helps melt away obstructions such as grease, and the hydrogen gas released stirs up the solids clogging the drain. Calculate the volume of H<sub>2</sub> formed at STP if 3.12 g of Al is treated with an excess of NaOH.

- 5.93** The volume of a sample of pure HCl gas was 189 mL at 25°C and 108 mmHg. It was completely dissolved in about 60 mL of water and titrated with an NaOH solution; 15.7 mL of the NaOH solution were required to neutralize the HCl. Calculate the molarity of the NaOH solution.
- 5.94** Propane (C<sub>3</sub>H<sub>8</sub>) burns in oxygen to produce carbon dioxide gas and water vapor. (a) Write a balanced equation for this reaction. (b) Calculate the number of liters of carbon dioxide measured at STP that could be produced from 7.45 g of propane.

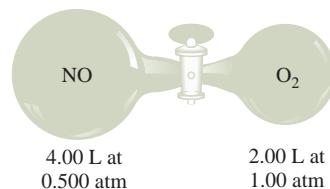
- 5.95** Consider the apparatus shown here. When a small amount of water is introduced into the flask by squeezing the bulb of the medicine dropper, water is squirted upward out of the long glass tubing. Explain this observation. (*Hint:* Hydrogen chloride gas is soluble in water.)



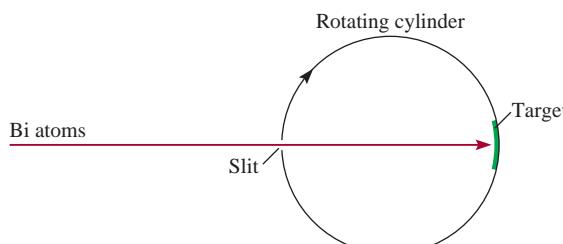
- 5.96** Nitric oxide (NO) reacts with molecular oxygen as follows:



Initially NO and O<sub>2</sub> are separated as shown in the figure. When the valve is opened, the reaction quickly goes to completion. Determine what gases remain at the end and calculate their partial pressures. Assume that the temperature remains constant at 25°C.



- 5.97** The apparatus shown in the diagram can be used to measure atomic and molecular speed. Suppose that a beam of metal atoms is directed at a rotating cylinder in a vacuum. A small opening in the cylinder allows the atoms to strike a target area. Because the cylinder is rotating, atoms traveling at different speeds will strike the target at different positions. In time, a layer of the metal will deposit on the target area, and the variation in its thickness is found to correspond to Maxwell's speed distribution. In one experiment it is found that at 850°C some bismuth (Bi) atoms struck the target at a point 2.80 cm from the spot directly opposite the slit. The diameter of the cylinder is 15.0 cm and it is rotating at 130 revolutions per second. (a) Calculate the speed (m/s) at which the target is moving. (*Hint:* The circumference of a circle is given by  $2\pi r$ , in which  $r$  is the radius.) (b) Calculate the time (in seconds) it takes for the target to travel 2.80 cm. (c) Determine the speed of the Bi atoms. Compare your result in (c) with the  $u_{\text{rms}}$  of Bi at 850°C. Comment on the difference.



- 5.98** Acidic oxides such as carbon dioxide react with basic oxides like calcium oxide (CaO) and barium oxide (BaO) to form salts (metal carbonates). (a) Write equations representing these two reactions. (b) A student placed a mixture of BaO and CaO of combined mass 4.88 g in a 1.46-L flask containing carbon dioxide gas at 35°C and 746 mmHg. After the reactions were complete, she found that the CO<sub>2</sub> pressure had dropped to 252 mmHg. Calculate the percent composition of the mixture.

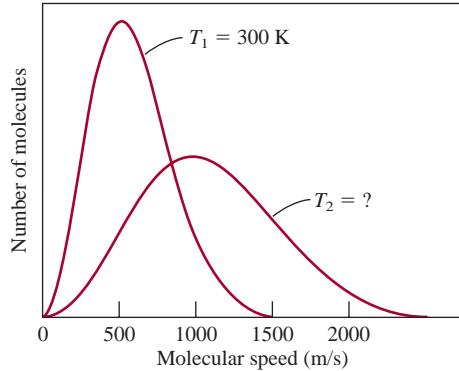
- 5.99 The running engine of an automobile produces carbon monoxide (CO), a toxic gas, at the rate of about 188 g CO per hour. A car is left idling at 20°C in a poorly ventilated garage that is 6.0 m long, 4.0 m wide, and 2.2 m high. (a) Calculate the rate of CO production in moles per minute. (b) How long would it take to build up a lethal concentration of CO of 1000 ppmv (parts per million by volume)?
- 5.100** Air entering the lungs ends up in tiny sacs called alveoli. It is from the alveoli that oxygen diffuses into the blood. The average radius of the alveoli is 0.0050 cm and the air inside contains 14 percent oxygen. Assuming that the pressure in the alveoli is 1.0 atm and the temperature is 37°C, calculate the number of oxygen molecules in one of the alveoli. (*Hint:* The volume of a sphere of radius  $r$  is  $\frac{4}{3}\pi r^3$ .)
- 5.101 It is said that every breath we take, on average, contains molecules that were once exhaled by Wolfgang Amadeus Mozart (1756–1791). These calculations demonstrate the validity of this statement. (a) Calculate the total number of molecules in the atmosphere. (*Hint:* Use the result in Problem 5.91 and 29.0 g/mol as the molar mass of air.) (b) Assuming the volume of every breath (inhale or exhale) is 500 mL, calculate the number of molecules exhaled in each breath at 37°C, which is human body temperature. (c) If Mozart's lifespan was exactly 35 years, what is the number of molecules exhaled in that period? (Given that an average person breathes 12 times per minute.) (d) Calculate the fraction of molecules in the atmosphere that were breathed out by Mozart. How many of Mozart's molecules do we breathe in with every inhalation of air? Round off your answer to one significant figure. (e) List three important assumptions in these calculations.
- 5.102** Under the same conditions of temperature and pressure, which of these gases would behave most ideally: Ne, N<sub>2</sub>, or CH<sub>4</sub>? Explain.
- 5.103 Based on your knowledge of the kinetic theory of gases, derive Graham's law of diffusion [Equation (5.17)].
- 5.104** A 6.11-g sample of a Cu-Zn alloy reacts with HCl acid to produce hydrogen gas. If the hydrogen gas has a volume of 1.26 L at 22°C and 728 mmHg, what is the percent of Zn in the alloy? (*Hint:* Cu does not react with HCl.)
- 5.105 Estimate the distance (in nanometers) between molecules of water vapor at 100°C and 1.0 atm. Assume ideal behavior. Repeat the calculation for liquid water at 100°C, given that the density of water is 0.96 g/cm<sup>3</sup> at that temperature. Comment on your results. (Assume water molecule to be a sphere with a diameter of 0.3 nm.) (*Hint:* First calculate the number density of water molecules. Next, convert the number density to linear density, that is, number of molecules in one direction.)
- 5.106** A stockroom supervisor measured the contents of a partially filled 25.0-gallon acetone drum on a day when the temperature was 18.0°C and atmospheric pressure was 750 mmHg, and found that 15.4 gallons of the solvent remained. After tightly sealing the drum, an assistant dropped the drum while carrying it upstairs to the organic laboratory. The drum was dented and its internal volume was decreased to 20.4 gallons. What is the total pressure inside the drum after the accident? The vapor pressure of acetone at 18.0°C is 400 mmHg. (*Hint:* At the time the drum was sealed, the pressure inside the drum, which is equal to the sum of the pressures of air and acetone, was equal to the atmospheric pressure.)
- 5.107 Lithium hydride reacts with water as follows:
- $$\text{LiH}(s) + \text{H}_2\text{O}(l) \longrightarrow \text{LiOH}(aq) + \text{H}_2(g)$$
- During World War II, U.S. pilots carried LiH tablets. In the event of a crash landing at sea, the LiH would react with the seawater and fill their life belts and lifeboats with hydrogen gas. How many grams of LiH are needed to fill a 4.1-L life belt at 0.97 atm and 12°C?
- 5.108** A sample of the gas discussed in Problem 5.38 is found to effuse through a porous barrier in 15.0 min. Under the same conditions of temperature and pressure, it takes N<sub>2</sub> 12.0 min to effuse through the same barrier. Calculate the molar mass of the gas and suggest what gas it might be.
- 5.109 Nickel forms a gaseous compound of the formula Ni(CO)<sub>x</sub>. What is the value of  $x$  given the fact that under the same conditions of temperature and pressure methane (CH<sub>4</sub>) effuses 3.3 times faster than the compound?

## SPECIAL PROBLEMS

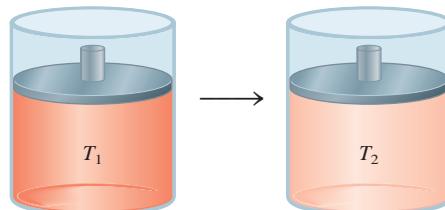
- 5.110** Apply your knowledge of the kinetic theory of gases to these situations.
- Does a single molecule have a temperature?
  - Two flasks of volumes  $V_1$  and  $V_2$  ( $V_2 > V_1$ ) contain the same number of helium atoms at the same

temperature. (i) Compare the root-mean-square (rms) speeds and average kinetic energies of the helium (He) atoms in the flasks. (ii) Compare the frequency and the force with which the He atoms collide with the walls of their containers.

- (c) Equal numbers of He atoms are placed in two flasks of the same volume at temperatures  $T_1$  and  $T_2$  ( $T_2 > T_1$ ) (i) Compare the rms speeds of the atoms in the two flasks. (ii) Compare the frequency and the force with which the He atoms collide with the walls of their containers.
- (d) Equal numbers of He and neon (Ne) atoms are placed in two flasks of the same volume and the temperature of both gases is 74°C. Comment on the validity of these statements: (i) The rms speed of He is equal to that of Ne. (ii) The average kinetic energies of the two gases are equal. (iii) The rms speed of each He atom is  $1.47 \times 10^3$  m/s.
- 5.111 Referring to the plot in Figure 5.19, (a) why do the plots of the gases dip before they rise? (b) Why do they all converge to 1 at very low  $P$ ? (c) What is the meaning of the intercept on the ideal gas line? Does the intercept mean that the gas has become an ideal gas?
- 5.112** Referring to Figure 5.15, we see that the maximum of each speed distribution plot is called the most probable speed ( $u_{\text{mp}}$ ) because it is the speed possessed by the largest number of molecules. It is given by  $u_{\text{mp}} = \sqrt{2RT/M}$ . (a) Compare  $u_{\text{mp}}$  with  $u_{\text{rms}}$  for nitrogen at 25°C. (b) The following diagram shows the Maxwell speed distribution curves for an ideal gas at two different temperatures  $T_1$  and  $T_2$ . Calculate the value of  $T_2$ .
- 



- 5.113 Use the kinetic theory of gases to explain why hot air rises.
- 5.114** One way to gain a physical understanding of  $b$  in the van der Waals equation is to calculate the “excluded volume.” Assume that the distance of closest approach between two similar atoms is the sum of their radii ( $2r$ ). (a) Calculate the volume around each atom into which the center of another atom cannot penetrate. (b) From your result in (a), calculate the excluded volume for 1 mole of the atoms, which is the constant  $b$ . How does this volume compare with the sum of the volumes of 1 mole of the atoms?
- 5.115 A 5.00-mole sample of  $\text{NH}_3$  gas is kept in a 1.92 L container at 300 K. If the van der Waals equation is assumed to give the correct answer for the pressure of the gas, calculate the percent error made in using the ideal gas equation to calculate the pressure.
- 5.116** The root-mean-square speed of a certain gaseous oxide is 493 m/s at 20°C. What is the molecular formula of the compound?
- 5.117 In 2.00 min, 29.7 mL of He effuse through a small hole. Under the same conditions of pressure and temperature, 10.0 mL of a mixture of CO and  $\text{CO}_2$  effuse through the hole in the same amount of time. Calculate the percent composition by volume of the mixture.
- 5.118** A gaseous reaction takes place at constant volume and constant pressure in a cylinder shown here. Which of the following equations best describes the reaction? The initial temperature ( $T_1$ ) is twice that of the final temperature ( $T_2$ ).
- $\text{A} + \text{B} \longrightarrow \text{C}$
  - $\text{AB} \longrightarrow \text{C} + \text{D}$
  - $\text{A} + \text{B} \longrightarrow \text{C} + \text{D}$
  - $\text{A} + \text{B} \longrightarrow 2\text{C} + \text{D}$



## ANSWERS TO PRACTICE EXERCISES

- 5.1** 0.986 atm. **5.2** 9.29 L. **5.3** 30.6 L. **5.4** 2.6 atm.  
**5.5** 44.1 g/mol. **5.6** 4.75 L. **5.7**  $\text{CH}_4$ : 1.29 atm;  $\text{C}_2\text{H}_6$ : 0.0657 atm;  $\text{C}_3\text{H}_8$ : 0.0181 atm. **5.8** 0.0653 g. **5.9** 321 m/s.

- 5.10** 146 g/mol. **5.11** 30.0 atm; 45.5 atm using the ideal gas equation.

Forest fire—an undesirable exothermic reaction.



## Energy Relationships in Chemical Reactions

### CHAPTER OUTLINE

- 6.1 The Nature of Energy and Types of Energy 172
- 6.2 Energy Changes in Chemical Reactions 173
- 6.3 Introduction to Thermodynamics 174
  - The First Law of Thermodynamics • Work and Heat
- 6.4 Enthalpy of Chemical Reactions 180
  - Enthalpy • Enthalpy of Reactions • Thermochemical Equations
    - A Comparison of  $\Delta H$  and  $\Delta E$
- 6.5 Calorimetry 185
  - Specific Heat and Heat Capacity • Constant-Volume Calorimetry • Constant-Pressure Calorimetry
- 6.6 Standard Enthalpy of Formation and Reaction 191
  - The Direct Method • The Indirect Method

### ESSENTIAL CONCEPTS

**Energy** The many different forms of energy are, at least in principle, interconvertible.

**First Law of Thermodynamics** The first law of thermodynamics, which is based on the law of conservation of energy, relates the internal energy change of a system to the heat change and the work done. It can also be expressed to show the relationship between the internal energy change and enthalpy change of a process.

**Thermochemistry** Most chemical reactions involve the absorption or release of heat. At constant pressure, the heat change is equal to the enthalpy change. The heat change is measured by a calorimeter. Constant-pressure and constant-volume calorimeters are devices for measuring heat changes under the stated conditions.

**Standard Enthalpy of Reaction** Standard enthalpy of reaction is the enthalpy change when the reaction is carried out at 1 atm pressure. It can be calculated from the standard enthalpies of formation of reactants and products. Hess's law enables us to measure the standard enthalpy of formation of a compound in an indirect way.



### Activity Summary

1. Interactivity: Conservation of Energy (6.3)
2. Animation: Heat Flow (6.4)

## 6.1 The Nature of Energy and Types of Energy

“Energy” is a much-used term that represents a rather abstract concept. For instance, when we feel tired, we might say we haven’t any *energy*; and we read about the need to find alternatives to nonrenewable *energy* sources. Unlike matter, energy is known and recognized by its effects. It cannot be seen, touched, smelled, or weighed.

**Energy** is usually defined as *the capacity to do work*. In Chapter 5 we defined work as “force  $\times$  distance,” but we will soon see that there are other kinds of work. All forms of energy are capable of doing work (that is, of exerting a force over a distance), but not all of them are equally relevant to chemistry. The energy contained in tidal waves, for example, can be harnessed to perform useful work, but the relationship between tidal waves and chemistry is minimal. Chemists define **work** as *directed energy change resulting from a process*. Kinetic energy—the energy produced by a moving object—is one form of energy that is of particular interest to chemists. Others include radiant energy, thermal energy, chemical energy, and potential energy.

**Radiant energy**, or *solar energy*, comes from the sun and is Earth’s primary energy source. Solar energy heats the atmosphere and Earth’s surface, stimulates the growth of vegetation through the process known as photosynthesis, and influences global climate patterns.

**Thermal energy** is *the energy associated with the random motion of atoms and molecules*. In general, thermal energy can be calculated from temperature measurements. The more vigorous the motion of the atoms and molecules in a sample of matter, the hotter the sample is and the greater its thermal energy. However, we need to distinguish carefully between thermal energy and temperature. A cup of coffee at 70°C has a higher temperature than a bathtub filled with warm water at 40°C, but much more thermal energy is stored in the bathtub water because it has a much larger volume and greater mass than the coffee and therefore more water molecules and more molecular motion.

**Chemical energy** is *stored within the structural units of chemical substances*; its quantity is determined by the type and arrangement of constituent atoms. When substances participate in chemical reactions, chemical energy is released, stored, or converted to other forms of energy.

**Potential energy** is *energy available by virtue of an object’s position*. For instance, because of its altitude, a rock at the top of a cliff has more potential energy and will make a bigger splash if it falls into the water below than a similar rock located partway down the cliff. Chemical energy can be considered a form of potential energy because it is associated with the relative positions and arrangements of atoms within a given substance.



As the water falls over the dam, its potential energy is converted to kinetic energy. Use of this energy to generate electricity is called hydroelectric power.

All forms of energy can be converted (at least in principle) from one form to another. We feel warm when we stand in sunlight because radiant energy is converted to thermal energy on our skin. When we exercise, chemical energy stored in our bodies is used to produce kinetic energy. When a ball starts to roll downhill, its potential energy is converted to kinetic energy. You can undoubtedly think of many other examples. Although energy can assume many different forms that are interconvertible, scientists have concluded that energy can be neither destroyed nor created. When one form of energy disappears, some other form of energy (of equal magnitude) must appear, and vice versa. This principle is summarized by the **law of conservation of energy**: *the total quantity of energy in the universe is assumed constant*.

Kinetic energy was introduced in Chapter 5.

## 6.2 Energy Changes in Chemical Reactions

Often the energy changes that take place during chemical reactions are of as much practical interest as the mass relationships we discussed in Chapter 3. For example, combustion reactions involving fuels such as natural gas and oil are carried out in daily life more for the thermal energy they release than for their products, which are water and carbon dioxide.

Almost all chemical reactions absorb or produce (release) energy, generally in the form of heat. It is important to understand the distinction between thermal energy and heat. **Heat** is the transfer of thermal energy between two bodies that are at different temperatures. Thus, we often speak of the “heat flow” from a hot object to a cold one. Although the term “heat” by itself implies the transfer of energy, we customarily talk of “heat absorbed” or “heat released” when describing the energy changes that occur during a process. **Thermochemistry** is the study of heat change in chemical reactions.

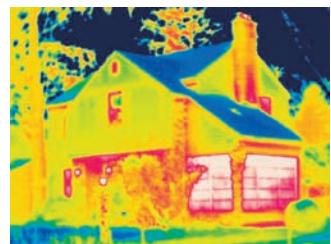
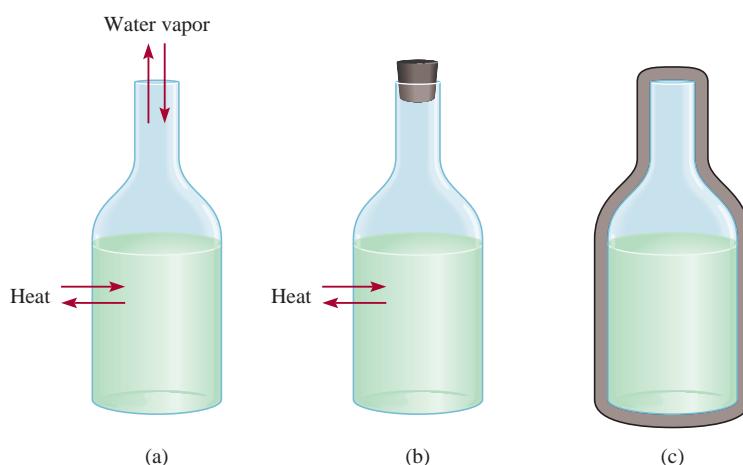
To analyze energy changes associated with chemical reactions we must first define the **system**, or the specific part of the universe that is of interest to us. For chemists, systems usually include substances involved in chemical and physical changes. For example, in an acid-base neutralization experiment, the system may be a beaker containing 50 mL of HCl to which 50 mL of NaOH is added. The **surroundings** are the rest of the universe outside the system.

There are three types of systems. An **open system** can exchange mass and energy, usually in the form of heat with its surroundings. For example, an open system may consist of a quantity of water in an open container, as shown in Figure 6.1(a). If we close the flask, as in Figure 6.1(b), so that no water vapor can escape from or condense into the container, we create a **closed system**, which allows the transfer of energy (heat) but not mass. By placing the water in a totally insulated container, we can construct an **isolated system**, which does not allow the transfer of either mass or energy, as shown in Figure 6.1(c).

The combustion of hydrogen gas in oxygen is one of many chemical reactions that release considerable quantities of energy (Figure 6.2):



In this case, we label the reacting mixture (hydrogen, oxygen, and water molecules) the **system** and the rest of the universe the **surroundings**. Because energy cannot be created or destroyed, any energy lost by the system must be gained by the surroundings. Thus,



This infrared photo shows where energy (heat) leaks through the house. The more red the color, the greater the energy is lost to the outside.

**Figure 6.1**

Three systems represented by water in a flask: (a) an open system, which allows the exchange of both energy and mass with surroundings; (b) a closed system, which allows the exchange of energy but not mass; and (c) an isolated system, which allows neither energy nor mass to be exchanged (here the flask is enclosed by a vacuum jacket).

**Figure 6.2**

The Hindenburg disaster. The Hindenburg, a German airship filled with hydrogen gas, was destroyed in a spectacular fire at Lakehurst, New Jersey, in 1937.



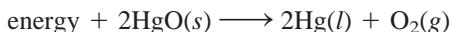
*Exo-* comes from the Greek word meaning “outside”; *endo-* means “within.”



On heating, HgO decomposes to give Hg and O<sub>2</sub>.

the heat generated by the combustion process is transferred from the system to its surroundings. This reaction is an example of an **exothermic process**, which is *any process that gives off heat*—that is, *transfers thermal energy to the surroundings*.

Now consider another reaction, the decomposition of mercury(II) oxide (HgO) at high temperatures:



This reaction is an **endothermic process**, in which *heat has to be supplied to the system* (that is, to HgO) by the surroundings.

In exothermic reactions, the total energy of the products is less than the total energy of the reactants. The difference is the heat supplied by the system to the surroundings. Just the opposite happens in endothermic reactions. Here, the difference between the energy of the products and the energy of the reactants is equal to the heat supplied to the system by the surroundings.

### 6.3 Introduction to Thermodynamics

Thermochemistry is part of a broader subject called **thermodynamics**, which is *the scientific study of the interconversion of heat and other kinds of energy*. The laws of thermodynamics provide useful guidelines for understanding the energetics and directions of processes. In this section we will concentrate on the first law of thermodynamics, which is particularly relevant to the study of thermochemistry. We will continue our discussion of thermodynamics in Chapter 18.

In thermodynamics, we study changes in the **state of a system**, which is defined by the values of all relevant macroscopic properties, for example, composition, energy, temperature, pressure, and volume. Energy, pressure, volume, and temperature are said to be **state functions**—properties that are determined by the state of the system, regardless of how that condition was achieved. In other words, when the state of a system changes, the magnitude of change in any state function depends only on the initial and final states of the system and not on how the change is accomplished.

The state of a given amount of a gas is specified by its volume, pressure, and temperature. Consider a gas at 2 atm, 300 K, and 1 L (the initial state). Suppose a process is carried out at constant temperature such that the gas pressure decreases to

**Figure 6.3**

The gain in gravitational potential energy that occurs when a person climbs from the base to the top of a mountain is independent of the path taken.

1 atm. According to Boyle's law, its volume must increase to 2 L. The final state then corresponds to 1 atm, 300 K, and 2 L. The change in volume ( $\Delta V$ ) is

$$\begin{aligned}\Delta V &= V_f - V_i \\ &= 2 \text{ L} - 1 \text{ L} \\ &= 1 \text{ L}\end{aligned}$$

The Greek letter *delta*,  $\Delta$ , symbolizes change. We use  $\Delta$  in this text always to mean final – initial.

where  $V_i$  and  $V_f$  denote the initial and final volume, respectively. No matter how we arrive at the final state (for example, the pressure of the gas can be increased first and then decreased to 1 atm), the change in volume is always 1 L. Thus, the volume of a gas is a state function. In a similar manner, we can show that pressure and temperature are also state functions.

Energy is another state function. Using potential energy as an example, we find that the net increase in gravitational potential energy when we go from the same starting point to the top of a mountain is always the same, regardless of how we get there (Figure 6.3).

Recall that an object possesses potential energy by virtue of its position or chemical composition.

## The First Law of Thermodynamics

The *first law of thermodynamics*, which is based on the law of conservation of energy, states that *energy can be converted from one form to another, but cannot be created or destroyed*.<sup>†</sup> How do we know this is so? It would be impossible to prove the validity of the first law of thermodynamics if we had to determine the total energy content of the universe. Even determining the total energy content of 1 g of iron, say, would be extremely difficult. Fortunately, we can test the validity of the first law by measuring only the *change* in the internal energy of a system between its *initial state* and its *final state* in a process. The change in internal energy  $\Delta E$  is given by

$$\Delta E = E_f - E_i$$

where  $E_i$  and  $E_f$  are the internal energies of the system in the initial and final states, respectively.

The internal energy of a system has two components: kinetic energy and potential energy. The kinetic energy component consists of various types of molecular motion and the movement of electrons within molecules. Potential energy is determined by the attractive interactions between electrons and nuclei and by repulsive interactions between electrons and between nuclei in individual molecules, as well as by interaction between molecules. It is impossible to measure all these contributions accurately, so we cannot calculate the total energy of a system with any certainty. Changes in energy, on the other hand, can be determined experimentally.



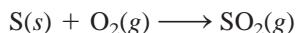
**Interactivity:**  
Conservation of Energy  
ARIS, Interactives

<sup>†</sup>See footnote on p. 30 (Chapter 2) for a discussion of mass and energy relationship in chemical reactions.



Sulfur burning in air to form  $\text{SO}_2$ .

Consider the reaction between 1 mole of sulfur and 1 mole of oxygen gas to produce 1 mole of sulfur dioxide:



In this case, our system is composed of the reactant molecules S and  $\text{O}_2$  and the product molecules  $\text{SO}_2$ . We do not know the internal energy content of either the reactant molecules or the product molecules, but we can accurately measure the *change* in energy content,  $\Delta E$ , given by

$$\Delta E = E(\text{product}) - E(\text{reactants})$$

$$= \text{energy content of 1 mol } \text{SO}_2(g) - \text{energy content of [1 mol } \text{S}(s) + 1 \text{ mol } \text{O}_2(g)]$$

We find that this reaction gives off heat. Therefore, the energy of the product is less than that of the reactants, and  $\Delta E$  is negative.

Interpreting the release of heat in this reaction to mean that some of the chemical energy contained in the molecules has been converted to thermal energy, we conclude that the transfer of energy from the system to the surroundings does not change the total energy of the universe. That is, the sum of the energy changes must be zero:

$$\Delta E_{\text{sys}} + \Delta E_{\text{surr}} = 0$$

or

$$\Delta E_{\text{sys}} = -\Delta E_{\text{surr}}$$

where the subscripts “sys” and “surr” denote system and surroundings, respectively. Thus, if one system undergoes an energy change  $\Delta E_{\text{sys}}$ , the rest of the universe, or the surroundings, must undergo a change in energy that is equal in magnitude but opposite in sign ( $-\Delta E_{\text{surr}}$ ); energy gained in one place must have been lost somewhere else. Furthermore, because energy can be changed from one form to another, the energy lost by one system can be gained by another system in a different form. For example, the energy lost by burning oil in a power plant may ultimately turn up in our homes as electrical energy, heat, light, and so on.

In chemistry, we are normally interested in the energy changes associated with the system (which may be a flask containing reactants and products), not with its surroundings. Therefore, a more useful form of the first law is

$$\Delta E = q + w \quad (6.1)$$

We use lowercase letters (such as  $w$  and  $q$ ) to represent thermodynamic quantities that are not state functions.

For convenience, we sometimes omit the word “internal” when discussing the energy of a system.

(We drop the subscript “sys” for simplicity.) Equation (6.1) says that the change in the internal energy,  $\Delta E$ , of a system is the sum of the heat exchange  $q$  between the system and the surroundings and the work done  $w$  on (or by) the system. The sign conventions for  $q$  and  $w$  are as follows:  $q$  is positive for an endothermic process and negative for an exothermic process and  $w$  is positive for work done on the system by the surroundings and negative for work done by the system on the surroundings. We can think of the first law of thermodynamics as an energy balance sheet, much like a money balance sheet kept in a bank that does currency exchange. You can withdraw or deposit money in either of two different currencies (like energy change due to heat exchange and work done). However, the value of your bank account depends only on the net amount of money left in it after these transactions, not on which currency you used.

Equation (6.1) may seem abstract, but it is actually quite logical. If a system loses heat to the surroundings or does work on the surroundings, we would expect its internal energy to decrease because those are energy-depleting processes. For this reason,

**TABLE 6.1** Sign Conventions for Work and Heat

Process	Sign
Work done by the system on the surroundings	−
Work done on the system by the surroundings	+
Heat absorbed by the system from the surroundings (endothermic process)	+
Heat absorbed by the surroundings from the system (exothermic process)	−

both  $q$  and  $w$  are negative. Conversely, if heat is added to the system or if work is done on the system, then the internal energy of the system would increase. In this case, both  $q$  and  $w$  are positive. Table 6.1 summarizes the sign conventions for  $q$  and  $w$ .

## Work and Heat

We will now look at the nature of work and heat in more detail.

### Work

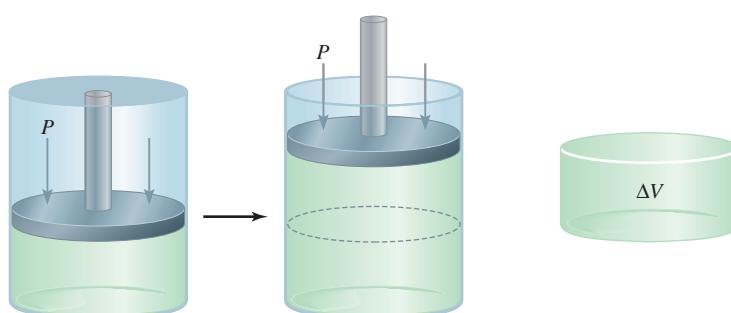
We have seen that work can be defined as force  $F$  multiplied by distance  $d$ :

$$w = Fd \quad (6.2)$$

In thermodynamics, work has a broader meaning that includes mechanical work (for example, a crane lifting a steel beam), electrical work (a battery supplying electrons to light the bulb of a flashlight), and surface work (blowing up a soap bubble). In this section we will concentrate on mechanical work; in Chapter 19 we will discuss the nature of electrical work.

One way to illustrate mechanical work is to study the expansion or compression of a gas. Many chemical and biological processes involve gas volume changes. Breathing and exhaling air involves the expansion and contraction of the tiny sacs called alveoli in the lungs. Another example is the internal combustion engine of the automobile. The successive expansion and compression of the cylinders due to the combustion of the gasoline-air mixture provide power to the vehicle. Figure 6.4 shows a gas in a cylinder fitted with a weightless, frictionless movable piston at a certain temperature, pressure, and volume. As it expands, the gas pushes the piston upward against a constant opposing external atmospheric pressure  $P$ . The work done by the gas on the surroundings is

$$w = -P\Delta V \quad (6.3)$$

**Figure 6.4**

The expansion of a gas against a constant external pressure (such as atmospheric pressure). The gas is in a cylinder fitted with a weightless movable piston. The work done is given by  $-P\Delta V$ .

where  $\Delta V$ , the change in volume, is given by  $V_f - V_i$ . The minus sign in Equation (6.3) takes care of the convention for  $w$ . For gas expansion,  $\Delta V > 0$ , so  $-P\Delta V$  is a negative quantity. For gas compression (work done on the system),  $\Delta V < 0$ , and  $-P\Delta V$  is a positive quantity.

Equation (6.3) derives from the fact that pressure  $\times$  volume can be expressed as (force/area)  $\times$  volume; that is,

$$P \times V = \frac{F}{d^2} \times d^3 = Fd = w$$

pressure      volume

where  $F$  is the opposing force and  $d$  has the dimension of length,  $d^2$  has the dimensions of area, and  $d^3$  has the dimensions of volume. Thus, the product of pressure and volume is equal to force times distance, or work. You can see that for a given increase in volume (that is, for a certain value of  $\Delta V$ ), the work done depends on the magnitude of the external, opposing pressure  $P$ . If  $P$  is zero (that is, if the gas is expanding against a vacuum), the work done must also be zero. If  $P$  is some positive, nonzero value, then the work done is given by  $-P\Delta V$ .

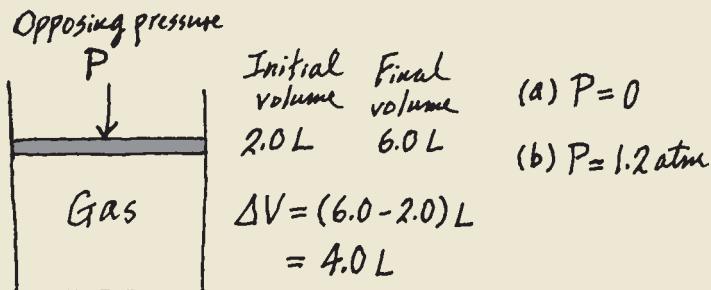
According to Equation (6.3), the units for work done by or on a gas are liters atmospheres. To express the work done in the more familiar unit of joules, we use the conversion factor (see Appendix 2).

$$1 \text{ L} \cdot \text{atm} = 101.3 \text{ J}$$

### Example 6.1

A certain gas expands in volume from 2.0 L to 6.0 L at constant temperature. Calculate the work done by the gas if it expands (a) against a vacuum and (b) against a constant pressure of 1.2 atm.

**Strategy** A simple sketch of the situation is helpful here:



The work done in gas expansion is equal to the product of the external, opposing pressure and the change in volume. What is the conversion factor between  $\text{L} \cdot \text{atm}$  and  $\text{J}$ ?

### Solution

(a) Because the external pressure is zero, no work is done in the expansion:

$$\begin{aligned} w &= -P\Delta V \\ &= -(0)(6.0 - 2.0) \text{ L} \\ &= 0 \end{aligned}$$

(Continued)

(b) The external, opposing pressure is 1.2 atm, so

$$\begin{aligned} w &= -P\Delta V \\ &= -(1.2 \text{ atm})(6.0 - 2.0) \text{ L} \\ &= -4.8 \text{ L} \cdot \text{atm} \end{aligned}$$

To convert the answer to joules, we write

$$\begin{aligned} w &= -4.8 \text{ L} \cdot \text{atm} \times \frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} \\ &= -4.9 \times 10^2 \text{ J} \end{aligned}$$

**Check** Because this is gas expansion (work is done by the system on the surroundings), the work done has a negative sign.

Similar problems: 6.15, 6.16.

**Practice Exercise** A gas expands from 264 mL to 971 mL at constant temperature. Calculate the work done (in joules) by the gas if it expands (a) against a vacuum and (b) against a constant pressure of 4.00 atm.

Example 6.1 shows that work is not a state function. Although the initial and final states are the same in (a) and (b), the amount of work done is different because the external, opposing pressures are different. We *cannot* write  $\Delta w = w_f - w_i$  for a change. Work done depends not only on the initial state and final state, but also on how the process is carried out, that is, on the path.

Because temperature is kept constant, you can use Boyle's law to show that the final pressure is the same in (a) and (b).

## Heat

The other component of internal energy is heat,  $q$ . Like work, heat is not a state function. For example, it takes 4184 J of energy to raise the temperature of 100 g of water from 20°C to 30°C. This energy can be gained (a) directly as heat energy from a Bunsen burner, without doing any work on the water; (b) by doing work on the water without adding heat energy (for example, by stirring the water with a magnetic stir bar); or (c) by some combination of the procedures described in (a) and (b). This simple illustration shows that heat associated with a given process, like work, depends on how the process is carried out. It is important to note that regardless of which procedure is taken, the change in internal energy of the system,  $\Delta E$ , depends on the sum of  $(q + w)$ . If changing the path from the initial state to the final state increases the value of  $q$ , then it will decrease the value of  $w$  by the same amount and vice versa, so that  $\Delta E$  remains unchanged.

In summary, heat and work are not state functions because they are not properties of a system. They manifest themselves only during a process (during a change). Thus, their values depend on the path of the process and vary accordingly.

## Example 6.2

The work done when a gas is compressed in a cylinder like that shown in Figure 6.4 is 462 J. During this process, there is a heat transfer of 128 J from the gas to the surroundings. Calculate the energy change for this process.

**Strategy** Compression is work done on the gas, so what is the sign for  $w$ ? Heat is released by the gas to the surroundings. Is this an endothermic or exothermic process? What is the sign for  $q$ ?

(Continued)

**Solution** To calculate the energy change of the gas, we need Equation (6.1). Work of compression is positive and because heat is released by the gas,  $q$  is negative. Therefore, we have

$$\begin{aligned}\Delta E &= q + w \\ &= -128 \text{ J} + 462 \text{ J} \\ &= 334 \text{ J}\end{aligned}$$

**Similar problems:** 6.17, 6.18.

**Practice Exercise** A gas expands and does  $P\cdot V$  work on the surroundings equal to 279 J. At the same time, it absorbs 216 J of heat from the surroundings. What is the change in energy of the system?

## 6.4 Enthalpy of Chemical Reactions

Our next step is to see how the first law of thermodynamics can be applied to processes carried out under different conditions. Specifically, we will consider a situation in which the volume of the system is kept constant and one in which the pressure applied on the system is kept constant. These are commonly encountered cases in the laboratory.

**P-V work means work of gas expansion or gas compression.**

If a chemical reaction is run at constant volume, then  $\Delta V = 0$  and no  $P\cdot V$  work will result from this change. From Equation (6.1) it follows that

$$\begin{aligned}\Delta E &= q - P\Delta V \\ &= q_v\end{aligned}\tag{6.4}$$

We add the subscript “ $v$ ” to remind us that this is a constant-volume process. This equality may seem strange at first, for we showed earlier that  $q$  is not a state function. The process is carried out under constant-volume conditions, however, so that the heat change can have only a specific value, which is equal to  $\Delta E$ .

### Enthalpy

Constant-volume conditions are often inconvenient and sometimes impossible to achieve. Most reactions occur under conditions of constant pressure (usually atmospheric pressure). If such a reaction results in a net increase in the number of moles of a gas, then the system does work on the surroundings (expansion). This follows from the fact that for the gas formed to enter the atmosphere, it must push the surrounding air back. Conversely, if more gas molecules are consumed than are produced, work is done on the system by the surroundings (compression). Finally, no work is done if there is no net change in the number of moles of gases from reactants to products.

In general, for a constant-pressure process we write

$$\begin{aligned}\Delta E &= q + w \\ &= q_p - P\Delta V \\ \text{or} \quad q_p &= \Delta E + P\Delta V\end{aligned}\tag{6.5}$$

where the subscript “ $p$ ” denotes constant-pressure condition.

We now introduce a new thermodynamic function of a system called ***enthalpy*** (***H***), which is defined by the equation

$$H = E + PV \quad (6.6)$$

where *E* is the internal energy of the system and *P* and *V* are the pressure and volume of the system, respectively. Because *E* and *PV* have energy units, enthalpy also has energy units. Furthermore, *E*, *P*, and *V* are all state functions, that is, the changes in (*E* + *PV*) depend only on the initial and final states. It follows, therefore, that the change in *H*, or  $\Delta H$ , also depends only on the initial and final states. Thus, *H* is a state function.

For any process, the change in enthalpy according to Equation (6.6) is given by

$$\Delta H = \Delta E + \Delta(PV) \quad (6.7)$$

If the pressure is held constant, then

$$\Delta H = \Delta E + P\Delta V \quad (6.8)$$

Comparing Equation (6.8) with Equation (6.5), we see that for a constant-pressure process,  $q_p = \Delta H$ . Again, although *q* is not a state function, the heat change at constant pressure is equal to  $\Delta H$  because the “path” is defined and therefore it can have only a specific value.

We now have two quantities— $\Delta E$  and  $\Delta H$ —that can be associated with a reaction. Both quantities measure energy changes, but under different conditions. If the reaction occurs under constant-volume conditions, then the heat change,  $q_v$ , is equal to  $\Delta E$ . On the other hand, when the reaction is carried out at constant pressure, the heat change,  $q_p$ , is equal to  $\Delta H$ .

In Section 6.5 we will discuss ways to measure heat changes at constant volume and constant pressure.

## Enthalpy of Reactions

Because most reactions are constant-pressure processes, we can equate the heat change in these cases to the change in enthalpy. For any reaction of the type



**Animation:**  
Heat Flow  
ARIS, Animations

we define the change in enthalpy, called the ***enthalpy of reaction***, ***ΔH***, as the difference between the enthalpies of the products and the enthalpies of the reactants:

$$\Delta H = H(\text{products}) - H(\text{reactants}) \quad (6.9)$$

The enthalpy of reaction can be positive or negative, depending on the process. For an endothermic process (heat absorbed by the system from the surroundings),  $\Delta H$  is positive (that is,  $\Delta H > 0$ ). For an exothermic process (heat released by the system to the surroundings),  $\Delta H$  is negative (that is,  $\Delta H < 0$ ).

An analogy for enthalpy change is a change in the balance in your bank account. Suppose your initial balance is \$100. After a transaction (deposit or withdrawal), the change in your bank balance,  $\Delta X$ , is given by

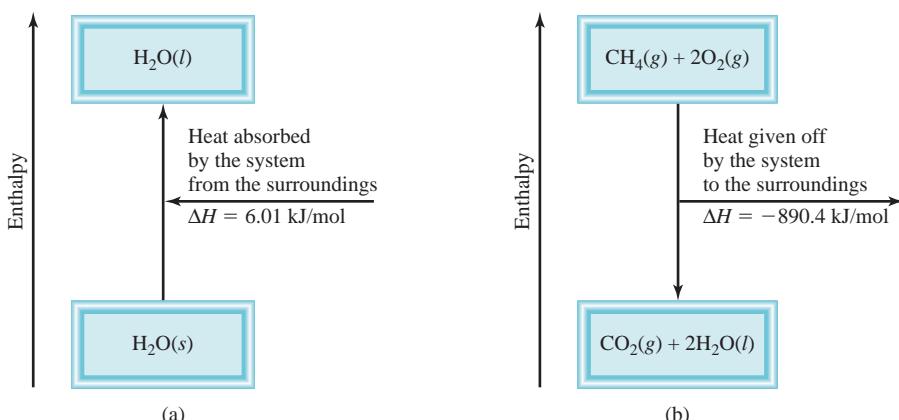
$$\Delta X = X_{\text{final}} - X_{\text{initial}}$$

where *X* represents the bank balance. If you deposit \$80 into your account, then  $\Delta X = \$180 - \$100 = \$80$ . This corresponds to an endothermic reaction. (The balance

This analogy assumes that you will not overdraw your bank account. The enthalpy of a substance cannot be negative.

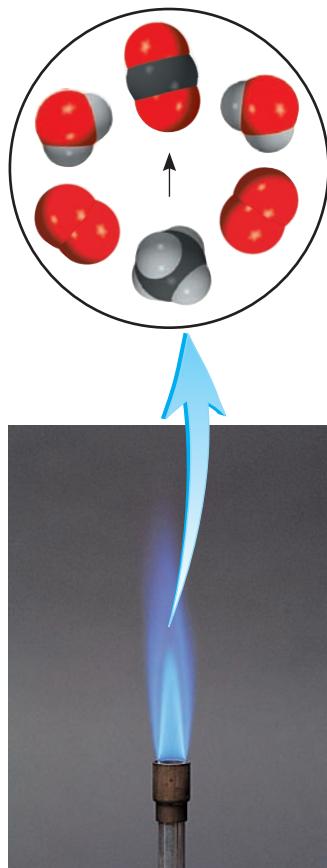
**Figure 6.5**

(a) Melting 1 mole of ice at 0°C (an endothermic process) results in an enthalpy increase in the system of 6.01 kJ. (b) Burning 1 mole of methane in oxygen gas (an exothermic process) results in an enthalpy decrease in the system of 890.4 kJ.



increases and so does the enthalpy of the system.) On the other hand, a withdrawal of \$60 means  $\Delta X = \$40 - \$100 = -\$60$ . The negative sign of  $\Delta X$  means your balance has decreased. Similarly, a negative value of  $\Delta H$  reflects a decrease in enthalpy of the system as a result of an exothermic process. The difference between this analogy and Equation (6.9) is that while you always know your exact bank balance, there is no way to know the enthalpies of individual products and reactants. In practice, we can measure only the *difference* in their values.

Now let us apply the idea of enthalpy changes to two common processes, the first involving a physical change, the second a chemical change.



Methane gas burning from a Bunsen burner.

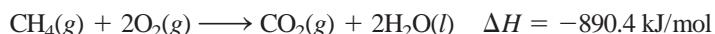
## Thermochemical Equations

At 0°C and a pressure of 1 atm, ice melts to form liquid water. Measurements show that for every mole of ice converted to liquid water under these conditions, 6.01 kilojoules (kJ) of heat energy are absorbed by the system (ice). Because the pressure is constant, the heat change is equal to the enthalpy change,  $\Delta H$ . Furthermore, this is an endothermic process, as expected for the energy-absorbing change of melting ice (Figure 6.5a). Therefore,  $\Delta H$  is a positive quantity. The equation for this physical change is



The “per mole” in the unit for  $\Delta H$  means that this is the enthalpy change *per mole of the reaction (or process) as it is written*, that is, when 1 mole of ice is converted to 1 mole of liquid water.

As another example, consider the combustion of methane ( $\text{CH}_4$ ), the principal component of natural gas:



From experience we know that burning natural gas releases heat to the surroundings, so it is an exothermic process. Under constant-pressure condition this heat change is equal to enthalpy change and  $\Delta H$  must have a negative sign (Figure 6.5b). Again, the per mole of reaction unit for  $\Delta H$  means that when 1 mole of  $\text{CH}_4$  reacts with 2 moles of  $\text{O}_2$  to yield 1 mole of  $\text{CO}_2$  and 2 moles of liquid  $\text{H}_2\text{O}$ , 890.4 kJ of heat are released to the surroundings.

The equations for the melting of ice and the combustion of methane are examples of **thermochemical equations**, which *show the enthalpy changes as well as the*

*mass relationships.* It is essential to specify a balanced equation when quoting the enthalpy change of a reaction. The following guidelines are helpful in writing and interpreting thermochemical equations:

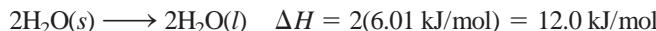
- When writing thermochemical equations, we must always specify the physical states of all reactants and products, because they help determine the actual enthalpy changes. For example, in the equation for the combustion of methane, if we show water vapor rather than liquid water as a product,



the enthalpy change is  $-802.4 \text{ kJ}$  rather than  $-890.4 \text{ kJ}$  because  $88.0 \text{ kJ}$  are needed to convert 2 moles of liquid water to water vapor; that is,

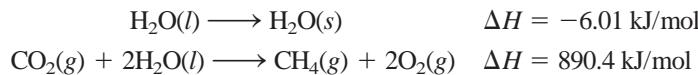


- If we multiply both sides of a thermochemical equation by a factor  $n$ , then  $\Delta H$  must also change by the same factor. Thus, for the melting of ice, if  $n = 2$ , we have



**Keep in mind that  $H$  is an extensive property.**

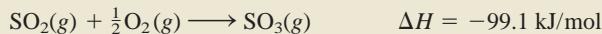
- When we reverse an equation, we change the roles of reactants and products. Consequently, the magnitude of  $\Delta H$  for the equation remains the same, but its sign changes. For example, if a reaction consumes thermal energy from its surroundings (that is, if it is endothermic), then the reverse reaction must release thermal energy back to its surroundings (that is, it must be exothermic) and the enthalpy change expression must also change its sign. Thus, reversing the melting of ice and the combustion of methane, the thermochemical equations become



and what was an endothermic process becomes exothermic, and vice versa.

### Example 6.3

Given the thermochemical equation



calculate the heat evolved when 74.6 g of  $\text{SO}_2$  (molar mass = 64.07 g/mol) is converted to  $\text{SO}_3$ .

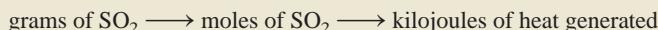
**Strategy** The thermochemical equation shows that for every mole of  $\text{SO}_2$  burned, 99.1 kJ of heat are given off (note the negative sign). Therefore, the conversion factor is

$$\frac{-99.1 \text{ kJ}}{1 \text{ mol SO}_2}$$

How many moles of  $\text{SO}_2$  are in 74.6 g of  $\text{SO}_2$ ? What is the conversion factor between grams and moles?

(Continued)

**Solution** We need to first calculate the number of moles of  $\text{SO}_2$  in 74.6 g of the compound and then find the number of kilojoules produced from the exothermic reaction. The sequence of conversions is as follows:



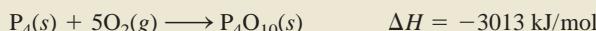
Therefore, the heat produced is given by

$$74.6 \text{ g } \text{SO}_2 \times \frac{1 \text{ mol } \text{SO}_2}{64.07 \text{ g } \text{SO}_2} \times \frac{-99.1 \text{ kJ}}{1 \text{ mol } \text{SO}_2} = -115 \text{ kJ}$$

**Check** Because 74.6 g is greater than the molar mass of  $\text{SO}_2$ , we expect the heat released to be larger than  $-99.1 \text{ kJ}$ . The negative sign indicates that this is an exothermic reaction.

**Similar problem:** 6.26.

**Practice Exercise** Calculate the heat evolved when 266 g of white phosphorus ( $\text{P}_4$ ) burns in air according to the equation



Sodium reacting with water to form hydrogen gas.

Recall that  $1 \text{ L} \cdot \text{atm} = 101.3 \text{ J}$ .

## A Comparison of $\Delta H$ and $\Delta E$

What is the relationship between  $\Delta H$  and  $\Delta E$  for a process? To find out, let us consider the reaction between sodium metal and water:



This thermochemical equation says that when two moles of sodium react with an excess of water, 367.5 kJ of heat are given off. Note that one of the products is hydrogen gas, which must push back air to enter the atmosphere. Consequently, some of the energy produced by the reaction is used to do work of pushing back a volume of air ( $\Delta V$ ) against atmospheric pressure ( $P$ ) (Figure 6.6). To calculate the change in internal energy, we rearrange Equation (6.8) as follows:

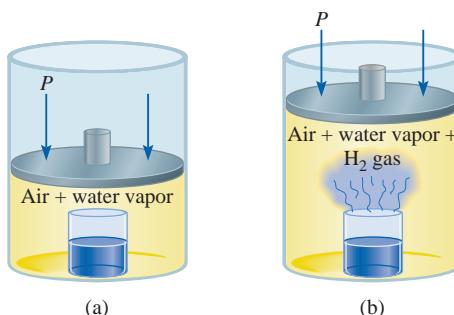
$$\Delta E = \Delta H - P\Delta V$$

If we assume the temperature to be  $25^\circ\text{C}$  and ignore the small change in the volume of the solution, we can show that the volume of 1 mole of  $\text{H}_2$  gas at 1.0 atm and 298 K is 24.5 L, so that  $-P\Delta V = -24.5 \text{ L} \cdot \text{atm}$  or  $-2.5 \text{ kJ}$ . Finally,

$$\begin{aligned} \Delta E &= -367.5 \text{ kJ/mol} - 2.5 \text{ kJ/mol} \\ &= -370.0 \text{ kJ/mol} \end{aligned}$$

**Figure 6.6**

(a) A beaker of water inside a cylinder fitted with a movable piston. The pressure inside is equal to the atmospheric pressure. (b) As the sodium metal reacts with water, hydrogen gas pushes the piston upward (doing work on the surroundings) until the pressure inside is again equal to that of outside.



This calculation shows that  $\Delta E$  and  $\Delta H$  are approximately the same. The reason  $\Delta H$  is smaller than  $\Delta E$  in magnitude is that some of the internal energy released is used to do gas expansion work, so less heat is evolved. For reactions that do not involve gases,  $\Delta V$  is usually very small and so  $\Delta E$  is practically the same as  $\Delta H$ .

Another way to calculate the internal energy change of a gaseous reaction is to assume ideal gas behavior and constant temperature. In this case,

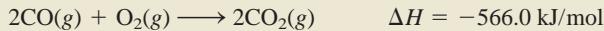
$$\begin{aligned}\Delta E &= \Delta H - \Delta(PV) \\ &= \Delta H - \Delta(nRT) \\ &= \Delta H - RT\Delta n\end{aligned}\quad (6.10)$$

where  $\Delta n$  is defined as

$$\Delta n = \text{number of moles of product gases} - \text{number of moles of reactant gases}$$

### Example 6.4

Calculate the change in internal energy when 2 moles of CO are converted to 2 moles of  $\text{CO}_2$  at 1 atm and 25°C:



**Strategy** We are given the enthalpy change,  $\Delta H$ , for the reaction and are asked to calculate the change in internal energy,  $\Delta E$ . Therefore, we need Equation (6.10). What is the change in the number of moles of gases?  $\Delta H$  is given in kilojoules, so what units should we use for  $R$ ?

**Solution** From the chemical equation we see that 3 moles of gases are converted to 2 moles of gases so that

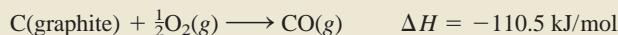
$$\begin{aligned}\Delta n &= \text{number of moles of product gas} - \text{number of moles of reactant gases} \\ &= 2 - 3 \\ &= -1\end{aligned}$$

Using 8.314 J/K · mol for  $R$  and  $T = 298 \text{ K}$  in Equation (6.10), we write

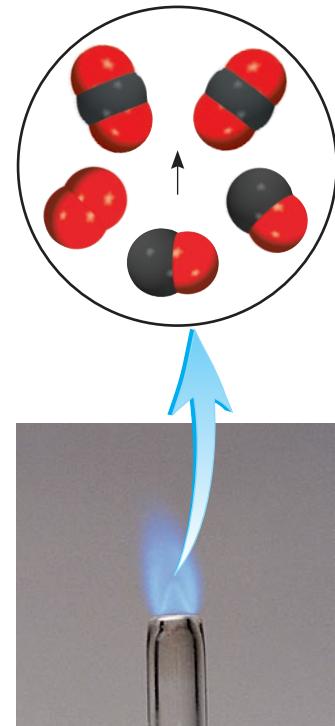
$$\begin{aligned}\Delta E &= \Delta H - RT\Delta n \\ &= -566.0 \text{ kJ/mol} - (8.314 \text{ J/K} \cdot \text{mol}) \left( \frac{1 \text{ kJ}}{1000 \text{ J}} \right) (298 \text{ K})(-1) \\ &= -563.5 \text{ kJ/mol}\end{aligned}$$

**Check** Knowing that the reacting gaseous system undergoes a compression (3 moles to 2 moles), is it reasonable to have  $\Delta H > \Delta E$  in magnitude?

**Practice Exercise** What is  $\Delta E$  for the formation of 1 mole of CO at 1 atm and 25°C?



For reactions that do not result in a change in the number of moles of gases from reactants to products [for example,  $\text{H}_2(g) + \text{Cl}_2(g) \longrightarrow 2\text{HCl}(g)$ ],  $\Delta E = \Delta H$ .



Carbon monoxide burns in air to form carbon dioxide.

**Similar problem: 6.27.**

## 6.5 Calorimetry

In the laboratory, heat changes in physical and chemical processes are measured with a *calorimeter*, a closed container designed specifically for this purpose. Our discussion of *calorimetry*, the measurement of heat changes, will depend on an understanding of specific heat and heat capacity, so let us consider them first.

**TABLE 6.2****The Specific Heats of Some Common Substances**

Substance	Specific Heat (J/g · °C)
Al	0.900
Au	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu	0.385
Fe	0.444
Hg	0.139
H <sub>2</sub> O	4.184
C <sub>2</sub> H <sub>5</sub> OH (ethanol)	2.46

**Specific Heat and Heat Capacity**

The **specific heat** (*s*) of a substance is *the amount of heat required to raise the temperature of one gram of the substance by one degree Celsius*. The **heat capacity** (*C*) of a substance is *the amount of heat required to raise the temperature of a given quantity of the substance by one degree Celsius*. Specific heat is an intensive property, whereas heat capacity is an extensive property. The relationship between the heat capacity and specific heat of a substance is

$$C = ms \quad (6.11)$$

where *m* is the mass of the substance in grams. For example, the specific heat of water is 4.184 J/g · °C, and the heat capacity of 60.0 g of water is

$$(60.0 \text{ g})(4.184 \text{ J/g} \cdot \text{°C}) = 251 \text{ J/}^{\circ}\text{C}$$

Note that specific heat has the units J/g · °C and heat capacity has the units J/°C. Table 6.2 shows the specific heat of some common substances.

If we know the specific heat and the amount of a substance, then the change in the sample's temperature ( $\Delta t$ ) will tell us the amount of heat (*q*) that has been absorbed or released in a particular process. The equations for calculating the heat change are given by

$$q = ms\Delta t \quad (6.12)$$

$$q = C\Delta t \quad (6.13)$$

where  $\Delta t$  is the temperature change:

$$\Delta t = t_{\text{final}} - t_{\text{initial}}$$

The sign convention for *q* is the same as that for enthalpy change; *q* is positive for endothermic processes and negative for exothermic processes.

**Example 6.5**

A 466-g sample of water is heated from 8.50°C to 74.60°C. Calculate the amount of heat absorbed (in kilojoules) by the water.

**Strategy** We know the quantity of water and the specific heat of water. With this information and the temperature rise, we can calculate the amount of heat absorbed (*q*).

**Solution** Using Equation (6.12), we write

$$\begin{aligned} q &= ms\Delta t \\ &= (466 \text{ g})(4.184 \text{ J/g} \cdot \text{°C})(74.60 \text{ °C} - 8.50 \text{ °C}) \\ &= 1.29 \times 10^5 \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \\ &= 129 \text{ kJ} \end{aligned}$$

(Continued)

**Check** The units g and °C cancel, and we are left with the desired unit kJ. Because heat is absorbed by the water from the surroundings, it has a positive sign.

Similar problem: 6.34.

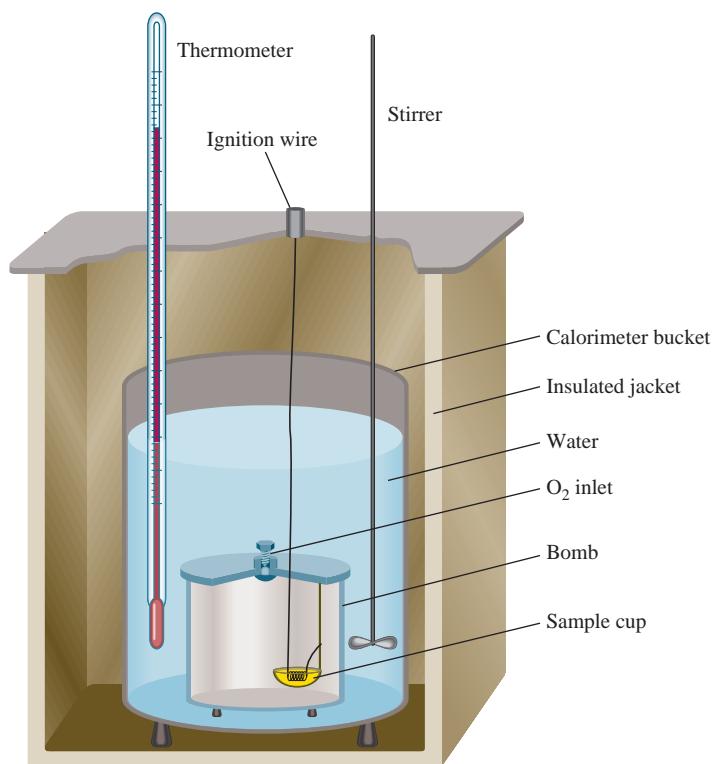
**Practice Exercise** An iron bar of mass 869 g cools from 94°C to 5°C. Calculate the heat released (in kilojoules) by the metal.

## Constant-Volume Calorimetry

Heat of combustion is usually measured by placing a known mass of a compound in a steel container called a *constant-volume bomb calorimeter*, which is filled with oxygen at about 30 atm of pressure. The closed bomb is immersed in a known amount of water, as shown in Figure 6.7. The sample is ignited electrically, and the heat produced by the combustion reaction can be calculated accurately by recording the rise in temperature of the water. The heat given off by the sample is absorbed by the water and the bomb. The special design of the calorimeter enables us to assume that no heat (or mass) is lost to the surroundings during the time it takes to make measurements. Therefore, we can call the bomb and the water in which it is submerged an isolated system. Because no heat enters or leaves the system throughout the process, the heat change of the system ( $q_{\text{system}}$ ) must be zero and we can write

$$\begin{aligned} q_{\text{system}} &= q_{\text{cal}} + q_{\text{rxn}} \\ &= 0 \end{aligned} \quad (6.14)$$

"Constant volume" refers to the volume of the container, which does not change during the reaction. Note that the container remains intact after the measurement. The term "bomb calorimeter" connotes the explosive nature of the reaction (on a small scale) in the presence of excess oxygen gas.



**Figure 6.7**  
A *constant-volume bomb calorimeter*. The calorimeter is filled with oxygen gas before it is placed in the bucket. The sample is ignited electrically, and the heat produced by the reaction can be accurately determined by measuring the temperature increase in the known amount of surrounding water.

where  $q_{\text{cal}}$  and  $q_{\text{rxn}}$  are the heat changes for the calorimeter and the reaction, respectively. Thus,

$$q_{\text{rxn}} = -q_{\text{cal}} \quad (6.15)$$

To calculate  $q_{\text{cal}}$ , we need to know the heat capacity of the calorimeter ( $C_{\text{cal}}$ ) and the temperature rise, that is

$$q_{\text{cal}} = C_{\text{cal}}\Delta t \quad (6.16)$$

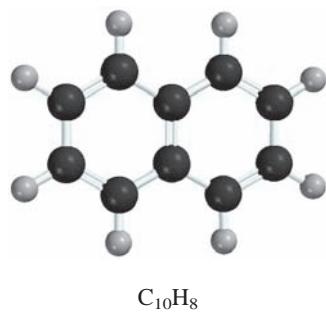
**Note that  $C_{\text{cal}}$  comprises both the bomb and the surrounding water.**

The quantity  $C_{\text{cal}}$  is calibrated by burning a substance with an accurately known heat of combustion. For example, it is known that the combustion of 1 g of benzoic acid ( $\text{C}_6\text{H}_5\text{COOH}$ ) releases 26.42 kJ of heat. If the temperature rise is  $4.673^\circ\text{C}$ , then the heat capacity of the calorimeter is given by

$$\begin{aligned} C_{\text{cal}} &= \frac{q_{\text{cal}}}{\Delta t} \\ &= \frac{26.42 \text{ kJ}}{4.673^\circ\text{C}} = 5.654 \text{ kJ}/^\circ\text{C} \end{aligned}$$

Once  $C_{\text{cal}}$  has been determined, the calorimeter can be used to measure the heat of combustion of other substances.

Note that because reactions in a bomb calorimeter occur under constant-volume rather than constant-pressure conditions, the heat changes *do not* correspond to the enthalpy change  $\Delta H$  (see Section 6.4). It is possible to correct the measured heat changes so that they correspond to  $\Delta H$  values, but the corrections usually are quite small so we will not concern ourselves with the details here. Finally, it is interesting to note that the energy contents of food and fuel (usually expressed in calories where 1 cal = 4.184 J) are measured with constant-volume calorimeters.



### Example 6.6

A quantity of 1.435 g of naphthalene ( $\text{C}_{10}\text{H}_8$ ), a pungent-smelling substance used in moth repellents, was burned in a constant-volume bomb calorimeter. Consequently, the temperature of the water rose from  $20.28^\circ\text{C}$  to  $25.95^\circ\text{C}$ . If the heat capacity of the bomb plus water was  $10.17 \text{ kJ}/^\circ\text{C}$ , calculate the heat of combustion of naphthalene on a molar basis; that is, find the molar heat of combustion.

**Strategy** Knowing the heat capacity and the temperature rise, how do we calculate the heat absorbed by the calorimeter? What is the heat generated by the combustion of 1.435 g of naphthalene? What is the conversion factor between grams and moles of naphthalene?

**Solution** The heat absorbed by the bomb and water is equal to the product of the heat capacity and the temperature change. From Equation (6.16), assuming no heat is lost to the surroundings, we write

$$\begin{aligned} q_{\text{cal}} &= C_{\text{cal}}\Delta t \\ &= (10.17 \text{ kJ}/^\circ\text{C})(25.95^\circ\text{C} - 20.28^\circ\text{C}) \\ &= 57.66 \text{ kJ} \end{aligned}$$

(Continued)

Because  $q_{\text{sys}} = q_{\text{cal}} + q_{\text{rxn}} = 0$ ,  $q_{\text{cal}} = -q_{\text{rxn}}$ . The heat change of the reaction is  $-57.66 \text{ kJ}$ . This is the heat released by the combustion of 1.435 g of C<sub>10</sub>H<sub>8</sub>; therefore, we can write the conversion factor as

$$\frac{-57.66 \text{ kJ}}{1.435 \text{ g C}_{10}\text{H}_8}$$

The molar mass of naphthalene is 128.2 g, so the heat of combustion of 1 mole of naphthalene is

$$\begin{aligned} \text{molar heat of combustion} &= \frac{-57.66 \text{ kJ}}{1.435 \text{ g C}_{10}\text{H}_8} \times \frac{128.2 \text{ g C}_{10}\text{H}_8}{1 \text{ mol C}_{10}\text{H}_8} \\ &= -5.151 \times 10^3 \text{ kJ/mol} \end{aligned}$$

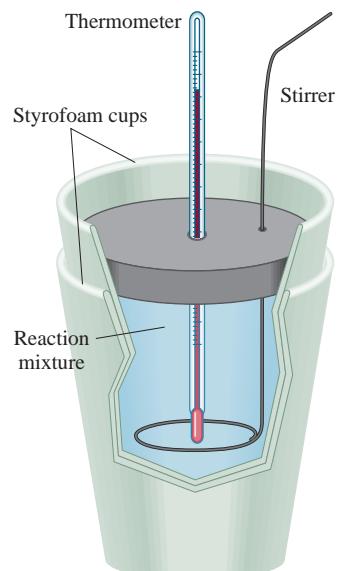
**Check** Knowing that the combustion reaction is exothermic and that the molar mass of naphthalene is much greater than 1.4 g, is the answer reasonable? Under the reaction conditions, can the heat change ( $-57.66 \text{ kJ}$ ) be equated to the enthalpy change of the reaction?

**Similar problem:** 6.37.

**Practice Exercise** A quantity of 1.922 g of methanol (CH<sub>3</sub>OH) was burned in a constant-volume bomb calorimeter. Consequently, the temperature of the water rose by 4.20°C. If the heat capacity of the bomb plus water was 10.4 kJ/°C, calculate the molar heat of combustion of methanol.

## Constant-Pressure Calorimetry

A simpler device than the constant-volume calorimeter is the constant-pressure calorimeter, which is used to determine the heat changes for noncombustion reactions. A crude constant-pressure calorimeter can be constructed from two Styrofoam coffee cups, as shown in Figure 6.8. This device measures the heat effects of a variety of reactions, such as acid-base neutralization, as well as the heat of solution and heat of dilution. Because the pressure is constant, the heat change for the process ( $q_{\text{rxn}}$ ) is equal to the enthalpy change ( $\Delta H$ ). As in the case of a constant-volume calorimeter, we treat the calorimeter as an isolated system. Furthermore, we neglect the small heat capacity of the coffee cups in our calculations. Table 6.3 lists some reactions that have been studied with the constant-pressure calorimeter.



**TABLE 6.3 Heats of Some Typical Reactions Measured at Constant Pressure**

Type of Reaction	Example	$\Delta H \text{ (kJ)}$
Heat of neutralization	HCl(aq) + NaOH(aq) → NaCl(aq) + H <sub>2</sub> O(l)	-56.2
Heat of ionization	H <sub>2</sub> O(l) → H <sup>+</sup> (aq) + OH <sup>-</sup> (aq)	56.2
Heat of fusion	H <sub>2</sub> O(s) → H <sub>2</sub> O(l)	6.01
Heat of vaporization	H <sub>2</sub> O(l) → H <sub>2</sub> O(g)	44.0*
Heat of reaction	MgCl <sub>2</sub> (s) + 2Na(l) → 2NaCl(s) + Mg(s)	-180.2

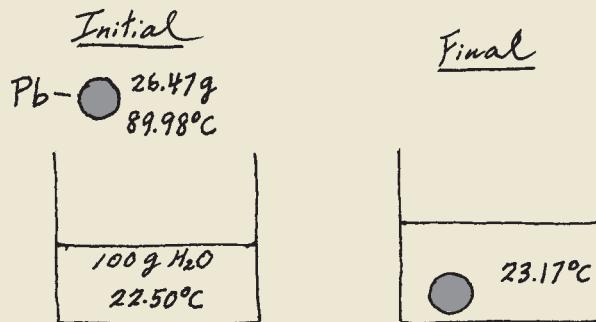
\*Measured at 25°C. At 100°C, the value is 40.79 kJ.

**Figure 6.8** A constant-pressure calorimeter made of two Styrofoam coffee cups. The outer cup helps to insulate the reacting mixture from the surroundings. Two solutions of known volume containing the reactants at the same temperature are carefully mixed in the calorimeter. The heat produced or absorbed by the reaction can be determined by measuring the temperature change.

### Example 6.7

A lead (Pb) pellet having a mass of 26.47 g at 89.98°C was placed in a constant-pressure calorimeter of negligible heat capacity containing 100.0 mL of water. The water temperature rose from 22.50°C to 23.17°C. What is the specific heat of the lead pellet?

**Strategy** A sketch of the initial and final situation is as follows:



We know the masses of water and the lead pellet as well as the initial and final temperatures. Assuming no heat is lost to the surroundings, we can equate the heat lost by the lead pellet to the heat gained by the water. Knowing the specific heat of water, we can then calculate the specific heat of lead.

**Solution** Treating the calorimeter as an isolated system (no heat lost to the surroundings), we write

$$q_{\text{Pb}} + q_{\text{H}_2\text{O}} = 0$$

or

$$q_{\text{Pb}} = -q_{\text{H}_2\text{O}}$$

The heat gained by the water is given by

$$q_{\text{H}_2\text{O}} = ms\Delta t$$

where  $m$  and  $s$  are the mass and specific heat and  $\Delta t = t_{\text{final}} - t_{\text{initial}}$ . Therefore,

$$\begin{aligned} q_{\text{H}_2\text{O}} &= (100.0 \text{ g})(4.184 \text{ J/g} \cdot ^\circ\text{C})(23.17^\circ\text{C} - 22.50^\circ\text{C}) \\ &= 280.3 \text{ J} \end{aligned}$$

Because the heat lost by the lead pellet is equal to the heat gained by the water, so  $q_{\text{Pb}} = -280.3 \text{ J}$ . Solving for the specific heat of Pb, we write

$$\begin{aligned} q_{\text{Pb}} &= ms\Delta t \\ -280.3 \text{ J} &= (26.47 \text{ g})(s)(23.17^\circ\text{C} - 89.98^\circ\text{C}) \\ s &= 0.158 \text{ J/g} \cdot ^\circ\text{C} \end{aligned}$$

**Similar problem: 6.76.**

**Check** The specific heat falls within the metals shown in Table 6.2.

**Practice Exercise** A 30.14-g stainless steel ball bearing at 117.82°C is placed in a constant-pressure calorimeter containing 120.0 mL of water at 18.44°C. If the specific heat of the ball bearing is 0.474 J/g · °C, calculate the final temperature of the water. Assume the calorimeter to have negligible heat capacity.

### Example 6.8

A quantity of  $1.00 \times 10^2$  mL of  $0.500\text{ M}$  HCl was mixed with  $1.00 \times 10^2$  mL of  $0.500\text{ M}$  NaOH in a constant-pressure calorimeter of negligible heat capacity. The initial temperature of the HCl and NaOH solutions was the same,  $22.50^\circ\text{C}$ , and the final temperature of the mixed solution was  $25.86^\circ\text{C}$ . Calculate the heat change for the neutralization reaction on a molar basis



Assume that the densities and specific heats of the solutions are the same as for water ( $1.00\text{ g/mL}$  and  $4.184\text{ J/g} \cdot {}^\circ\text{C}$ , respectively).

**Strategy** Because the temperature rose, the neutralization reaction is exothermic. How do we calculate the heat absorbed by the combined solution? What is the heat of the reaction? What is the conversion factor for expressing the heat of reaction on a molar basis?

**Solution** Assuming no heat is lost to the surroundings,  $q_{\text{sys}} = q_{\text{soln}} + q_{\text{rxn}} = 0$ , so  $q_{\text{rxn}} = -q_{\text{soln}}$ , where  $q_{\text{soln}}$  is the heat absorbed by the combined solution. Because the density of the solution is  $1.00\text{ g/mL}$ , the mass of a 100-mL solution is 100 g. Thus,

$$\begin{aligned} q_{\text{soln}} &= ms\Delta t \\ &= (1.00 \times 10^2\text{ g} + 1.00 \times 10^2\text{ g})(4.184\text{ J/g} \cdot {}^\circ\text{C})(25.86^\circ\text{C} - 22.50^\circ\text{C}) \\ &= 2.81 \times 10^3\text{ J} \\ &= 2.81\text{ kJ} \end{aligned}$$

Because  $q_{\text{rxn}} = -q_{\text{soln}}$ ,  $q_{\text{rxn}} = -2.81\text{ kJ}$ .

From the molarities given, the number of moles of both HCl and NaOH in  $1.00 \times 10^2$  mL solution is

$$\frac{0.500\text{ mol}}{1\text{ L}} \times 0.100\text{ L} = 0.0500\text{ mol}$$

Therefore, the heat of neutralization when 1.00 mole of HCl reacts with 1.00 mole of NaOH is

$$\text{heat of neutralization} = \frac{-2.81\text{ kJ}}{0.0500\text{ mol}} = -56.2\text{ kJ/mol}$$

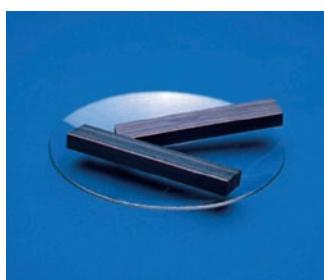
**Check** Is the sign consistent with the nature of the reaction? Under the reaction condition, can the heat change be equated to the enthalpy change?

**Similar problem:** 6.38.

**Practice Exercise** A quantity of  $4.00 \times 10^2$  mL of  $0.600\text{ M}$   $\text{HNO}_3$  is mixed with  $4.00 \times 10^2$  mL of  $0.300\text{ M}$   $\text{Ba}(\text{OH})_2$  in a constant-pressure calorimeter of negligible heat capacity. The initial temperature of both solutions is the same at  $18.46^\circ\text{C}$ . What is the final temperature of the solution? (Use the result in Example 6.8 for your calculation.)

## 6.6 Standard Enthalpy of Formation and Reaction

So far we have learned that we can determine the enthalpy change that accompanies a reaction by measuring the heat absorbed or released (at constant pressure). From Equation (6.9) we see that  $\Delta H$  can also be calculated if we know the actual enthalpies of all reactants and products. However, as mentioned earlier, there is no way to measure the *absolute* value of the enthalpy of a substance. Only values *relative* to an arbitrary



Graphite (top) and diamond (bottom).

reference can be determined. This problem is similar to the one geographers face in expressing the elevations of specific mountains or valleys. Rather than trying to devise some type of “absolute” elevation scale (perhaps based on distance from the center of Earth?), by common agreement all geographic heights and depths are expressed relative to sea level, an arbitrary reference with a defined elevation of “zero” meters or feet. Similarly, chemists have agreed on an arbitrary reference point for enthalpy.

The “sea level” reference point for all enthalpy expressions is called the ***standard enthalpy of formation*** ( $\Delta H_f^\circ$ ). Substances are said to be in the ***standard state*** at 1 atm,<sup>†</sup> hence the term “standard enthalpy.” The superscript “ $^\circ$ ” represents standard-state conditions (1 atm), and the subscript “f” stands for formation. By convention, *the standard enthalpy of formation of any element in its most stable form is zero*. Take the element oxygen as an example. Molecular oxygen ( $O_2$ ) is more stable than the other allotropic form of oxygen, ozone ( $O_3$ ), at 1 atm and 25°C. Thus, we can write  $\Delta H_f^\circ(O_2) = 0$ , but  $\Delta H_f^\circ(O_3) \neq 0$ . Similarly, graphite is a more stable allotropic form of carbon than diamond at 1 atm and 25°C, so we have  $\Delta H_f^\circ(C, \text{graphite}) = 0$  and  $\Delta H_f^\circ(C, \text{diamond}) \neq 0$ . Based on this reference for elements, we can now define the standard enthalpy of formation of a compound as *the heat change that results when 1 mole of the compound is formed from its elements at a pressure of 1 atm*. Table 6.4 lists the standard enthalpies of formation for a number of elements and compounds. (For a more complete list of  $\Delta H_f^\circ$  values, see Appendix 2.) Note that although the standard state does not specify a temperature, we will always use  $\Delta H_f^\circ$  values measured at 25°C for our discussion because most of the thermodynamic data are collected at this temperature.

The importance of the standard enthalpies of formation is that once we know their values, we can readily calculate the ***standard enthalpy of reaction***,  $\Delta H_{\text{rxn}}^\circ$ , defined as *the enthalpy of a reaction carried out at 1 atm*. For example, consider the hypothetical reaction



where  $a$ ,  $b$ ,  $c$ , and  $d$  are stoichiometric coefficients. For this reaction  $\Delta H_{\text{rxn}}^\circ$  is given by

$$\Delta H_{\text{rxn}}^\circ = [c\Delta H_f^\circ(C) + d\Delta H_f^\circ(D)] - [a\Delta H_f^\circ(A) + b\Delta H_f^\circ(B)] \quad (6.17)$$

We can generalize Equation (6.17) as

$$\Delta H_{\text{rxn}}^\circ = \Sigma n\Delta H_f^\circ(\text{products}) - \Sigma m\Delta H_f^\circ(\text{reactants}) \quad (6.18)$$

where  $m$  and  $n$  denote the stoichiometric coefficients for the reactants and products, and  $\Sigma$  (sigma) means “the sum of.” Note that in calculations, the stoichiometric coefficients are just numbers without units.

To use Equation (6.18) to calculate  $\Delta H_{\text{rxn}}^\circ$  we must know the  $\Delta H_f^\circ$  values of the compounds that take part in the reaction. To determine these values we can apply the direct method or the indirect method.

### The Direct Method

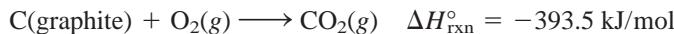
This method of measuring  $\Delta H_f^\circ$  works for compounds that can be readily synthesized from their elements. Suppose we want to know the enthalpy of formation of carbon dioxide. We must measure the enthalpy of the reaction when carbon

<sup>†</sup>In thermodynamics, the standard pressure is defined as 1 bar, where 1 bar =  $10^5$  Pa = 0.987 atm. Because 1 bar differs from 1 atm by only 1.3 percent, we will continue to use 1 atm as the standard pressure. Note that the normal melting point and boiling point of a substance are defined in terms of 1 atm.

**TABLE 6.4** Standard Enthalpies of Formation of Some Inorganic Substances at 25°C

Substance	$\Delta H_f^\circ$ (kJ/mol)	Substance	$\Delta H_f^\circ$ (kJ/mol)
Ag(s)	0	H <sub>2</sub> O <sub>2</sub> (l)	-187.6
AgCl(s)	-127.04	Hg(l)	0
Al(s)	0	I <sub>2</sub> (s)	0
Al <sub>2</sub> O <sub>3</sub> (s)	-1669.8	HI(g)	25.94
Br <sub>2</sub> (l)	0	Mg(s)	0
HBr(g)	-36.2	MgO(s)	-601.8
C(graphite)	0	MgCO <sub>3</sub> (s)	-1112.9
C(diamond)	1.90	N <sub>2</sub> (g)	0
CO(g)	-110.5	NH <sub>3</sub> (g)	-46.3
CO <sub>2</sub> (g)	-393.5	NO(g)	90.4
Ca(s)	0	NO <sub>2</sub> (g)	33.85
CaO(s)	-635.6	N <sub>2</sub> O <sub>4</sub> (g)	9.66
CaCO <sub>3</sub> (s)	-1206.9	N <sub>2</sub> O(g)	81.56
Cl <sub>2</sub> (g)	0	O(g)	249.4
HCl(g)	-92.3	O <sub>2</sub> (g)	0
Cu(s)	0	O <sub>3</sub> (g)	142.2
CuO(s)	-155.2	S(rhombic)	0
F <sub>2</sub> (g)	0	S(monoclinic)	0.30
HF(g)	-268.61	SO <sub>2</sub> (g)	-296.1
H(g)	218.2	SO <sub>3</sub> (g)	-395.2
H <sub>2</sub> (g)	0	H <sub>2</sub> S(g)	-20.15
H <sub>2</sub> O(g)	-241.8	ZnO(s)	-347.98
H <sub>2</sub> O(l)	-285.8	ZnS(s)	-202.9

(graphite) and molecular oxygen in their standard states are converted to carbon dioxide in its standard state:



We know from experience that this combustion easily goes to completion. Thus, from Equation (6.17) we can write

$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= \Delta H_f^\circ(\text{CO}_2, \text{g}) - [\Delta H_f^\circ(\text{C, graphite}) + \Delta H_f^\circ(\text{O}_2, \text{g})] \\ &= -393.5 \text{ kJ/mol} \end{aligned}$$

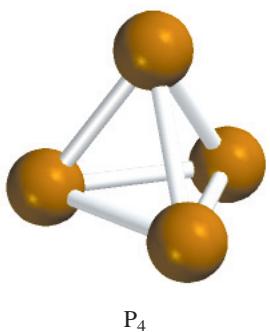
Because both graphite and O<sub>2</sub> are stable allotropic forms of the elements, it follows that  $\Delta H_f^\circ(\text{C, graphite})$  and  $\Delta H_f^\circ(\text{O}_2, \text{g})$  are zero. Therefore,

$$\Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ(\text{CO}_2, \text{g}) = -393.5 \text{ kJ/mol}$$

or

$$\Delta H_f^\circ(\text{CO}_2, \text{g}) = -393.5 \text{ kJ/mol}$$

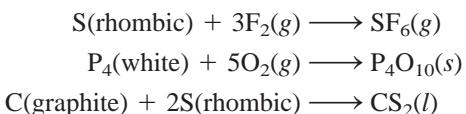
Note that arbitrarily assigning zero  $\Delta H_f^\circ$  for each element in its most stable form at the standard state does not affect our calculations in any way. Remember, in thermochemistry we are interested only in enthalpy *changes* because they can be



White phosphorus burns in air to form  $\text{P}_4\text{O}_{10}$ .

determined experimentally whereas the absolute enthalpy values cannot. The choice of a zero “reference level” for enthalpy makes calculations easier to handle. Again referring to the terrestrial altitude analogy, we find that Mt. Everest is 8708 ft higher than Mt. McKinley. This difference in altitude is unaffected by the decision to set sea level at 0 ft or at 1000 ft.

Other compounds that can be studied by the direct method are  $\text{SF}_6$ ,  $\text{P}_4\text{O}_{10}$ , and  $\text{CS}_2$ . The equations representing their syntheses are



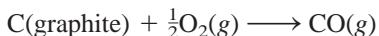
Note that S(rhombic) and P(white) are the most stable allotropes of sulfur and phosphorus, respectively, at 1 atm and 25°C, so their  $\Delta H_f^\circ$  values are zero.

### The Indirect Method

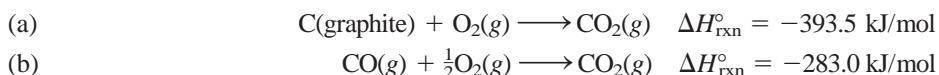
Many compounds cannot be directly synthesized from their elements. In some cases, the reaction proceeds too slowly, or side reactions produce substances other than the desired compound. In these cases,  $\Delta H_f^\circ$  can be determined by an indirect approach, which is based on Hess’s law of heat summation, or simply Hess’s law, named after the Swiss chemist Germain Hess. **Hess’s law** can be stated as follows: *When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.* In other words, if we can break down the reaction of interest into a series of reactions for which  $\Delta H_{\text{rxn}}^\circ$  can be measured, we can calculate  $\Delta H_{\text{rxn}}^\circ$  for the overall reaction. Hess’s law is based on the fact that because  $H$  is a state function,  $\Delta H$  depends only on the initial and final state (that is, only on the nature of reactants and products). The enthalpy change would be the same whether the overall reaction takes place in one step or many steps.

An analogy for Hess’s law is as follows. Suppose you go from the first floor to the sixth floor of a building by elevator. The gain in your gravitational potential energy (which corresponds to the enthalpy change for the overall process) is the same whether you go directly there or stop at each floor on your way up (breaking the trip into a series of steps).

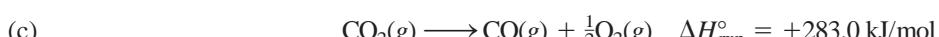
Let’s say we are interested in the standard enthalpy of formation of carbon monoxide (CO). We might represent the reaction as



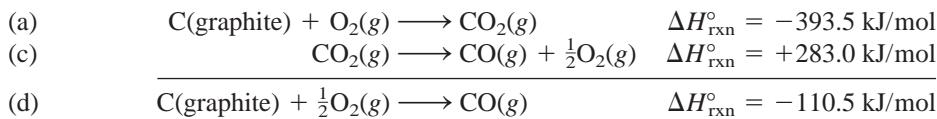
However, burning graphite also produces some carbon dioxide ( $\text{CO}_2$ ), so we cannot measure the enthalpy change for CO directly as shown. Instead, we must employ an indirect route, based on Hess’s law. It is possible to carry out the following two separate reactions, which do go to completion:



First, we reverse Equation (b) to get



Because chemical equations can be added and subtracted just like algebraic equations, we carry out the operation (a) + (c) and obtain



Thus,  $\Delta H_f^{\circ}(\text{CO}) = -110.5 \text{ kJ/mol}$ . Looking back, we see that the overall reaction is the formation of  $\text{CO}_2$  [Equation (a)], which can be broken down into two parts [Equations (d) and (b)]. Figure 6.9 shows the overall scheme of our procedure.

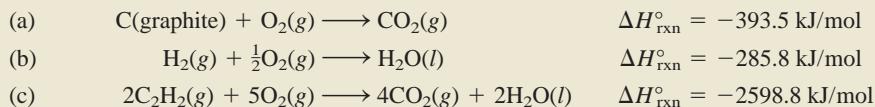
The general rule in applying Hess's law is to arrange a series of chemical equations (corresponding to a series of steps) in such a way that, when added together, all species will cancel except for the reactants and products that appear in the overall reaction. This means that we want the elements on the left and the compound of interest on the right of the arrow. Further, we often need to multiply some or all of the equations representing the individual steps by the appropriate coefficients.

### Example 6.9

Calculate the standard enthalpy of formation of acetylene ( $\text{C}_2\text{H}_2$ ) from its elements:

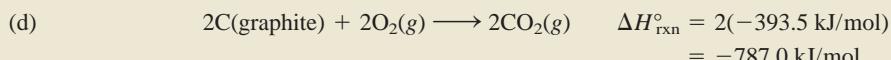


The equations for each step and the corresponding enthalpy changes are

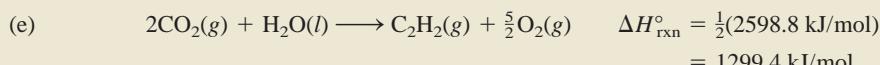


**Strategy** Our goal here is to calculate the enthalpy change for the formation of  $\text{C}_2\text{H}_2$  from its elements C and  $\text{H}_2$ . The reaction does not occur directly, however, so we must use an indirect route using the information given by Equations (a), (b), and (c).

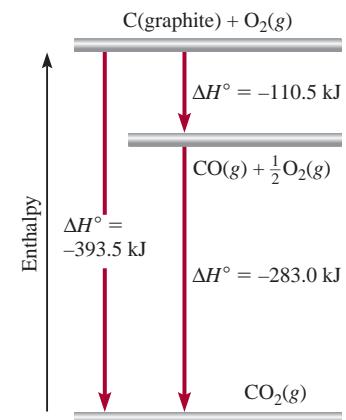
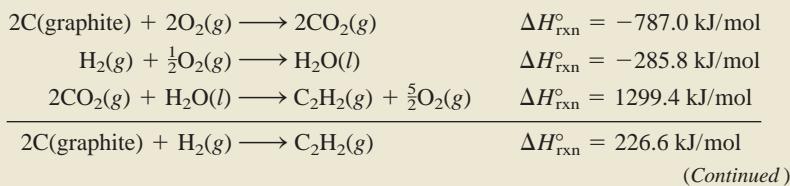
**Solution** Looking at the synthesis of  $\text{C}_2\text{H}_2$ , we need 2 moles of graphite as reactant. So we multiply Equation (a) by 2 to get



Next, we need 1 mole of  $\text{H}_2$  as a reactant and this is provided by Equation (b). Last, we need 1 mole of  $\text{C}_2\text{H}_2$  as a product. Equation (c) has 2 moles of  $\text{C}_2\text{H}_2$  as a reactant so we need to reverse the equation and divide it by 2:

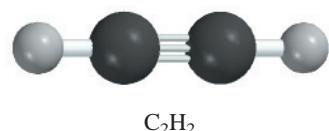


Adding Equations (d), (b), and (e) together, we get



**Figure 6.9**

The enthalpy change for the formation of 1 mole of  $\text{CO}_2$  from graphite and  $\text{O}_2$  can be broken into two steps according to Hess's law.



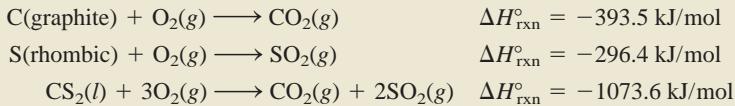
An oxyacetylene torch has a high flame temperature ( $3000^{\circ}\text{C}$ ) and is used to weld metals.

(Continued)

Therefore,  $\Delta H_f^\circ = \Delta H_{rxn}^\circ = 226.6 \text{ kJ/mol}$ . The  $\Delta H_f^\circ$  value means that when 1 mole of  $\text{C}_2\text{H}_2$  is synthesized from 2 moles of C(graphite) and 1 mole of  $\text{H}_2$ , 226.6 kJ of heat are absorbed by the reacting system from the surroundings. Thus, this is an endothermic process.

**Similar problems:** 6.62, 6.63.

**Practice Exercise** Calculate the standard enthalpy of formation of carbon disulfide ( $\text{CS}_2$ ) from its elements, given that



The molten iron formed in a thermite reaction is run down into a mold between the ends of two railroad rails. On cooling, the rails are welded together.

### Example 6.10

The thermite reaction involves aluminum and iron(III) oxide



This reaction is highly exothermic and the liquid iron formed is used to weld metals. Calculate the heat released in kilojoules per gram of Al reacted with  $\text{Fe}_2\text{O}_3$ . The  $\Delta H_f^\circ$  for  $\text{Fe}(l)$  is 12.40 kJ/mol.

**Strategy** The enthalpy of a reaction is the difference between the sum of the enthalpies of the products and the sum of the enthalpies of the reactants. The enthalpy of each species (reactant or product) is given by the product of the stoichiometric coefficient and the standard enthalpy of formation of the species.

**Solution** Using the given  $\Delta H_f^\circ$  value for  $\text{Fe}(l)$  and other  $\Delta H_f^\circ$  values in Appendix 3 and Equation (6.18), we write

$$\begin{aligned} \Delta H_{rxn}^\circ &= [\Delta H_f^\circ(\text{Al}_2\text{O}_3) + 2\Delta H_f^\circ(\text{Fe})] - [2\Delta H_f^\circ(\text{Al}) + \Delta H_f^\circ(\text{Fe}_2\text{O}_3)] \\ &= [(-1669.8 \text{ kJ/mol}) + 2(12.40 \text{ kJ/mol})] - [2(0) + (-822.2 \text{ kJ/mol})] \\ &= -822.8 \text{ kJ/mol} \end{aligned}$$

This is the amount of heat released for two moles of Al reacted. We use the following ratio

$$\frac{-822.8 \text{ kJ}}{2 \text{ mol Al}}$$

to convert to kJ/g Al. The molar mass of Al is 26.98 g, so

$$\begin{aligned} \text{heat released per gram of Al} &= \frac{-822.8 \text{ kJ}}{2 \text{ mol Al}} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \\ &= -15.25 \text{ kJ/g} \end{aligned}$$

**Check** Is the negative sign consistent with the exothermic nature of the reaction? As a quick check, we see that 2 moles of Al weigh about 54 g and give off about 823 kJ of heat when reacted with  $\text{Fe}_2\text{O}_3$ . Therefore, the heat given off per gram of Al reacted is approximately  $-830 \text{ kJ}/54 \text{ g}$  or  $-15.4 \text{ kJ/g}$ .

**Similar problems:** 6.54, 6.57.

**Practice Exercise** Benzene ( $\text{C}_6\text{H}_6$ ) burns in air to produce carbon dioxide and liquid water. Calculate the heat released (in kilojoules) per gram of the compound reacted with oxygen. The standard enthalpy of formation of benzene is 49.04 kJ/mol.

In general, the more negative the standard enthalpy of formation of a compound the more stable is the compound. Thus, in the thermite reaction the less stable  $\text{Fe}_2\text{O}_3$  is converted to the more stable  $\text{Al}_2\text{O}_3$ , and we expect the reaction to release a large amount of heat.

## KEY EQUATIONS

$$\Delta E = q + w \quad (6.1)$$

$$w = -P\Delta V \quad (6.3)$$

$$H = E + PV \quad (6.6)$$

$$\Delta H = \Delta E + P\Delta V \quad (6.8)$$

$$\Delta E = \Delta H - RT\Delta n \quad (6.10)$$

$$C = ms \quad (6.11)$$

$$q = ms\Delta t \quad (6.12)$$

$$q = C\Delta t \quad (6.13)$$

$$\Delta H_{\text{rxn}}^{\circ} = \sum n\Delta H_f^{\circ}(\text{products}) - \sum m\Delta H_f^{\circ}(\text{reactants}) \quad (6.18)$$

Mathematical statement of the first law of thermodynamics.

Calculating work done in gas expansion or compression.

Definition of enthalpy.

Calculating enthalpy (or energy) change for a constant-pressure process.

Calculating enthalpy (or energy) change for a constant-temperature process.

Definition of heat capacity.

Calculating heat change in term of specific heat.

Calculating heat change in terms of heat capacity.

Calculating standard enthalpy of reaction.

## SUMMARY OF FACTS AND CONCEPTS

- Energy is the capacity to do work. There are many forms of energy and they are all interconvertible. The law of conservation of energy states that the total amount of energy in the universe always stays the same.
- Any process that gives off heat to the surroundings is called an exothermic process; any process that absorbs heat from the surroundings is an endothermic process.
- The state of a system is defined by variables such as composition, volume, temperature, and pressure. The change in a state function for a system depends only on the initial and final states of the system, and not on the path by which the change is accomplished. Energy is a state function; work and heat are not.
- Energy can be converted from one form to another, but it cannot be created or destroyed (first law of thermodynamics). In chemistry we are concerned mainly with thermal energy, electrical energy, and mechanical energy, which is usually associated with pressure-volume work.
- The change in enthalpy ( $\Delta H$ , usually given in kilojoules) is a measure of the heat of a reaction (or any other process) at constant pressure. Enthalpy is a state function. A change in enthalpy  $\Delta H$  is equal to  $\Delta E + P\Delta V$  for a constant-pressure process. For chemical reactions at constant temperature,  $\Delta H$  is given by  $\Delta E + RT\Delta n$ , where  $\Delta n$  is the difference between moles of gaseous products and moles of gaseous reactants.
- Constant-volume and constant-pressure calorimeters are used to measure heat changes of physical and chemical processes.
- Hess's law states that the overall enthalpy change in a reaction is equal to the sum of enthalpy changes for the individual steps that make up the overall reaction. The standard enthalpy of a reaction can be calculated from the standard enthalpies of formation of reactants and products.

## KEY WORDS

Calorimetry, p. 185	First law of thermodynamics, p. 175	Potential energy, p. 172	State of a system, p. 174
Chemical energy, p. 172	Heat, p. 173	Radiant energy, p. 172	Surroundings, p. 173
Closed system, p. 173	Heat capacity ( $C$ ), p. 186	Specific heat ( $s$ ), p. 186	System, p. 173
Endothermic process, p. 174	Hess's law, p. 194	Standard enthalpy of formation ( $\Delta H_f^\circ$ ), p. 192	Thermal energy, p. 172
Energy, p. 172	Isolated system, p. 173	Standard enthalpy of reaction ( $\Delta H_{rxn}^\circ$ ), p. 192	Thermochemical equation, p. 182
Enthalpy ( $H$ ), p. 181	Law of conservation of energy, p. 172	Standard state, p. 192	Thermochemistry, p. 173
Enthalpy of reaction ( $\Delta H$ ), p. 181	Open system, p. 173	State function, p. 174	Thermodynamics, p. 174
Exothermic process, p. 174			Work, p. 172

## QUESTIONS AND PROBLEMS

### Definitions

#### Review Questions

- 6.1 Define these terms: system, surroundings, open system, closed system, isolated system, thermal energy, chemical energy, potential energy, kinetic energy, law of conservation of energy.
- 6.2 What is heat? How does heat differ from thermal energy? Under what condition is heat transferred from one system to another?
- 6.3 What are the units for energy commonly employed in chemistry?
- 6.4 A truck initially traveling at 60 km per hour is brought to a complete stop at a traffic light. Does this change violate the law of conservation of energy? Explain.
- 6.5 These are various forms of energy: chemical, heat, light, mechanical, and electrical. Suggest ways of interconverting these forms of energy.
- 6.6 Describe the interconversions of forms of energy occurring in these processes: (a) You throw a softball up into the air and catch it. (b) You switch on a flashlight. (c) You ride the ski lift to the top of the hill and then ski down. (d) You strike a match and let it burn down.

### Energy Changes in Chemical Reactions

#### Review Questions

- 6.7 Define these terms: thermochemistry, exothermic process, endothermic process.
- 6.8 Stoichiometry is based on the law of conservation of mass. On what law is thermochemistry based?
- 6.9 Describe two exothermic processes and two endothermic processes.

- 6.10 Decomposition reactions are usually endothermic, whereas combination reactions are usually exothermic. Give a qualitative explanation for these trends.

### First Law of Thermodynamics

#### Review Questions

- 6.11 On what law is the first law of thermodynamics based? Explain the sign conventions in the equation  $\Delta E = q + w$ .
- 6.12 Explain what is meant by a state function. Give two examples of quantities that are state functions and two that are not.
- 6.13 The internal energy of an ideal gas depends only on its temperature. Do a first-law analysis of this process. A sample of an ideal gas is allowed to expand at constant temperature against atmospheric pressure. (a) Does the gas do work on its surroundings? (b) Is there heat exchange between the system and the surroundings? If so, in which direction? (c) What is  $\Delta E$  for the gas for this process?
- 6.14 Consider these changes.
  - (a)  $\text{Hg}(l) \longrightarrow \text{Hg}(g)$
  - (b)  $3\text{O}_2(g) \longrightarrow 2\text{O}_3(g)$
  - (c)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(s) \longrightarrow \text{CuSO}_4(s) + 5\text{H}_2\text{O}(g)$
  - (d)  $\text{H}_2(g) + \text{F}_2(g) \longrightarrow 2\text{HF}(g)$

At constant pressure, in which of the reactions is work done by the system on the surroundings? By the surroundings on the system? In which of them is no work done?

#### Problems

- 6.15 A sample of nitrogen gas expands in volume from 1.6 L to 5.4 L at constant temperature. Calculate the

work done in joules if the gas expands (a) against a vacuum, (b) against a constant pressure of 0.80 atm, and (c) against a constant pressure of 3.7 atm.

- 6.16** A gas expands in volume from 26.7 mL to 89.3 mL at constant temperature. Calculate the work done (in joules) if the gas expands (a) against a vacuum, (b) against a constant pressure of 1.5 atm, and (c) against a constant pressure of 2.8 atm.

- 6.17 A gas expands and does  $P\text{-}V$  work on the surroundings equal to 325 J. At the same time, it absorbs 127 J of heat from the surroundings. Calculate the change in energy of the gas.

- 6.18** The work done to compress a gas is 74 J. As a result, 26 J of heat is given off to the surroundings. Calculate the change in energy of the gas.

- 6.19 Calculate the work done when 50.0 g of tin dissolves in excess acid at 1.00 atm and 25°C:



Assume ideal gas behavior.

- 6.20** Calculate the work done in joules when 1.0 mole of water vaporizes at 1.0 atm and 100°C. Assume that the volume of liquid water is negligible compared with that of steam at 100°C, and ideal gas behavior.

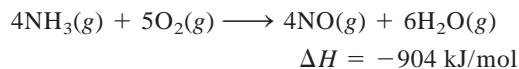
## Enthalpy of Chemical Reactions

### Review Questions

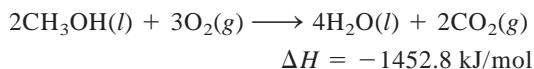
- 6.21 Define these terms: enthalpy, enthalpy of reaction. Under what condition is the heat of a reaction equal to the enthalpy change of the same reaction?

- 6.22 In writing thermochemical equations, why is it important to indicate the physical state (that is, gaseous, liquid, solid, or aqueous) of each substance?

- 6.23 Explain the meaning of this thermochemical equation:



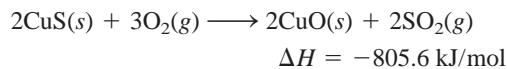
- 6.24 Consider this reaction:



What is the value of  $\Delta H$  if (a) the equation is multiplied throughout by 2, (b) the direction of the reaction is reversed so that the products become the reactants and vice versa, (c) water vapor instead of liquid water is formed as the product?

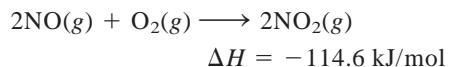
### Problems

- 6.25 The first step in the industrial recovery of copper from the copper sulfide ore is roasting, that is, the conversion of CuS to CuO by heating:

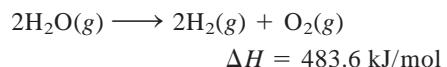


Calculate the heat evolved (in kJ) per gram of CuS roasted.

- 6.26** Determine the amount of heat (in kJ) given off when  $1.26 \times 10^4$  g of NO<sub>2</sub> are produced according to the equation

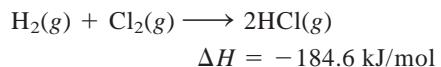


- 6.27 Consider the reaction



If 2.0 moles of H<sub>2</sub>O(g) are converted to H<sub>2</sub>(g) and O<sub>2</sub>(g) against a pressure of 1.0 atm at 125°C, what is  $\Delta E$  for this reaction?

- 6.28** Consider the reaction



If 3 moles of H<sub>2</sub> react with 3 moles of Cl<sub>2</sub> to form HCl, calculate the work done against a pressure of 1.0 atm at 25°C. What is  $\Delta E$  for this reaction? Assume the reaction goes to completion.

## Calorimetry

### Review Questions

- 6.29 What is the difference between specific heat and heat capacity? What are the units for these two quantities? Which is the intensive property and which is the extensive property?

- 6.30 Define calorimetry and describe two commonly used calorimeters. In a calorimetric measurement, why is it important that we know the heat capacity of the calorimeter? How is this value determined?

### Problems

- 6.31 Consider the following data:

Metal	Al	Cu
Mass (g)	10	30
Specific heat (J/g · °C)	0.900	0.385
Temperature (°C)	40	60

When these two metals are placed in contact, which of the following will take place?

- Heat will flow from Al to Cu because Al has a larger specific heat.
- Heat will flow from Cu to Al because Cu has a larger mass.
- Heat will flow from Cu to Al because Cu has a larger heat capacity.
- Heat will flow from Cu to Al because Cu is at a higher temperature.
- No heat will flow in either direction.

- 6.32** Consider two metals A and B, each having a mass of 100 g and an initial temperature of 20°C. The specific heat of A is larger than that of B. Under the same heating conditions, which metal would take longer to reach a temperature of 21°C?
- 6.33 A piece of silver of mass 362 g has a heat capacity of 85.7 J/°C. What is the specific heat of silver?
- 6.34** A 6.22-kg piece of copper metal is heated from 20.5°C to 324.3°C. Calculate the heat absorbed (in kJ) by the metal.
- 6.35 Calculate the amount of heat liberated (in kJ) from 366 g of mercury when it cools from 77.0°C to 12.0°C.
- 6.36** A sheet of gold weighing 10.0 g and at a temperature of 18.0°C is placed flat on a sheet of iron weighing 20.0 g and at a temperature of 55.6°C. What is the final temperature of the combined metals? Assume that no heat is lost to the surroundings. (*Hint:* The heat gained by the gold must be equal to the heat lost by the iron. The specific heats of the metals are given in Table 6.2.)
- 6.37 A 0.1375-g sample of solid magnesium is burned in a constant-volume bomb calorimeter that has a heat capacity of 3024 J/°C. The temperature increases by 1.126°C. Calculate the heat given off by the burning Mg, in kJ/g and in kJ/mol.
- 6.38** A quantity of  $2.00 \times 10^2$  mL of 0.862 M HCl is mixed with  $2.00 \times 10^2$  mL of 0.431 M Ba(OH)<sub>2</sub> in a constant-pressure calorimeter of negligible heat capacity. The initial temperature of the HCl and Ba(OH)<sub>2</sub> solutions is the same at 20.48°C. For the process
- $$\text{H}^+(aq) + \text{OH}^-(aq) \longrightarrow \text{H}_2\text{O}(l)$$
- the heat of neutralization is –56.2 kJ/mol. What is the final temperature of the mixed solution?

## Standard Enthalpy of Formation and Reaction

### Review Questions

- 6.39 What is meant by the standard-state condition?
- 6.40 How are the standard enthalpies of formation of an element and of a compound determined?
- 6.41 What is meant by the standard enthalpy of a reaction?
- 6.42 Write the equation for calculating the enthalpy of a reaction. Define all the terms.
- 6.43 State Hess's law. Explain, with one example, the usefulness of Hess's law in thermochemistry.
- 6.44 Describe how chemists use Hess's law to determine the  $\Delta H_f^\circ$  of a compound by measuring its heat (enthalpy) of combustion.

### Problems

- 6.45 Which of the following standard enthalpy of formation values is not zero at 25°C? Na(s), Ne(g), CH<sub>4</sub>(g), S<sub>8</sub>(s), Hg(l), H(g).

- 6.46** The  $\Delta H_f^\circ$  values of the two allotropes of oxygen, O<sub>2</sub> and O<sub>3</sub>, are 0 and 142.2 kJ/mol, respectively, at 25°C. Which is the more stable form at this temperature?
- 6.47 Which is the more negative quantity at 25°C:  $\Delta H_f^\circ$  for H<sub>2</sub>O(l) or  $\Delta H_f^\circ$  for H<sub>2</sub>O(g)?
- 6.48** Predict the value of  $\Delta H_f^\circ$  (greater than, less than, or equal to zero) for these elements at 25°C: (a) Br<sub>2</sub>(g) and Br<sub>2</sub>(l), (b) I<sub>2</sub>(g) and I<sub>2</sub>(s).
- 6.49 In general, compounds with negative  $\Delta H_f^\circ$  values are more stable than those with positive  $\Delta H_f^\circ$  values. H<sub>2</sub>O<sub>2</sub>(l) has a negative  $\Delta H_f^\circ$  (see Table 6.4). Why, then, does H<sub>2</sub>O<sub>2</sub>(l) have a tendency to decompose to H<sub>2</sub>O(l) and O<sub>2</sub>(g)?
- 6.50** Suggest ways (with appropriate equations) that would enable you to measure the  $\Delta H_f^\circ$  values of Ag<sub>2</sub>O(s) and CaCl<sub>2</sub>(s) from their elements. No calculations are necessary.
- 6.51 Calculate the heat of decomposition for this process at constant pressure and 25°C:
- $$\text{CaCO}_3(s) \longrightarrow \text{CaO}(s) + \text{CO}_2(g)$$
- (Look up the standard enthalpy of formation of the reactant and products in Table 6.4.)
- 6.52** The standard enthalpies of formation of ions in aqueous solutions are obtained by arbitrarily assigning a value of zero to H<sup>+</sup> ions; that is,  $\Delta H_f^\circ[\text{H}^+(aq)] = 0$ .
- (a) For the following reaction
- $$\text{HCl}(g) \xrightarrow{\text{H}_2\text{O}} \text{H}^+(aq) + \text{Cl}^-(aq)$$
- $$\Delta H^\circ = -74.9 \text{ kJ/mol}$$
- calculate  $\Delta H_f^\circ$  for the Cl<sup>–</sup> ions.
- (b) Given that  $\Delta H_f^\circ$  for OH<sup>–</sup> ions is –229.6 kJ/mol, calculate the enthalpy of neutralization when 1 mole of a strong monoprotic acid (such as HCl) is titrated by 1 mole of a strong base (such as KOH) at 25°C.
- 6.53 Calculate the heats of combustion for the following reactions from the standard enthalpies of formation listed in Appendix 2:
- (a)  $2\text{H}_2(g) + \text{O}_2(g) \longrightarrow 2\text{H}_2\text{O}(l)$
- (b)  $2\text{C}_2\text{H}_2(g) + 5\text{O}_2(g) \longrightarrow 4\text{CO}_2(g) + 2\text{H}_2\text{O}(l)$
- 6.54** Calculate the heats of combustion for the following reactions from the standard enthalpies of formation listed in Appendix 2:
- (a)  $\text{C}_2\text{H}_4(g) + 3\text{O}_2(g) \longrightarrow 2\text{CO}_2(g) + 2\text{H}_2\text{O}(l)$
- (b)  $2\text{H}_2\text{S}(g) + 3\text{O}_2(g) \longrightarrow 2\text{H}_2\text{O}(l) + 2\text{SO}_2(g)$
- 6.55 Methanol, ethanol, and *n*-propanol are three common alcohols. When 1.00 g of each of these alcohols is burned in air, heat is liberated as shown by the following data: (a) methanol (CH<sub>3</sub>OH), –22.6 kJ;

(b) ethanol ( $C_2H_5OH$ ),  $-29.7\text{ kJ}$ ; (c) *n*-propanol ( $C_3H_7OH$ ),  $-33.4\text{ kJ}$ . Calculate the heats of combustion of these alcohols in  $\text{kJ/mol}$ .

- 6.56** The standard enthalpy change for the following reaction is  $436.4\text{ kJ/mol}$ :



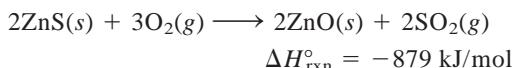
Calculate the standard enthalpy of formation of atomic hydrogen ( $H$ ).

- 6.57** From the standard enthalpies of formation, calculate  $\Delta H_{\text{rxn}}^{\circ}$  for the reaction



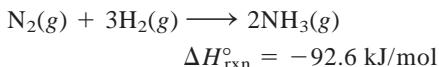
For  $C_6H_{12}(l)$ ,  $\Delta H_f^{\circ} = -151.9\text{ kJ/mol}$ .

- 6.58** The first step in the industrial recovery of zinc from the zinc sulfide ore is roasting, that is, the conversion of  $ZnS$  to  $ZnO$  by heating:



Calculate the heat evolved (in  $\text{kJ}$ ) per gram of  $ZnS$  roasted.

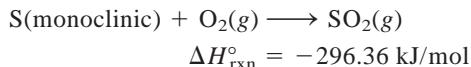
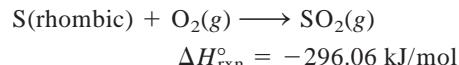
- 6.59** Determine the amount of heat (in  $\text{kJ}$ ) given off when  $1.26 \times 10^4\text{ g}$  of ammonia are produced according to the equation



Assume that the reaction takes place under standard-state conditions at  $25^\circ\text{C}$ .

- 6.60** At  $850^\circ\text{C}$ ,  $CaCO_3$  undergoes substantial decomposition to yield  $CaO$  and  $CO_2$ . Assuming that the  $\Delta H_f^{\circ}$  values of the reactant and products are the same at  $850^\circ\text{C}$  as they are at  $25^\circ\text{C}$ , calculate the enthalpy change (in  $\text{kJ}$ ) if  $66.8\text{ g}$  of  $CO_2$  are produced in one reaction.

- 6.61** From these data,

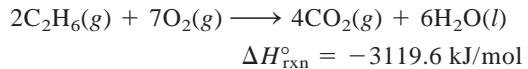
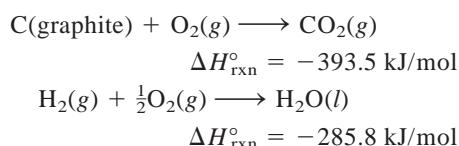


calculate the enthalpy change for the transformation



(Monoclinic and rhombic are different allotropic forms of elemental sulfur.)

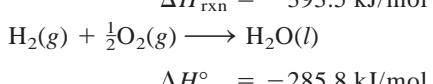
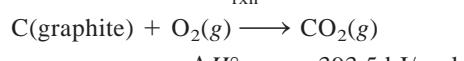
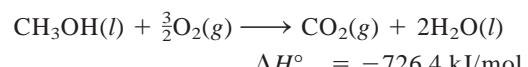
- 6.62** From the following data,



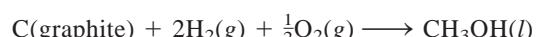
calculate the enthalpy change for the reaction



- 6.63** From the following heats of combustion,



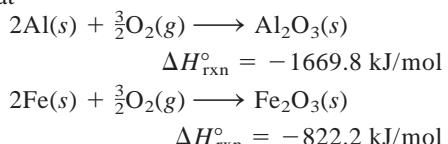
calculate the enthalpy of formation of methanol ( $CH_3OH$ ) from its elements:



- 6.64** Calculate the standard enthalpy change for the reaction



given that



## Additional Problems

- 6.65** The convention of arbitrarily assigning a zero enthalpy value for the most stable form of each element in the standard state at  $25^\circ\text{C}$  is a convenient way of dealing with enthalpies of reactions. Explain why this convention cannot be applied to nuclear reactions.

- 6.66** Consider the following two reactions:



Determine the enthalpy change for the process



- 6.67** The standard enthalpy change  $\Delta H^\circ$  for the thermal decomposition of silver nitrate according to the following equation is  $+78.67\text{ kJ}$ :



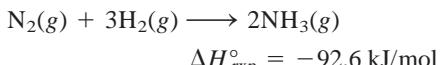
The standard enthalpy of formation of  $AgNO_3(s)$  is  $-123.02\text{ kJ/mol}$ . Calculate the standard enthalpy of formation of  $AgNO_2(s)$ .

- 6.68** Hydrazine,  $N_2H_4$ , decomposes according to the following reaction:



(a) Given that the standard enthalpy of formation of hydrazine is 50.42 kJ/mol, calculate  $\Delta H^\circ$  for its decomposition. (b) Both hydrazine and ammonia burn in oxygen to produce  $H_2O(l)$  and  $N_2(g)$ . Write balanced equations for each of these processes and calculate  $\Delta H^\circ$  for each of them. On a mass basis (per kg), would hydrazine or ammonia be the better fuel?

6.69 Consider the reaction



If 2.0 moles of  $N_2$  react with 6.0 moles of  $H_2$  to form  $NH_3$ , calculate the work done (in joules) against a pressure of 1.0 atm at 25°C. What is  $\Delta E$  for this reaction? Assume the reaction goes to completion.

6.70 Calculate the heat released when 2.00 L of  $Cl_2(g)$  with a density of 1.88 g/L react with an excess of sodium metal as 25°C and 1 atm to form sodium chloride.

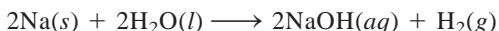
6.71 Photosynthesis produces glucose,  $C_6H_{12}O_6$ , and oxygen from carbon dioxide and water:



(a) How would you determine experimentally the  $\Delta H_{rxn}^\circ$  value for this reaction? (b) Solar radiation produces about  $7.0 \times 10^{14}$  kg glucose a year on Earth. What is the corresponding  $\Delta H^\circ$  change?

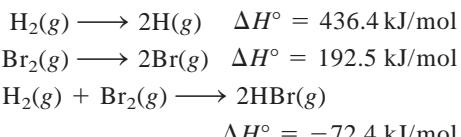
6.72 A 2.10-mole sample of crystalline acetic acid, initially at 17.0°C, is allowed to melt at 17.0°C and is then heated to 118.1°C (its normal boiling point) at 1.00 atm. The sample is allowed to vaporize at 118.1°C and is then rapidly quenched to 17.0°C, so that it recrystallizes. Calculate  $\Delta H^\circ$  for the total process as described.

6.73 Calculate the work done in joules by the reaction

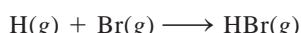


when 0.34 g of Na reacts with water to form hydrogen gas at 0°C and 1.0 atm.

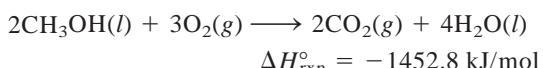
6.74 You are given the following data:



Calculate  $\Delta H^\circ$  for the reaction



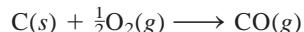
6.75 Methanol ( $CH_3OH$ ) is an organic solvent and is also used as a fuel in some automobile engines. From the following data, calculate the standard enthalpy of formation of methanol:



6.76 A 44.0-g sample of an unknown metal at 99.0°C was placed in a constant-pressure calorimeter containing 80.0 g of water at 24.0°C. The final temperature of the system was found to be 28.4°C. Calculate the specific heat of the metal. (The heat capacity of the calorimeter is 12.4 J/C.)

6.77 A 1.00-mole sample of ammonia at 14.0 atm and 25°C in a cylinder fitted with a movable piston expands against a constant external pressure of 1.00 atm. At equilibrium, the pressure and volume of the gas are 1.00 atm and 23.5 L, respectively. (a) Calculate the final temperature of the sample. (b) Calculate  $q$ ,  $w$ , and  $\Delta E$  for the process. The specific heat of ammonia is 0.0258 J/g · °C.

6.78 Producer gas (carbon monoxide) is prepared by passing air over red-hot coke:



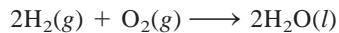
Water gas (mixture of carbon monoxide and hydrogen) is prepared by passing steam over red-hot coke:



For many years, both producer gas and water gas were used as fuels in industry and for domestic cooking. The large-scale preparation of these gases was carried out alternately, that is, first producer gas, then water gas, and so on. Using thermochemical reasoning, explain why this procedure was chosen.

6.79 If energy is conserved, how can there be an energy crisis?

6.80 The so-called hydrogen economy is based on hydrogen produced from water using solar energy. The gas is then burned as a fuel:



A primary advantage of hydrogen as a fuel is that it is nonpolluting. A major disadvantage is that it is a gas and therefore is harder to store than liquids or solids. Calculate the volume of hydrogen gas at 25°C and 1.00 atm required to produce an amount of energy equivalent to that produced by the combustion of a gallon of octane ( $C_8H_{18}$ ). The density of octane is 2.66 kg/gal, and its standard enthalpy of formation is −249.9 kJ/mol.

6.81 The combustion of what volume of ethane ( $C_2H_6$ ), measured at 23.0°C and 752 mmHg, would be required to heat 855 g of water from 25.0°C to 98.0°C?

6.82 The heat of vaporization of a liquid ( $\Delta H_{vap}$ ) is the energy required to vaporize 1.00 g of the liquid at its boiling point. In one experiment, 60.0 g of liquid nitrogen (boiling point −196°C) are poured into a Styrofoam cup containing  $2.00 \times 10^2$  g of water at 55.3°C. Calculate the molar heat of vaporization of liquid nitrogen if the final temperature of the water is 41.0°C.

6.83 Calculate the work done (in joules) when 1.0 mole of water is frozen at 0°C and 1.0 atm. The volumes of one mole of water and ice at 0°C are 0.0180 L and 0.0196 L, respectively.

**6.84** For which of the following reactions does  $\Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ$ ?

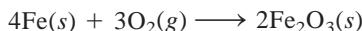
- (a)  $\text{H}_2(g) + \text{S}(\text{rhombic}) \longrightarrow \text{H}_2\text{S}(g)$
- (b)  $\text{C}(\text{diamond}) + \text{O}_2(g) \longrightarrow \text{CO}_2(g)$
- (c)  $\text{H}_2(g) + \text{CuO}(s) \longrightarrow \text{H}_2\text{O}(l) + \text{Cu}(s)$
- (d)  $\text{O}(g) + \text{O}_2(g) \longrightarrow \text{O}_3(g)$

6.85 A quantity of 0.020 mole of a gas initially at 0.050 L and 20°C undergoes a constant-temperature expansion until its volume is 0.50 L. Calculate the work done (in joules) by the gas if it expands (a) against a vacuum and (b) against a constant pressure of 0.20 atm. (c) If the gas in (b) is allowed to expand unchecked until its pressure is equal to the external pressure, what would its final volume be before it stopped expanding, and what would be the work done?

**6.86** (a) For most efficient use, refrigerator freezer compartments should be fully packed with food. What is the thermochemical basis for this recommendation? (b) Starting at the same temperature, tea and coffee remain hot longer in a thermal flask than chicken noodle soup. Explain.

6.87 Calculate the standard enthalpy change for the fermentation process. (See Problem 3.72.)

**6.88** Portable hot packs are available for skiers and people engaged in other outdoor activities in a cold climate. The air-permeable paper packet contains a mixture of powdered iron, sodium chloride, and other components, all moistened by a little water. The exothermic reaction that produces the heat is a very common one—the rusting of iron:



When the outside plastic envelope is removed,  $\text{O}_2$  molecules penetrate the paper, causing the reaction to begin. A typical packet contains 250 g of iron to warm your hands or feet for up to 4 h. How much heat (in kJ) is produced by this reaction? (*Hint:* See Appendix 2 for  $\Delta H_f^\circ$  values.)

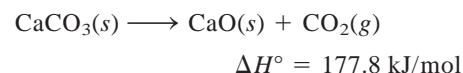
6.89 A person ate 0.50 lb of cheese (an energy intake of 4000 kJ). Suppose that none of the energy was stored in his body. What mass (in grams) of water would he need to perspire in order to maintain his original temperature? (It takes 44.0 kJ to vaporize 1 mole of water.)

**6.90** The total volume of the Pacific Ocean is estimated to be  $7.2 \times 10^8 \text{ km}^3$ . A medium-sized atomic bomb produces  $1.0 \times 10^{15} \text{ J}$  of energy upon explosion. Calculate the number of atomic bombs needed to release enough energy to raise the temperature of the water in the Pacific Ocean by 1°C.

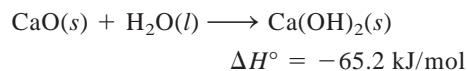
6.91 A 19.2-g quantity of dry ice (solid carbon dioxide) is allowed to sublime (evaporate) in an apparatus like the one shown in Figure 6.4. Calculate the expansion work done against a constant external pressure of 0.995 atm and at a constant temperature of 22°C. Assume that the initial volume of dry ice is negligible and that  $\text{CO}_2$  behaves like an ideal gas.

**6.92** The enthalpy of combustion of benzoic acid ( $\text{C}_6\text{H}_5\text{COOH}$ ) is commonly used as the standard for calibrating constant-volume bomb calorimeters; its value has been accurately determined to be  $-3226.7 \text{ kJ/mol}$ . When 1.9862 g of benzoic acid are burned in a calorimeter, the temperature rises from 21.84°C to 25.67°C. What is the heat capacity of the bomb? (Assume that the quantity of water surrounding the bomb is exactly 2000 g.)

6.93 Lime is a term that includes calcium oxide ( $\text{CaO}$ , also called quicklime) and calcium hydroxide [ $\text{Ca}(\text{OH})_2$ , also called slaked lime]. It is used in the steel industry to remove acidic impurities, in air-pollution control to remove acidic oxides such as  $\text{SO}_2$ , and in water treatment. Quicklime is made industrially by heating limestone ( $\text{CaCO}_3$ ) above 2000°C:

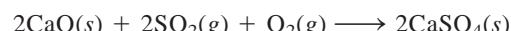


Slaked lime is produced by treating quicklime with water:



The exothermic reaction of quicklime with water and the rather small specific heats of both quicklime ( $0.946 \text{ J/g} \cdot ^\circ\text{C}$ ) and slaked lime ( $1.20 \text{ J/g} \cdot ^\circ\text{C}$ ) make it hazardous to store and transport lime in vessels made of wood. Wooden sailing ships carrying lime would occasionally catch fire when water leaked into the hold. (a) If a 500-g sample of water reacts with an equimolar amount of  $\text{CaO}$  (both at an initial temperature of 25°C), what is the final temperature of the product,  $\text{Ca}(\text{OH})_2$ ? Assume that the product absorbs all of the heat released in the reaction. (b) Given that the standard enthalpies of formation of  $\text{CaO}$  and  $\text{H}_2\text{O}$  are  $-635.6 \text{ kJ/mol}$  and  $-285.8 \text{ kJ/mol}$ , respectively, calculate the standard enthalpy of formation of  $\text{Ca}(\text{OH})_2$ .

**6.94** Calcium oxide ( $\text{CaO}$ ) is used to remove sulfur dioxide generated by coal-burning power stations:



Calculate the enthalpy change for this process if  $6.6 \times 10^5 \text{ g}$  of  $\text{SO}_2$  are removed by this process every day.

6.95 A balloon 16 m in diameter is inflated with helium at 18°C. (a) Calculate the mass of He in the balloon, assuming ideal behavior. (b) Calculate the work done

(in joules) during the inflation process if the atmospheric pressure is 98.7 kPa.

- 6.96** (a) A person drinks four glasses of cold water ( $3.0^{\circ}\text{C}$ ) every day. The volume of each glass is  $2.5 \times 10^2$  mL. How much heat (in kJ) does the body have to supply to raise the temperature of the water to  $37^{\circ}\text{C}$ , the body temperature? (b) How much heat would your body lose if you were to ingest  $8.0 \times 10^2$  g of snow at  $0^{\circ}\text{C}$  to quench thirst? (The amount of heat necessary to melt snow is 6.01 kJ/mol.)
- 6.97** Determine the standard enthalpy of formation of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) from its standard enthalpy of combustion ( $-1367.4$  kJ/mol).
- 6.98** Ice at  $0^{\circ}\text{C}$  is placed in a Styrofoam cup containing 361 g of a soft drink at  $23^{\circ}\text{C}$ . The specific heat of the drink is about the same as that of water. Some ice remains after the ice and soft drink reach an equilibrium temperature of  $0^{\circ}\text{C}$ . Determine the mass of ice that has melted. Ignore the heat capacity of the cup. (Hint: It takes 334 J to melt 1 g of ice at  $0^{\circ}\text{C}$ .)
- 6.99** A gas company in Massachusetts charges \$1.30 for  $15 \text{ ft}^3$  of natural gas ( $\text{CH}_4$ ) measured at  $20^{\circ}\text{C}$  and 1.0 atm. Calculate the cost of heating 200 mL of water (enough to make a cup of coffee or tea) from

$20^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ . Assume that only 50 percent of the heat generated by the combustion is used to heat the water; the rest of the heat is lost to the surroundings.

- 6.100** Calculate the internal energy of a Goodyear blimp filled with helium gas at  $1.2 \times 10^5$  Pa. The volume of the blimp is  $5.5 \times 10^3$  m $^3$ . If all the energy were used to heat 10.0 tons of copper at  $21^{\circ}\text{C}$ , calculate the final temperature of the metal. (Hint: See Section 5.6 for help in calculating the internal energy of a gas. 1 ton =  $9.072 \times 10^5$  g.)
- 6.101** Decomposition reactions are usually endothermic, whereas combination reactions are usually exothermic. Give a qualitative explanation for these trends.
- 6.102** Acetylene ( $\text{C}_2\text{H}_2$ ) can be made by reacting calcium carbide ( $\text{CaC}_2$ ) with water. (a) Write an equation for the reaction. (b) What is the maximum amount of heat (in kilojoules) that can be obtained from the combustion of acetylene, starting with 74.6 g of  $\text{CaC}_2$ ?
- 6.103** When 1.034 g of naphthalene ( $\text{C}_{10}\text{H}_8$ ) are burned in a constant-volume bomb calorimeter at 298 K, 41.56 kJ of heat are evolved. Calculate  $\Delta E$  and  $\Delta H$  for the reaction on a molar basis.

## SPECIAL PROBLEMS

- 6.104** (a) A snowmaking machine contains a mixture of compressed air and water vapor at about 20 atm. When the mixture is sprayed into the atmosphere it expands so rapidly that, as a good approximation, no heat exchange occurs between the system (air and water) and its surroundings. (In thermodynamics, such a process is called an adiabatic process.) Do a first law of thermodynamics analysis to show how snow is formed under these conditions.
- (b) If you have ever pumped air into a bicycle tire, you probably noticed a warming effect at the valve stem. The action of the pump compresses the air inside the pump and the tire. The process is rapid enough to be treated as an adiabatic process. Apply the first law of thermodynamics to account for the warming effect.
- (c) A driver's manual states that the stopping distance quadruples as the speed doubles; that is, if it takes 30 ft to stop a car traveling at 25 mph, then it would take 120 ft to stop a car moving at 50 mph. Justify this statement by using the first law of thermodynamics. Assume that when a car is stopped, its kinetic energy ( $\frac{1}{2}mv^2$ ) is totally converted to heat.
- 6.105** Why are cold, damp air and hot, humid air more uncomfortable than dry air at the same temperatures? (The specific heats of water vapor and air are approximately  $1.9 \text{ J/g} \cdot ^{\circ}\text{C}$  and  $1.0 \text{ J/g} \cdot ^{\circ}\text{C}$ , respectively.)
- 6.106** The average temperature in deserts is high during the day but quite cool at night, whereas that in regions along the coastline is more moderate. Explain.
- 6.107** From a thermochemical point of view, explain why a carbon dioxide fire extinguisher or water should not be used on a magnesium fire.
- 6.108** A 4.117-g impure sample of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) was burned in a constant-volume calorimeter having a heat capacity of  $19.65 \text{ kJ}/^{\circ}\text{C}$ . If the rise in temperature is  $3.134^{\circ}\text{C}$ , calculate the percent by mass of the glucose in the sample. Assume that the impurities are unaffected by the combustion process. See Appendix 3 for thermodynamic data.
- 6.109** Construct a table with the headings  $q$ ,  $w$ ,  $\Delta E$ , and  $\Delta H$ . For each of the following processes, deduce whether each of the quantities listed is positive (+), negative (-), or zero (0). (a) Freezing of benzene. (b) Compression of an ideal gas at constant temperature. (c) Reaction of sodium with water. (d) Boiling

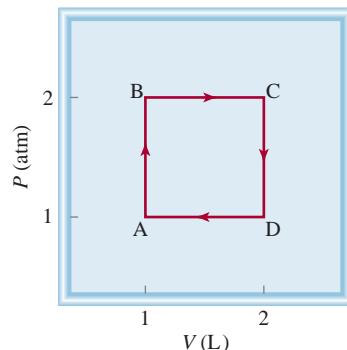
liquid ammonia. (e) Heating a gas at constant volume. (f) Melting of ice.

- 6.110** The combustion of 0.4196 g of a hydrocarbon releases 17.55 kJ of heat. The masses of the products are  $\text{CO}_2 = 1.419$  g and  $\text{H}_2\text{O} = 0.290$  g. (a) What is the empirical formula of the compound? (b) If the approximate molar mass of the compound is 76 g, calculate its standard enthalpy of formation.

- 6.111** Metabolic activity in the human body releases approximately  $1.0 \times 10^4$  kJ of heat per day. Assuming the body is 50 kg of water, how much would the body temperature rise if it were an isolated system? How much water must the body eliminate as perspiration to maintain the normal body temperature (98.6°F)? Comment on your results. The heat of vaporization of water may be taken as 2.41 kJ/g.

- 6.112** Starting at A, an ideal gas undergoes a cyclic process involving expansion and compression at constant

temperature, as shown here. Calculate the total work done. Does your result support the notion that work is not a state function?



## ANSWERS TO PRACTICE EXERCISES

- 6.1** (a) 0, (b) -286 J.   **6.2** -63 J.   **6.3**  $-6.47 \times 10^3$  kJ.  
**6.4** -111.7 kJ/mol.   **6.5** -34.3 kJ.   **6.6** -728 kJ/mol.

- 6.7** 21.19°C.   **6.8** 22.49°C.   **6.9** 87.3 kJ/mol.  
**6.10** -41.83 kJ/g.



"Neon lights" is a generic term for atomic emission involving various noble gases, mercury, and phosphor. The UV light from excited mercury atoms causes phosphor-coated tubes to fluoresce white light and other colors.

## The Electronic Structure of Atoms

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### ESSENTIAL CONCEPTS

**Planck's Quantum Theory** To explain the dependence of radiation emitted by objects on wavelength, Planck proposed that atoms and molecules could emit (or absorb) energy in discrete quantities called quanta. Planck's theory revolutionized physics.

**The Advent of Quantum Mechanics** Planck's work led to the explanation of the photoelectric effect by Einstein, who postulated that light consists of particles called photons, and the emission spectrum of the hydrogen atom by Bohr. Further advancements to quantum theory were made by de Broglie, who demonstrated that an electron possesses both particle and wave properties, and Heisenberg, who derived an inherent limitation to measuring submicroscopic systems. These developments culminated in the Schrödinger equation, which describes the behavior and energy of electrons, atoms, and molecules.

**The Hydrogen Atom** The solution to the Schrödinger equation for the hydrogen atom shows quantized energies for the electron and a set of wave functions called atomic orbitals. The atomic orbitals are labeled with specific quantum numbers; the orbitals tell us the regions in which an electron can be located. The results obtained for hydrogen, with minor modifications, can be applied to more complex atoms.

**The Building-Up Principle** The periodic table can be constructed by increasing atomic number and adding electrons in a stepwise fashion. Specific guidelines (the Pauli exclusion principle and Hund's rule) help us write ground-state electron configurations of the elements, which tell us how electrons are distributed among the atomic orbitals.

### Interactive



### Activity Summary

1. Interactivity: Wavelength, Frequency, Amplitude (7.1)
2. Animation: Emission Spectra (7.3)
3. Interactivity: Orbital Shapes and Energy (7.7)
4. Animation: Electron Configurations (7.8)
5. Interactivity: Pauli Exclusion Principle (7.8)
6. Interactivity: Orbital Filling Rules (7.8)

## 7.1 From Classical Physics to Quantum Theory

Early attempts to understand atoms and molecules met with only limited success. By assuming that molecules behave like rebounding balls, physicists were able to predict and explain some macroscopic phenomena, such as the pressure exerted by a gas. However, their model did not account for the stability of molecules; that is, it could not explain the forces that hold atoms together. It took a long time to realize—and an even longer time to accept—that the properties of atoms and molecules are *not* governed by the same laws that work so well for larger objects.

The new era in physics started in 1900 with a young German physicist named Max Planck. While analyzing the data on the radiation emitted by solids heated to various temperatures, Planck discovered that atoms and molecules emit energy only in certain discrete quantities, or *quanta*. Physicists had always assumed that energy is continuous, which meant that any amount of energy could be released in a radiation process, so Planck's *quantum theory* turned physics upside down. Indeed, the flurry of research that ensued altered our concept of nature forever.

To understand quantum theory, we must know something about the nature of waves. A *wave* can be thought of as *a vibrating disturbance by which energy is transmitted*. The speed of a wave depends on the type of wave and the nature of the medium through which the wave is traveling (for example, air, water, or a vacuum). *The distance between identical points on successive waves* is called the *wavelength  $\lambda$*  (lambda). The *frequency  $\nu$*  (nu) of the wave is *the number of waves that pass through a particular point in one second*. The *amplitude* is *the vertical distance from the mid-line of a wave to the peak or trough* (Figure 7.1a). Figure 7.1b shows two waves that have the same amplitude but different wavelengths and frequencies.

An important property of a wave traveling through space is its speed ( $u$ ), which is given by the product of its wavelength and its frequency:

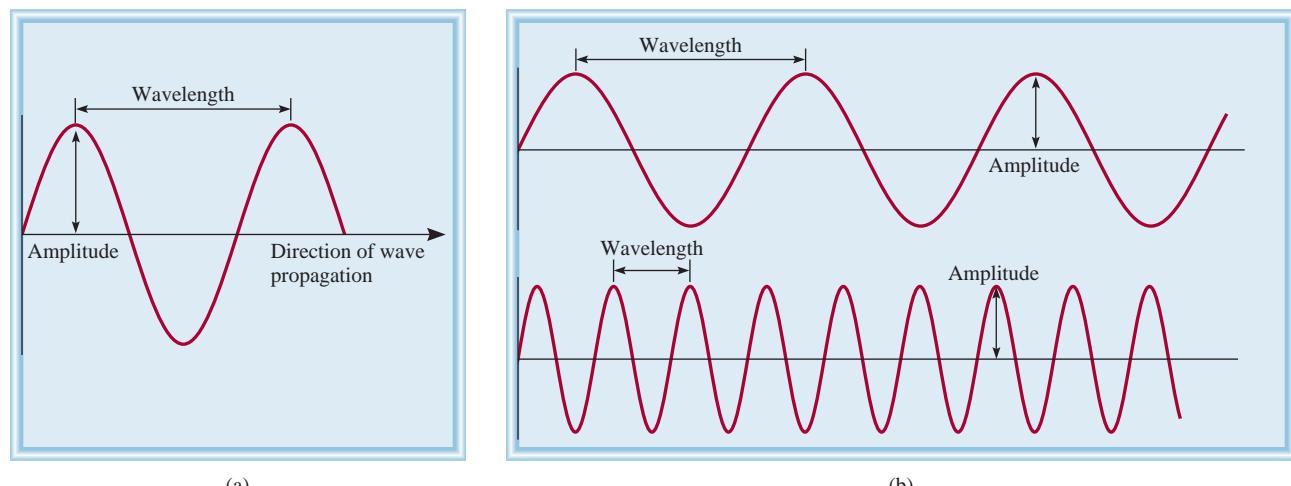
$$u = \lambda\nu \quad (7.1)$$



Ocean water waves.



**Interactivity:**  
Wavelength, Frequency,  
Amplitude  
Online Learning Center,  
Interactives



**Figure 7.1**

(a) Wavelength and amplitude. (b) Two waves having different wavelengths and frequencies. The wavelength of the top wave is three times that of the lower wave, but its frequency is only one-third that of the lower wave. Both waves have the same amplitude and speed.

The inherent “sensibility” of Equation (7.1) becomes apparent if we analyze the physical dimensions involved in the three terms. The wavelength ( $\lambda$ ) expresses the length of a wave, or distance/wave. The frequency ( $\nu$ ) indicates the number of these waves that pass any reference point per unit of time, or waves/time. Thus, the product of these terms results in dimensions of distance/time, which is speed:

$$\frac{\text{distance}}{\text{time}} = \frac{\text{distance}}{\text{wave}} \times \frac{\text{waves}}{\text{time}}$$

Wavelength is usually expressed in units of meters, centimeters, or nanometers, and frequency is measured in hertz (Hz), where

$$1 \text{ Hz} = 1 \text{ cycle/s}$$

The word “cycle” may be left out and the frequency expressed as, for example, 25/s (read as “25 per second”).

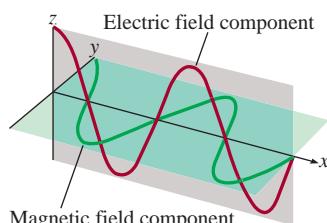
## Electromagnetic Radiation

There are many kinds of waves, such as water waves, sound waves, and light waves. In 1873 James Clerk Maxwell proposed that visible light consists of electromagnetic waves. According to Maxwell’s theory, an **electromagnetic wave** has an electric field component and a magnetic field component. These two components have the same wavelength and frequency, and hence the same speed, but they travel in mutually perpendicular planes (Figure 7.2). The significance of Maxwell’s theory is that it provides a mathematical description of the general behavior of light. In particular, his model accurately describes how energy in the form of radiation can be propagated through space as vibrating electric and magnetic fields. **Electromagnetic radiation** is the emission and transmission of energy in the form of electromagnetic waves.

Electromagnetic waves travel  $3.00 \times 10^8$  meters per second (rounded off), or 186,000 miles per second, in a vacuum. This speed does differ from one medium to another, but not enough to distort our calculations significantly. By convention, we use the symbol  $c$  for the speed of electromagnetic waves, or as it is more commonly called, the *speed of light*. The wavelength of electromagnetic waves is usually given in nanometers (nm).

**Sound waves and water waves are not electromagnetic waves, but X rays and radio waves are.**

A more accurate value for the speed of light is given on the inside back cover of the book.



**Figure 7.2**

The electric field and magnetic field components of an electromagnetic wave. These two components have the same wavelength, frequency, and amplitude, but they vibrate in two mutually perpendicular planes.

### Example 7.1

The wavelength of the green light from a traffic signal is centered at 522 nm. What is the frequency of this radiation?

**Strategy** We are given the wavelength of an electromagnetic wave and asked to calculate its frequency. Rearranging Equation (7.1) and replacing  $u$  with  $c$  (the speed of light) gives

$$\nu = \frac{c}{\lambda}$$

**Solution** Because the speed of light is given in meters per second, it is convenient to first convert wavelength to meters. Recall that  $1 \text{ nm} = 1 \times 10^{-9} \text{ m}$  (see Table 1.3). We write

$$\begin{aligned}\lambda &= 522 \text{ nm} \times \frac{1 \times 10^{-9} \text{ m}}{1 \text{ nm}} = 522 \times 10^{-9} \text{ m} \\ &= 5.22 \times 10^{-7} \text{ m}\end{aligned}$$

(Continued)

Substituting in the wavelength and the speed of light ( $3.00 \times 10^8$  m/s), the frequency is

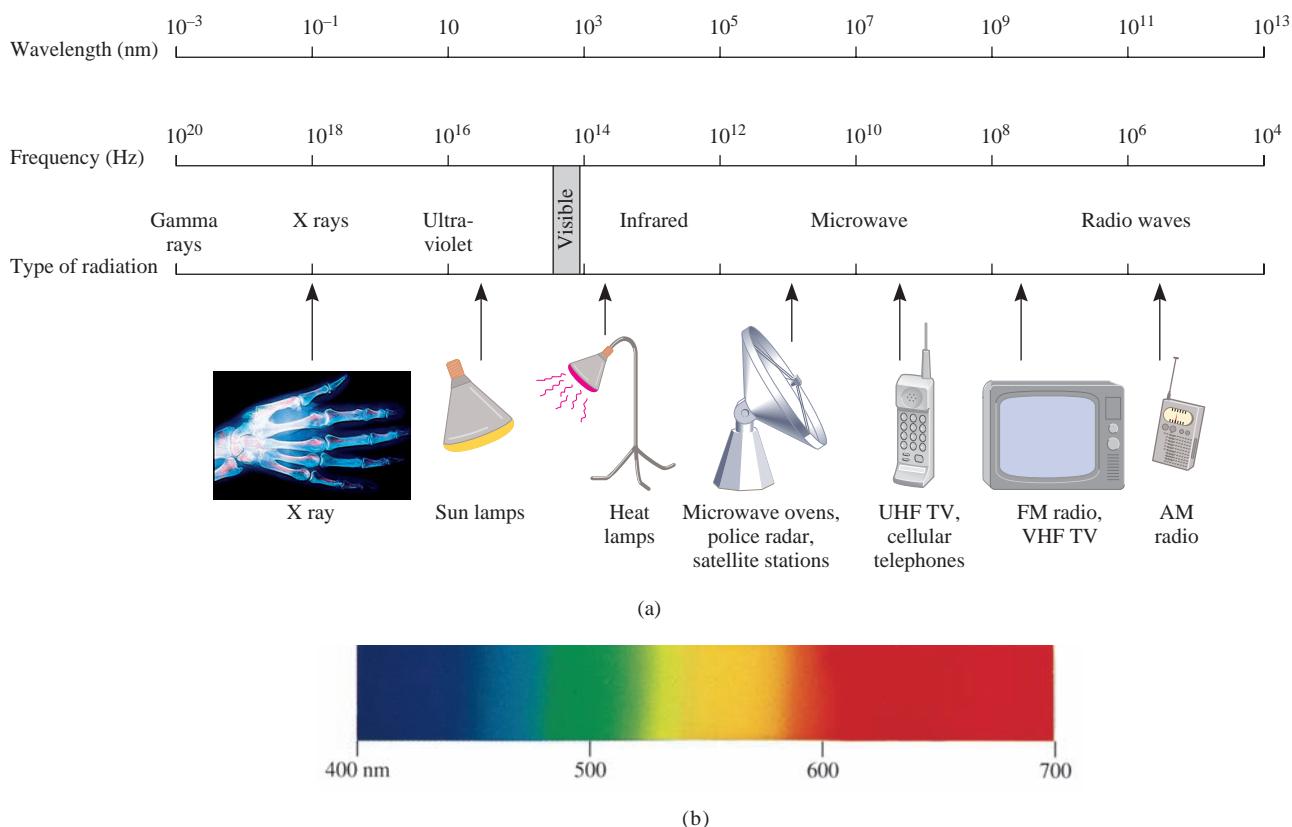
$$\nu = \frac{3.00 \times 10^8 \text{ m/s}}{5.22 \times 10^{-7} \text{ m}} \\ = 5.75 \times 10^{14}/\text{s}, \text{ or } 5.75 \times 10^{14} \text{ Hz}$$

**Check** The answer shows that  $5.75 \times 10^{14}$  waves pass a fixed point every second. This very high frequency is in accordance with the very high speed of light.

**Similar problem:** 7.7.

**Practice Exercise** What is the wavelength (in meters) of an electromagnetic wave whose frequency is  $3.64 \times 10^7$  Hz?

Figure 7.3 shows various types of electromagnetic radiation, which differ from one another in wavelength and frequency. The long radio waves are emitted by large antennas, such as those used by broadcasting stations. The shorter, visible light waves are produced by the motions of electrons within atoms and molecules. The shortest



**Figure 7.3**

(a) Types of electromagnetic radiation. Gamma rays have the shortest wavelength and highest frequency; radio waves have the longest wavelength and the lowest frequency. Each type of radiation is spread over a specific range of wavelengths (and frequencies). (b) Visible light ranges from a wavelength of 400 nm (violet) to 700 nm (red).

waves, which also have the highest frequency, are associated with  $\gamma$  (gamma) rays, which result from changes within the nucleus of the atom (see Chapter 2). As we will see shortly, the higher the frequency, the more energetic the radiation. Thus, ultraviolet radiation, X rays, and  $\gamma$  rays are high-energy radiation.

## Planck's Quantum Theory

When solids are heated, they emit electromagnetic radiation over a wide range of wavelengths. The dull red glow of an electric heater and the bright white light of a tungsten lightbulb are examples of radiation from heated solids.

Measurements taken in the latter part of the nineteenth century showed that the amount of radiation energy emitted by an object at a certain temperature depends on its wavelength. Attempts to account for this dependence in terms of established wave theory and thermodynamic laws were only partially successful. One theory explained short-wavelength dependence but failed to account for the longer wavelengths. Another theory accounted for the longer wavelengths but failed for short wavelengths. It seemed that something fundamental was missing from the laws of classical physics.

Planck solved the problem with an assumption that departed drastically from accepted concepts. Classical physics assumed that atoms and molecules could emit (or absorb) any arbitrary amount of radiant energy. Planck said that atoms and molecules could emit (or absorb) energy only in discrete quantities, like small packages or bundles. Planck gave the name ***quantum*** to the smallest quantity of energy that can be emitted (or absorbed) in the form of electromagnetic radiation. The energy  $E$  of a single quantum of energy is given by

$$E = h\nu \quad (7.2)$$

where  $h$  is called *Planck's constant* and  $\nu$  is the frequency of radiation. The value of Planck's constant is  $6.63 \times 10^{-34}$  J·s. Because  $\nu = c/\lambda$ , Equation (7.2) can also be expressed as

$$E = h\frac{c}{\lambda} \quad (7.3)$$

According to quantum theory, energy is always emitted in multiples of  $h\nu$ ; for example,  $h\nu$ ,  $2 h\nu$ ,  $3 h\nu$ , . . . , but never, for example,  $1.67 h\nu$  or  $4.98 h\nu$ . At the time Planck presented his theory, he could not explain why energies should be fixed or quantized in this manner. Starting with this hypothesis, however, he had no trouble correlating the experimental data for emission by solids over the *entire* range of wavelengths; they all supported the quantum theory.

The idea that energy should be quantized or “bundled” may seem strange, but the concept of quantization has many analogies. For example, an electric charge is also quantized; there can be only whole-number multiples of  $e$ , the charge of one electron. Matter itself is quantized because the numbers of electrons, protons, and neutrons and the numbers of atoms in a sample of matter must also be integers. Our money system is based on a “quantum” of value called a penny. Even processes in living systems involve quantized phenomena. The eggs laid by hens are quantized, and a pregnant cat gives birth to an integral number of kittens, not to one-half or three-quarters of a kitten.

## 7.2 The Photoelectric Effect

In 1905, only 5 years after Planck presented his quantum theory, the German-American physicist Albert Einstein used the theory to solve another mystery in physics, the **photoelectric effect**, a phenomenon in which *electrons are ejected from the surface of certain metals exposed to light of at least a certain minimum frequency*, called *the threshold frequency* (Figure 7.4). The number of electrons ejected was proportional to the intensity (or brightness) of the light, but the energies of the ejected electrons were not. Below the threshold frequency no electrons were ejected no matter how intense the light.

The photoelectric effect could not be explained by the wave theory of light. Einstein, however, made an extraordinary assumption. He suggested that a beam of light is really a stream of particles. These *particles of light* are now called **photons**. Using Planck's quantum theory of radiation as a starting point, Einstein deduced that each photon must possess energy  $E$ , given by the equation

$$E = h\nu$$

This equation has the same form as Equation (7.2) because, as we will see shortly, electromagnetic radiation is emitted as well as absorbed in the form of photons.

where  $\nu$  is the frequency of light. Electrons are held in a metal by attractive forces, and so removing them from the metal requires light of a sufficiently high frequency (which corresponds to sufficiently high energy) to break them free. Shining a beam of light onto a metal surface can be thought of as shooting a beam of particles—photons—at the metal atoms. If the frequency of photons is such that  $h\nu$  is exactly equal to the energy that binds the electrons in the metal, then the light will have just enough energy to knock the electrons loose. If we use light of a higher frequency, then not only will the electrons be knocked loose, but they will also acquire some kinetic energy. This situation is summarized by the equation

$$h\nu = \text{KE} + W$$

where KE is the kinetic energy of the ejected electron and  $W$  is called the *work function*, which is a measure of how strongly held the electron is in the metal. Rewriting the preceding equation as

$$\text{KE} = h\nu - W$$

shows that the more energetic the photon (that is, the higher its frequency), the greater the kinetic energy of the ejected electron.

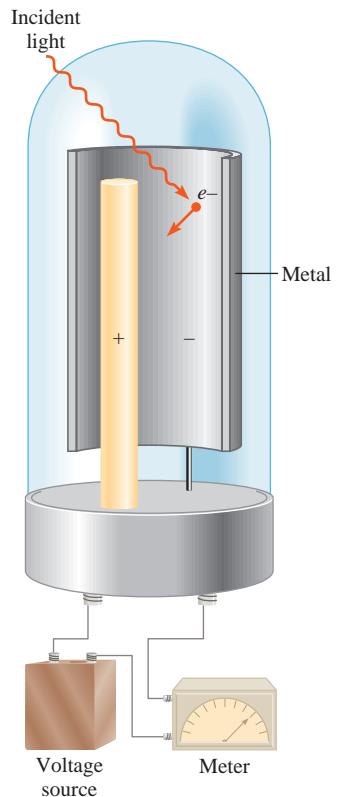
Now consider two beams of light having the same frequency (which is greater than the threshold frequency) but different intensities. The more intense beam of light consists of a larger number of photons; consequently, it ejects more electrons from the metal's surface than the weaker beam of light. Thus, the more intense the light, the greater the number of electrons emitted by the target metal; the higher the frequency of the light, the greater the kinetic energy of the ejected electrons.

### Example 7.2

Calculate the energy (in joules) of (a) a photon with a wavelength of  $5.00 \times 10^4$  nm (infrared region) and (b) a photon with a wavelength of  $5.00 \times 10^{-2}$  nm (X ray region).

**Strategy** In both (a) and (b) we are given the wavelength of a photon and asked to calculate its energy. We need to use Equation (7.3) to calculate the energy. Planck's constant is given in the text and also on the back inside cover.

(Continued)



**Figure 7.4**

An apparatus for studying the photoelectric effect. Light of a certain frequency falls on a clean metal surface. Ejected electrons are attracted toward the positive electrode. The flow of electrons is registered by a detecting meter.

**Solution** (a) From Equation (7.3),

$$\begin{aligned} E &= h \frac{c}{\lambda} \\ &= \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{(5.00 \times 10^4 \text{ nm}) \frac{1 \times 10^{-9} \text{ m}}{1 \text{ nm}}} \\ &= 3.98 \times 10^{-21} \text{ J} \end{aligned}$$

This is the energy of a single photon with a  $5.00 \times 10^4 \text{ nm}$  wavelength.

- (b) Following the same procedure as in (a), we can show that the energy of the photon that has a wavelength of  $5.00 \times 10^{-2} \text{ nm}$  is  $3.98 \times 10^{-15} \text{ J}$ .

**Check** Because the energy of a photon increases with decreasing wavelength, we see that an “X ray” photon is  $1 \times 10^6$ , or a million times, more energetic than an “infrared” photon.

**Similar problem:** 7.15.

**Practice Exercise** The energy of a photon is  $5.87 \times 10^{-20} \text{ J}$ . What is its wavelength (in nanometers)?

Einstein’s theory of light posed a dilemma for scientists. On the one hand, it explains the photoelectric effect satisfactorily. On the other hand, the particle theory of light is not consistent with the known wave behavior of light. The only way to resolve the dilemma is to accept the idea that light possesses *both* particlelike and wavelike properties. Depending on the experiment, light behaves either as a wave or as a stream of particles. This concept was totally alien to the way physicists had thought about matter and radiation, and it took a long time for them to accept it. We will see in Section 7.4 that a dual nature (particles and waves) is not unique to light but is characteristic of all matter, including electrons.

## 7.3 Bohr’s Theory of the Hydrogen Atom

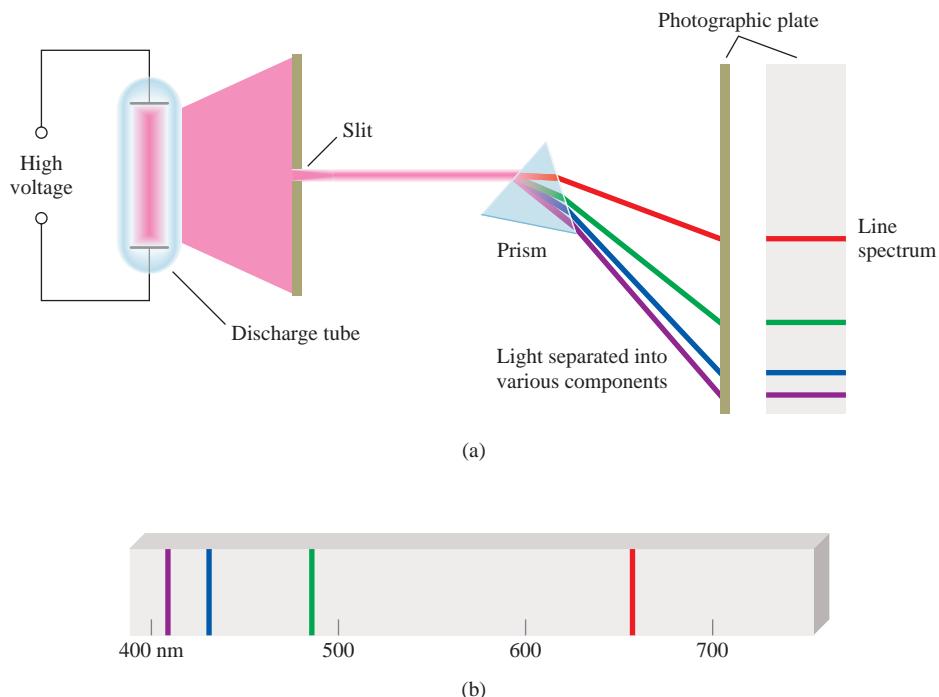
Einstein’s work paved the way for the solution of yet another nineteenth-century “mystery” in physics: the emission spectra of atoms.

### Emission Spectra

Ever since the seventeenth century, when Newton showed that sunlight is composed of various color components that can be recombined to produce white light, chemists and physicists have studied the characteristics of *emission spectra*, that is, *either continuous or line spectra of radiation emitted by substances*. The emission spectrum of a substance can be seen by energizing a sample of material either with thermal energy or with some other form of energy (such as a high-voltage electrical discharge if the substance is gaseous). A “red-hot” or “white-hot” iron bar freshly removed from a high-temperature source produces a characteristic glow. This visible glow is the portion of its emission spectrum that is sensed by eye. The warmth of the same iron bar represents another portion of its emission spectrum—the infrared region. A feature common to the emission spectra of the sun and of a heated solid is that both are continuous; that is, all wavelengths of visible light are represented in the spectra (see the visible region in Figure 7.3).



**Animation:**  
Emission spectra  
Online Learning Center,  
Animations



**Figure 7.5**  
 (a) An experimental arrangement for studying the emission spectra of atoms and molecules. The gas under study is in a discharge tube containing two electrodes. As electrons flow from the negative electrode to the positive electrode, they collide with the gas. This collision process eventually leads to the emission of light by the atoms (or molecules). The emitted light is separated into its components by a prism. Each component color is focused at a definite position, according to its wavelength, and forms a colored image of the slit on the photographic plate. The colored images are called spectral lines. (b) The line emission spectrum of hydrogen atoms.

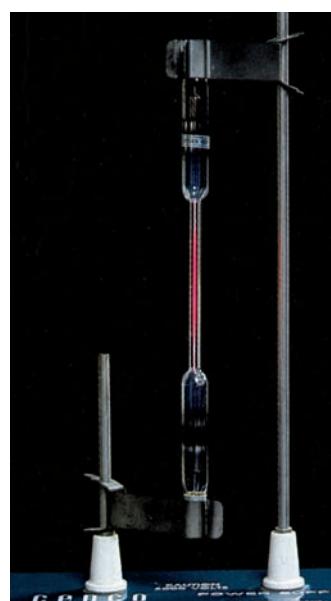
The emission spectra of atoms in the gas phase, on the other hand, do not show a continuous spread of wavelengths from red to violet; rather, the atoms produce bright lines in different parts of the visible spectrum. These **line spectra** are the light emission only at specific wavelengths. Figure 7.5 is a schematic diagram of a discharge tube that is used to study emission spectra, and Figure 7.6 shows the color emitted by hydrogen atoms in a discharge tube.

Every element has a unique emission spectrum. The characteristic lines in atomic spectra can be used in chemical analysis to identify unknown atoms, much as fingerprints are used to identify people. When the lines of the emission spectrum of a known element exactly match the lines of the emission spectrum of an unknown sample, the identity of the sample is established. Although the utility of this procedure was recognized some time ago in chemical analysis, the origin of these lines was unknown until early in the twentieth century.

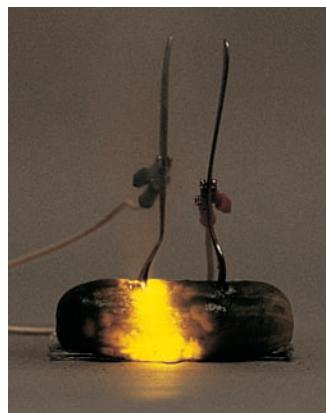
## Emission Spectrum of the Hydrogen Atom

In 1913, not too long after Planck's and Einstein's discoveries, a theoretical explanation of the emission spectrum of the hydrogen atom was presented by the Danish physicist Niels Bohr. Bohr's treatment is very complex and is no longer considered to be correct in all its details. Thus, we will concentrate only on his important assumptions and final results, which do account for the spectral lines.

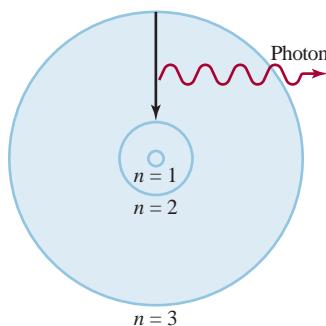
According to the laws of classical physics, an electron moving in an orbit of a hydrogen atom would experience an acceleration toward the nucleus by radiating away energy in the form of electromagnetic waves. Thus, such an electron would quickly spiral into the nucleus and annihilate itself with the proton. To explain why this does not happen, Bohr postulated that the electron is allowed to occupy only certain orbits of specific energies. In other words, the energies of the electron are quantized. An electron in any of the allowed orbits will not radiate energy and therefore will not



**Figure 7.6**  
 Color emitted by hydrogen atoms in a discharge tube. The color observed results from the combination of the colors emitted in the visible spectrum.



When a high voltage is applied between the forks, some of the sodium ions in the pickle are converted to sodium atoms in an excited state. These atoms emit the characteristic yellow light as they relax to the ground state.



**Figure 7.7**  
The emission process in an excited hydrogen atom, according to Bohr's theory. An electron originally in a higher-energy orbit ( $n = 3$ ) falls back to a lower-energy orbit ( $n = 2$ ). As a result, a photon with energy  $h\nu$  is given off. The value of  $h\nu$  is equal to the difference in energies of the two orbits occupied by the electron in the emission process. For simplicity, only three orbits are shown.

spiral into the nucleus. Bohr attributed the emission of radiation by an energized hydrogen atom to the electron dropping from a higher-energy orbit to a lower one and giving up a quantum of energy (a photon) in the form of light (Figure 7.7). Bohr showed that the energies that an electron in hydrogen atom can occupy are given by

$$E_n = -R_H \left( \frac{1}{n^2} \right) \quad (7.4)$$

where  $R_H$ , the Rydberg constant (after the Swedish physicist Johannes Rydberg), has the value  $2.18 \times 10^{-18}$  J. The number  $n$  is an integer called the principal quantum number; it has the values  $n = 1, 2, 3, \dots$ .

The negative sign in Equation (7.4) is an arbitrary convention, signifying that the energy of the electron in the atom is *lower* than the energy of a *free electron*, which is an electron that is infinitely far from the nucleus. The energy of a free electron is arbitrarily assigned a value of zero. Mathematically, this corresponds to setting  $n$  equal to infinity in Equation (7.4), so that  $E_\infty = 0$ . As the electron gets closer to the nucleus (as  $n$  decreases),  $E_n$  becomes larger in absolute value, but also more negative. The most negative value, then, is reached when  $n = 1$ , which corresponds to the most stable energy state. We call this the **ground state**, or the **ground level**, which refers to *the lowest energy state of a system* (which is an atom in our discussion). The stability of the electron diminishes for  $n = 2, 3, \dots$ . Each of these levels is called an **excited state**, or **excited level**, which is *higher in energy than the ground state*. A hydrogen electron for which  $n$  is greater than 1 is said to be in an excited state. The radius of each circular orbit in Bohr's model depends on  $n^2$ . Thus, as  $n$  increases from 1 to 2 to 3, the orbit radius increases very rapidly. The higher the excited state, the farther away the electron is from the nucleus (and the less tightly it is held by the nucleus).

Bohr's theory enables us to explain the line spectrum of the hydrogen atom. Radiant energy absorbed by the atom causes the electron to move from a lower-energy state (characterized by a smaller  $n$  value) to a higher-energy state (characterized by a larger  $n$  value). Conversely, radiant energy (in the form of a photon) is emitted when the electron moves from a higher-energy state to a lower-energy state. The quantized movement of the electron from one energy state to another is analogous to the movement of a tennis ball either up or down a set of stairs (Figure 7.8). The ball can be on any of several steps but never between steps. The journey from a lower step to a higher one is an energy-requiring process, whereas movement from a higher step to a lower step is an energy-releasing process. The quantity of energy involved in either type of change is determined by the distance between the beginning and ending steps. Similarly, the amount of energy needed to move an electron in the Bohr atom depends on the difference in energy levels between the initial and final states.

To apply Equation (7.4) to the emission process in a hydrogen atom, let us suppose that the electron is initially in an excited state characterized by the principal quantum number  $n_i$ . During emission, the electron drops to a lower energy state characterized by the principal quantum number  $n_f$  (the subscripts i and f denote the initial and final states, respectively). This lower energy state may be either a less excited state or the ground state. The difference between the energies of the initial and final states is

$$\Delta E = E_f - E_i$$

From Equation (7.4),

$$E_f = -R_H \left( \frac{1}{n_f^2} \right)$$

**TABLE 7.1** The Various Series in Atomic Hydrogen Emission Spectrum

Series	$n_f$	$n_i$	Spectrum Region
Lyman	1	2, 3, 4, . . .	Ultraviolet
Balmer	2	3, 4, 5, . . .	Visible and ultraviolet
Paschen	3	4, 5, 6, . . .	Infrared
Brackett	4	5, 6, 7, . . .	Infrared

and

$$E_i = -R_H \left( \frac{1}{n_i^2} \right)$$

Therefore,

$$\begin{aligned} \Delta E &= \left( \frac{-R_H}{n_f^2} \right) - \left( \frac{-R_H}{n_i^2} \right) \\ &= R_H \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \end{aligned}$$

Because this transition results in the emission of a photon of frequency  $\nu$  and energy  $h\nu$ , we can write

$$\Delta E = h\nu = R_H \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \quad (7.5)$$

When a photon is emitted,  $n_i > n_f$ . Consequently the term in parentheses is negative and  $\Delta E$  is negative (energy is lost to the surroundings). When energy is absorbed,  $n_i < n_f$  and the term in parentheses is positive, so  $\Delta E$  is positive. Each spectral line in the emission spectrum corresponds to a particular transition in a hydrogen atom. When we study a large number of hydrogen atoms, we observe all possible transitions and hence the corresponding spectral lines. The brightness of a spectral line depends on how many photons of the same wavelength are emitted.

The emission spectrum of hydrogen includes a wide range of wavelengths from the infrared to the ultraviolet. Table 7.1 lists the series of transitions in the hydrogen spectrum; they are named after their discoverers. The Balmer series was particularly easy to study because a number of its lines fall in the visible range.

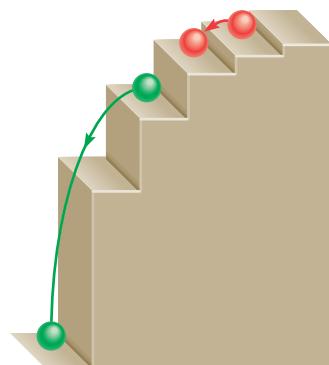
Figure 7.7 shows a single transition. However, it is more informative to express transitions as shown in Figure 7.9. Each horizontal line represents an allowed energy level for the electron in a hydrogen atom. The energy levels are labeled with their principal quantum numbers.

### Example 7.3

What is the wavelength of a photon (in nanometers) emitted during a transition from the  $n_i = 5$  state to the  $n_f = 2$  state in the hydrogen atom?

**Strategy** We are given the initial and final states in the emission process. We can calculate the energy of the emitted photon using Equation (7.5). Then from Equations (7.2)

(Continued)

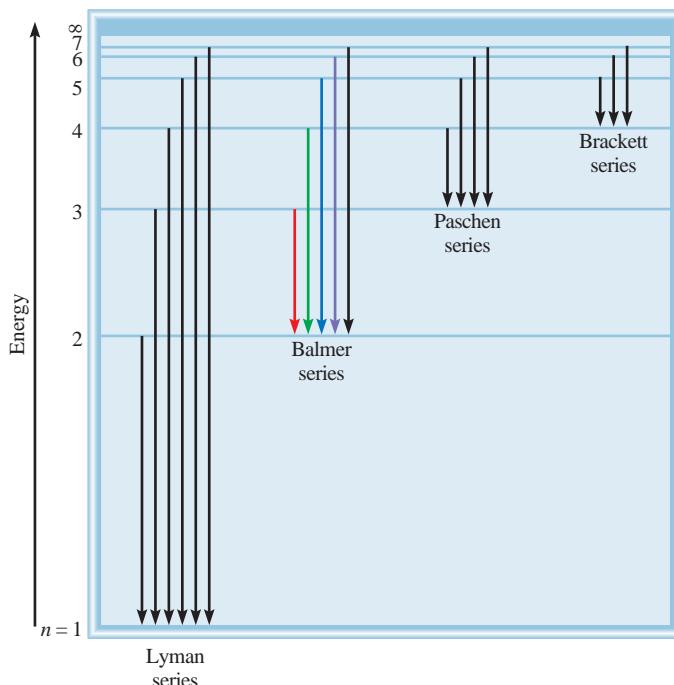


**Figure 7.8**

A mechanical analogy for the emission processes. The ball can rest on any step but not between steps.

**Figure 7.9**

The energy levels in the hydrogen atom and the various emission series. Each energy level corresponds to the energy associated with an allowed energy state for an orbit, as postulated by Bohr and shown in Figure 7.7. The emission lines are labeled according to the scheme in Table 7.1.



and (7.1) we can solve for the wavelength of the photon. The value of Rydberg's constant is given in the text.

**Solution** From Equation (7.5) we write

$$\begin{aligned}\Delta E &= R_H \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \\ &= 2.18 \times 10^{-18} \text{ J} \left( \frac{1}{5^2} - \frac{1}{2^2} \right) \\ &= -4.58 \times 10^{-19} \text{ J}\end{aligned}$$

The negative sign is in accord with our convention that energy is given off to the surroundings.

The negative sign indicates that this is energy associated with an emission process. To calculate the wavelength, we will omit the minus sign for  $\Delta E$  because the wavelength of the photon must be positive. Because  $\Delta E = h\nu$  or  $\nu = \Delta E/h$ , we can calculate the wavelength of the photon by writing

$$\begin{aligned}\lambda &= \frac{c}{\nu} \\ &= \frac{ch}{\Delta E} \\ &= \frac{(3.00 \times 10^8 \text{ m/s})(6.63 \times 10^{-34} \text{ J} \cdot \text{s})}{4.58 \times 10^{-19} \text{ J}} \\ &= 4.34 \times 10^{-7} \text{ m} \\ &= 4.34 \times 10^{-7} \text{ m} \times \left( \frac{1 \text{ nm}}{1 \times 10^{-9} \text{ m}} \right) = 434 \text{ nm}\end{aligned}$$

(Continued)

**Check** The wavelength is in the visible region of the electromagnetic region (see Figure 7.3). This is consistent with the fact that because  $n_f = 2$ , this transition gives rise to a spectral line in the Balmer series (see Table 7.1).

Similar problems: 7.31, 7.32.

**Practice Exercise** What is the wavelength (in nanometers) of a photon emitted during a transition from  $n_i = 6$  to  $n_f = 4$  state in the H atom?

## 7.4 The Dual Nature of the Electron

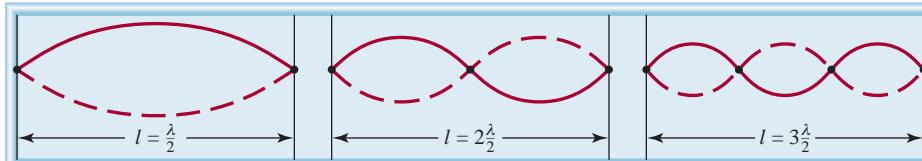
Physicists were both mystified and intrigued by Bohr's theory. They questioned why the energies of the hydrogen electron are quantized. Or, phrasing the question in a more concrete way, Why is the electron in a Bohr atom restricted to orbiting the nucleus at certain fixed distances? For a decade no one, not even Bohr himself, had a logical explanation. In 1924 the French physicist Louis de Broglie provided a solution to this puzzle. De Broglie reasoned that if light waves can behave like a stream of particles (photons), then perhaps particles such as electrons can possess wave properties. According to de Broglie, an electron bound to the nucleus behaves like a *standing wave*. Standing waves can be generated by plucking, say, a guitar string (Figure 7.10). The waves are described as standing, or stationary, because they do not travel along the string. Some points on the string, called **nodes**, do not move at all; that is, *the amplitude of the wave at these points is zero*. There is a node at each end, and there may be nodes between the ends. The greater the frequency of vibration, the shorter the wavelength of the standing wave and the greater the number of nodes. As Figure 7.10 shows, there can be only certain wavelengths in any of the allowed motions of the string.

De Broglie argued that if an electron does behave like a standing wave in the hydrogen atom, the length of the wave must fit the circumference of the orbit exactly (Figure 7.11). Otherwise the wave would partially cancel itself on each successive orbit. Eventually the amplitude of the wave would be reduced to zero, and the wave would not exist.

The relation between the circumference of an allowed orbit ( $2\pi r$ ) and the wavelength ( $\lambda$ ) of the electron is given by

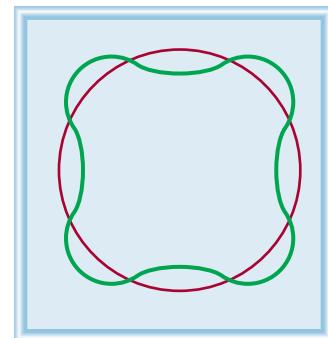
$$2\pi r = n\lambda \quad (7.6)$$

where  $r$  is the radius of the orbit,  $\lambda$  is the wavelength of the electron wave, and  $n = 1, 2, 3, \dots$ . Because  $n$  is an integer, it follows that  $r$  can have only certain values as  $n$  increases from 1 to 2 to 3 and so on. And because the energy of the electron depends on the size of the orbit (or the value of  $r$ ), its value must be quantized.

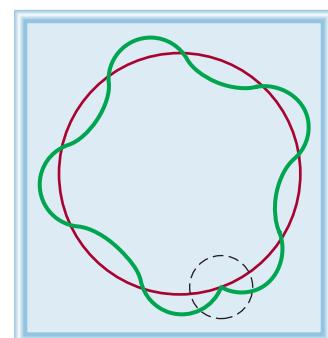


**Figure 7.10**

The standing waves generated by plucking a guitar string. Each dot represents a node. The length of the string ( $l$ ) must be equal to a whole number times one-half the wavelength ( $\lambda/2$ ).



(a)



(b)

**Figure 7.11**

(a) The circumference of the orbit is equal to an integral number of wavelengths. This is an allowed orbit. (b) The circumference of the orbit is not equal to an integral number of wavelengths. As a result, the electron wave does not close in on itself. This is a nonallowed orbit.

De Broglie's reasoning led to the conclusion that waves can behave like particles and particles can exhibit wavelike properties. De Broglie deduced that the particle and wave properties are related by the expression

$$\lambda = \frac{h}{mu} \quad (7.7)$$

where  $\lambda$ ,  $m$ , and  $u$  are the wavelengths associated with a moving particle, its mass, and its velocity, respectively. Equation (7.7) implies that a particle in motion can be treated as a wave, and a wave can exhibit the properties of a particle. Note that the left side of Equation (7.7) involves the wavelike property of wavelength, whereas the right side makes references to mass, a distinctly particlelike property.

### Example 7.4

Calculate the wavelength of the “particle” in the following two cases: (a) The fastest serve in tennis is about 150 miles per hour, or 68 m/s. Calculate the wavelength associated with a  $6.0 \times 10^{-2}$ -kg tennis ball traveling at this speed. (b) Calculate the wavelength associated with an electron ( $9.1094 \times 10^{-31}$  kg) moving at 68 m/s.

**Strategy** We are given the mass and the speed of the particle in (a) and (b) and asked to calculate the wavelength so we need Equation (7.7). Note that because the units of Planck's constants are  $J \cdot s$ ,  $m$  and  $u$  must be in kg and m/s ( $1 J = 1 \text{ kg m}^2/\text{s}^2$ ), respectively.

**Solution** (a) Using Equation (7.7) we write

$$\begin{aligned}\lambda &= \frac{h}{mu} \\ &= \frac{6.63 \times 10^{-34} \text{ J} \cdot \text{s}}{(6.0 \times 10^{-2} \text{ kg}) \times 68 \text{ m/s}} \\ &= 1.6 \times 10^{-34} \text{ m}\end{aligned}$$

**Comment** This is an exceedingly small wavelength considering that the size of an atom itself is on the order of  $1 \times 10^{-10}$  m. For this reason, the wave properties of a tennis ball cannot be detected by any existing measuring device.

(b) In this case,

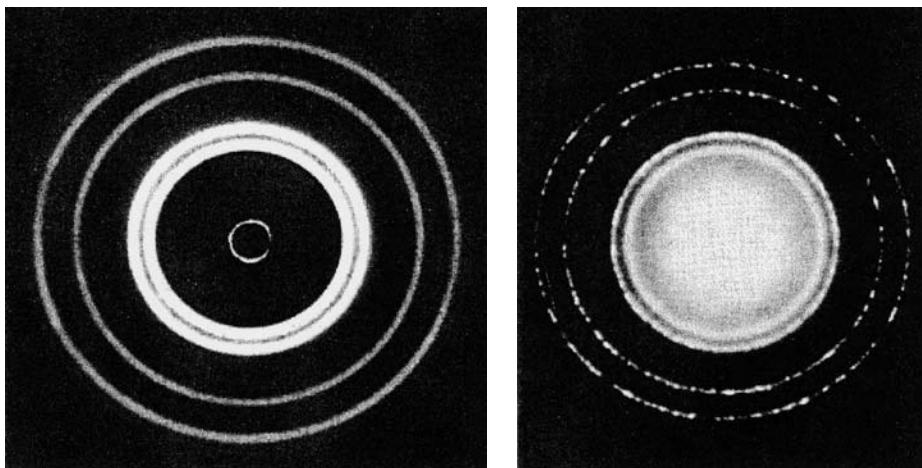
$$\begin{aligned}\lambda &= \frac{h}{mu} \\ &= \frac{6.63 \times 10^{-34} \text{ J} \cdot \text{s}}{(9.1094 \times 10^{-31} \text{ kg}) \times 68 \text{ m/s}} \\ &= 1.1 \times 10^{-5} \text{ m}\end{aligned}$$

**Comment** This wavelength ( $1.1 \times 10^{-5}$  m or  $1.1 \times 10^4$  nm) is in the infrared region. This calculation shows that only electrons (and other submicroscopic particles) have measurable wavelengths.

**Similar problems:** 7.40, 7.41.

**Practice Exercise** Calculate the wavelength (in nanometers) of a H atom (mass =  $1.674 \times 10^{-27}$  kg) moving at  $7.00 \times 10^2$  cm/s.

Example 7.4 shows that although de Broglie's equation can be applied to diverse systems, the wave properties become observable only for submicroscopic objects. This

**Figure 7.12**

*Left: X-ray diffraction pattern of aluminum foil. Right: Electron diffraction of aluminum foil. The similarity of these two patterns shows that electrons can behave like X rays and display wave properties.*

distinction is due to the smallness of Planck's constant,  $h$ , which appears in the numerator in Equation (7.7).

Shortly after de Broglie introduced his equation, Clinton Davisson and Lester Germer in the United States and G. P. Thomson in England demonstrated that electrons do indeed possess wavelike properties. By directing a beam of electrons through a thin piece of gold foil, Thomson obtained a set of concentric rings on a screen, similar to the pattern observed when X rays (which are waves) were used. Figure 7.12 shows such a pattern for aluminum.

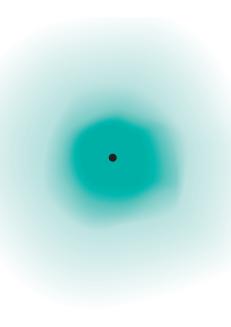
## 7.5 Quantum Mechanics

The spectacular success of Bohr's theory was followed by a series of disappointments. Bohr's approach could not account for the emission spectra of atoms containing more than one electron, such as atoms of helium and lithium. Nor did it explain why extra lines appear in the hydrogen emission spectrum when a magnetic field is applied. Another problem arose with the discovery that electrons are wavelike: How can the "position" of a wave be specified? We cannot define the precise location of a wave because a wave extends in space.

The dual nature of electrons was particularly troublesome because of the electron's exceedingly small mass. To describe the problem of trying to locate a subatomic particle that behaves like a wave, the German physicist Werner Heisenberg formulated what is now known as the **Heisenberg uncertainty principle**: *It is impossible to know simultaneously both the momentum (mass times velocity) and the position of a particle with certainty.* In other words, to get a precise measurement of the momentum of a particle we must settle for less precise knowledge of the particle's position, and vice versa. Applying the Heisenberg uncertainty principle to the hydrogen atom, we see that it is inherently impossible to know simultaneously both the precise location and precise momentum of the electron. Thus, it is not appropriate to imagine the electron circling the nucleus in well-defined orbits.

To be sure, Bohr made a significant contribution to our understanding of atoms, and his suggestion that the energy of an electron in an atom is quantized remains unchallenged. But his theory did not provide a complete description of electronic behavior in atoms. In 1926 the Austrian physicist Erwin Schrödinger, using a complicated mathematical technique, formulated an equation that describes the behavior

**In reality,** Bohr's theory accounted for the observed emission spectra of  $\text{He}^+$  and  $\text{Li}^{2+}$  ions, as well as that of hydrogen. However, all three systems have one feature in common—each contains a single electron. Thus, the Bohr model worked successfully only for the hydrogen atom and for "hydrogen-like ions."



and energies of submicroscopic particles in general, an equation analogous to Newton's laws of motion for macroscopic objects. The *Schrödinger equation* requires advanced calculus to solve, and we will not discuss it here. It is important to know, however, that the equation incorporates both particle behavior, in terms of mass  $m$ , and wave behavior, in terms of a *wave function*  $\psi$  (psi), which depends on the location in space of the system (such as an electron in an atom).

The wave function itself has no direct physical meaning. However, the probability of finding the electron in a certain region in space is proportional to the square of the wave function,  $\psi^2$ . The idea of relating  $\psi^2$  to probability stemmed from a wave theory analogy. According to wave theory, the intensity of light is proportional to the square of the amplitude of the wave, or  $\psi^2$ . The most likely place to find a photon is where the intensity is greatest, that is, where the value of  $\psi^2$  is greatest. A similar argument associates  $\psi^2$  with the likelihood of finding an electron in regions surrounding the nucleus.

Schrödinger's equation began a new era in physics and chemistry, for it launched a new field, *quantum mechanics* (also called *wave mechanics*). We now refer to the developments in quantum theory from 1913—the time Bohr presented his analysis for the hydrogen atom—to 1926 as “old quantum theory.”

**Figure 7.13**

A representation of the electron density distribution surrounding the nucleus in the hydrogen atom. It shows a high probability of finding the electron closer to the nucleus.

## The Quantum Mechanical Description of the Hydrogen Atom

The Schrödinger equation specifies the possible energy states the electron can occupy in a hydrogen atom and identifies the corresponding wave functions ( $\psi$ ). These energy states and wave functions are characterized by a set of quantum numbers (to be discussed shortly), with which we can construct a comprehensive model of the hydrogen atom.

Although quantum mechanics tells us that we cannot pinpoint an electron in an atom, it does define the region where the electron might be at a given time. The concept of **electron density** gives the probability that an electron will be found in a particular region of an atom. The square of the wave function,  $\psi^2$ , defines the distribution of electron density in three-dimensional space around the nucleus. Regions of high electron density represent a high probability of locating the electron, whereas the opposite holds for regions of low electron density (Figure 7.13).

To distinguish the quantum mechanical description of an atom from Bohr's model, we speak of an atomic orbital, rather than an orbit. An **atomic orbital** can be thought of as the wave function of an electron in an atom. When we say that an electron is in a certain orbital, we mean that the distribution of the electron density or the probability of locating the electron in space is described by the square of the wave function associated with that orbital. An atomic orbital, therefore, has a characteristic energy, as well as a characteristic distribution of electron density.

The Schrödinger equation works nicely for the simple hydrogen atom with its one proton and one electron, but it turns out that it cannot be solved exactly for any atom containing more than one electron! Fortunately, chemists and physicists have learned to get around this kind of difficulty by approximation. For example, although the behavior of electrons in **many-electron atoms** (that is, atoms containing two or more electrons) is not the same as in the hydrogen atom, we assume that the difference is probably not too great. Thus, we can use the energies and wave functions obtained from the hydrogen atom as good approximations of the behavior of electrons in more complex atoms. In fact, this approach provides fairly reliable descriptions of electronic behavior in many-electron atoms.

Although the helium atom has only two electrons, in quantum mechanics it is regarded as a many-electron atom.

## 7.6 Quantum Numbers

In quantum mechanics, three ***quantum numbers*** are required to *describe the distribution of electrons in hydrogen and other atoms*. These numbers are derived from the mathematical solution of the Schrödinger equation for the hydrogen atom. They are called the *principal quantum number*, the *angular momentum quantum number*, and the *magnetic quantum number*. These quantum numbers will be used to describe atomic orbitals and to label electrons that reside in them. A fourth quantum number—the *spin quantum number*—describes the behavior of a specific electron and completes the description of electrons in atoms.

### The Principal Quantum Number ( $n$ )

The principal quantum number ( $n$ ) can have integral values 1, 2, 3, and so forth; it corresponds to the quantum number in Equation (7.4). In a hydrogen atom, the value of  $n$  determines the energy of an orbital. As we will see shortly, this is not the case for a many-electron atom. The principal quantum number also relates to the average distance of the electron from the nucleus in a particular orbital. The larger  $n$  is, the greater the average distance of an electron in the orbital from the nucleus and therefore the larger the orbital.

Equation (7.4) holds only for the hydrogen atom.

### The Angular Momentum Quantum Number ( $\ell$ )

The angular momentum quantum number ( $\ell$ ) tells us the “shape” of the orbitals (see Section 7.7). The values of  $\ell$  depend on the value of the principal quantum number,  $n$ . For a given value of  $n$ ,  $\ell$  has possible integral values from 0 to  $(n - 1)$ . If  $n = 1$ , there is only one possible value of  $\ell$ ; that is,  $\ell = n - 1 = 1 - 1 = 0$ . If  $n = 2$ , there are two values of  $\ell$ , given by 0 and 1. If  $n = 3$ , there are three values of  $\ell$ , given by 0, 1, and 2. The value of  $\ell$  is generally designated by the letters *s*, *p*, *d*, . . . as follows:

$\ell$	0	1	2	3	4	5
Name of orbital	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>	<i>h</i>

Thus, if  $\ell = 0$ , we have an *s* orbital; if  $\ell = 1$ , we have a *p* orbital; and so on.

A collection of orbitals with the same value of  $n$  is frequently called a shell. One or more orbitals with the same  $n$  and  $\ell$  values are referred to as a subshell. For example, the shell with  $n = 2$  is composed of two subshells,  $\ell = 0$  and 1 (the allowed values for  $n = 2$ ). These subshells are called the  $2s$  and  $2p$  subshells where 2 denotes the value of  $n$ , and *s* and *p* denote the values of  $\ell$ .

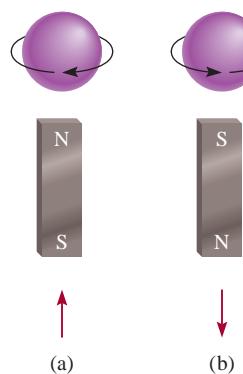
Remember that the “2” in  $2s$  refers to the value of  $n$  and the “*s*” symbolizes the value of  $\ell$ .

### The Magnetic Quantum Number ( $m_\ell$ )

The magnetic quantum number ( $m_\ell$ ) describes the orientation of the orbital in space (to be discussed in Section 7.7). Within a subshell, the value of  $m_\ell$  depends on the value of the angular momentum quantum number,  $\ell$ . For a certain value of  $\ell$ , there are  $(2\ell + 1)$  integral values of  $m_\ell$  as follows:

$$-\ell, (-\ell + 1), \dots, 0, \dots, (+\ell - 1), +\ell$$

If  $\ell = 0$ , then  $m_\ell = 0$ . If  $\ell = 1$ , then there are  $[(2 \times 1) + 1]$ , or three values of  $m_\ell$ , namely,  $-1, 0$ , and  $1$ . If  $\ell = 2$ , there are  $[(2 \times 2) + 1]$ , or five values of  $m_\ell$ , namely,  $-2, -1, 0, 1$ , and  $2$ . The number of  $m_\ell$  values indicates the number of orbitals in a subshell with a particular  $\ell$  value.

**Figure 7.14**

The (a) clockwise and (b) counterclockwise spins of an electron. The magnetic fields generated by these two spinning motions are analogous to those from the two magnets. The upward and downward arrows are used to denote the direction of spin.



**Interactivity:**  
Orbital Shapes and Energy  
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Interactives

To conclude our discussion of these three quantum numbers, let us consider a situation in which  $n = 2$  and  $\ell = 1$ . The values of  $n$  and  $\ell$  indicate that we have a  $2p$  subshell, and in this subshell we have *three*  $2p$  orbitals (because there are three values of  $m_\ell$ , given by  $-1, 0$ , and  $1$ ).

## The Electron Spin Quantum Number ( $m_s$ )

Experiments on the emission spectra of hydrogen and sodium atoms indicated that lines in the emission spectra could be split by the application of an external magnetic field. The only way physicists could explain these results was to assume that electrons act like tiny magnets. If electrons are thought of as spinning on their own axes, as Earth does, their magnetic properties can be accounted for. According to electromagnetic theory, a spinning charge generates a magnetic field, and it is this motion that causes an electron to behave like a magnet. Figure 7.14 shows the two possible spinning motions of an electron, one clockwise and the other counterclockwise. To take the electron spin into account, it is necessary to introduce a fourth quantum number, called the electron spin quantum number ( $m_s$ ), which has a value of  $+\frac{1}{2}$  or  $-\frac{1}{2}$ .

## 7.7 Atomic Orbitals

Table 7.2 shows the relation between quantum numbers and atomic orbitals. We see that when  $\ell = 0$ ,  $(2\ell + 1) = 1$  and there is only one value of  $m_\ell$ , thus, we have an  $s$  orbital. When  $\ell = 1$ ,  $(2\ell + 1) = 3$ , so there are three values of  $m_\ell$  or three  $p$  orbitals, labeled  $p_x$ ,  $p_y$ , and  $p_z$ . When  $\ell = 2$ ,  $(2\ell + 1) = 5$  and there are five values of  $m_\ell$ , and the corresponding five  $d$  orbitals are labeled with more elaborate subscripts. In the following sections we will consider the  $s$ ,  $p$ , and  $d$  orbitals separately.

### ***s* Orbitals**

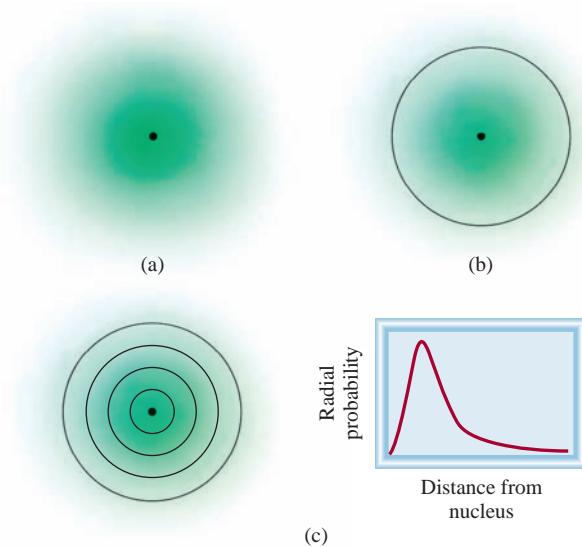
One of the important questions we ask when studying the properties of atomic orbitals is, What are the shapes of the orbitals? Strictly speaking, an orbital does not have a

That the wave function for an orbital theoretically has no outer limit as one moves outward from the nucleus raises interesting philosophical questions regarding the sizes of atoms. Chemists have agreed on an operational definition of atomic size, as we will see in Chapter 8.

**TABLE 7.2** Relation Between Quantum Numbers and Atomic Orbitals

$n$	$\ell$	$m_\ell$	Number of Orbitals	Atomic Orbital Designations
1	0	0	1	$1s$
2	0	0	1	$2s$
	1	$-1, 0, 1$	3	$2p_x, 2p_y, 2p_z$
3	0	0	1	$3s$
	1	$-1, 0, 1$	3	$3p_x, 3p_y, 3p_z$
	2	$-2, -1, 0, 1, 2$	5	$3d_{xy}, 3d_{yz}, 3d_{xz}, 3d_{x^2-y^2}, 3d_{z^2}$
.	.	.	.	.
.	.	.	.	.

An  $s$  subshell has one orbital, a  $p$  subshell has three orbitals, and a  $d$  subshell has five orbitals.

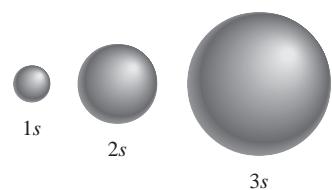
**Figure 7.15**

(a) Plot of electron density in the hydrogen 1s orbital as a function of the distance from the nucleus. The electron density falls off rapidly as the distance from the nucleus increases. (b) Boundary surface diagram of the hydrogen 1s orbital. (c) A more realistic way of viewing electron density distribution is to divide the 1s orbital into successive spherical thin shells. A plot of the probability of finding the electron in each shell, called radial probability, as a function of distance shows a maximum at 52.9 pm from the nucleus. Interestingly, this is equal to the radius of the innermost orbit in the Bohr model.

well-defined shape because the wave function characterizing the orbital extends from the nucleus to infinity. In that sense, it is difficult to say what an orbital looks like. On the other hand, it is certainly convenient to think of orbitals as having specific shapes, particularly in discussing the formation of chemical bonds between atoms, as we will do in Chapters 9 and 10.

Although in principle an electron can be found anywhere, we know that most of the time it is quite close to the nucleus. Figure 7.15(a) shows the distribution of electron density in a hydrogen 1s orbital moving outward from the nucleus. As you can see, the electron density falls off rapidly as the distance from the nucleus increases. Roughly speaking, there is about a 90 percent probability of finding the electron within a sphere of radius 100 pm ( $1 \text{ pm} = 1 \times 10^{-12} \text{ m}$ ) surrounding the nucleus. Thus, we can represent the 1s orbital by drawing a **boundary surface diagram** that encloses about 90 percent of the total electron density in an orbital, as shown in Figure 7.15(b). A 1s orbital represented in this manner is merely a sphere.

Figure 7.16 shows boundary surface diagrams for the 1s, 2s, and 3s hydrogen atomic orbitals. All s orbitals are spherical in shape but differ in size, which increases as the principal quantum number increases. Although the details of electron density variation within each boundary surface are lost, there is no serious disadvantage. For us the most important features of atomic orbitals are their shapes and *relative* sizes, which are adequately represented by boundary surface diagrams.



## p Orbitals

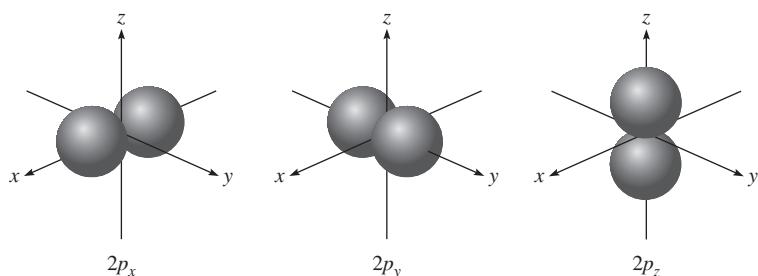
It should be clear that the p orbitals start with the principal quantum number  $n = 2$ . If  $n = 1$ , then the angular momentum quantum number  $\ell$  can assume only the value of zero; therefore, there is only a 1s orbital. As we saw earlier, when  $\ell = 1$ , the magnetic quantum number  $m_\ell$  can have values of  $-1, 0$ , and  $1$ . Starting with  $n = 2$  and  $\ell = 1$ , we therefore have three 2p orbitals:  $2p_x$ ,  $2p_y$ , and  $2p_z$  (Figure 7.17). The letter subscripts indicate the axes along which the orbitals are oriented. These three p

**Figure 7.16**

Boundary surface diagrams of the hydrogen 1s, 2s, and 3s orbitals. Each sphere contains about 90 percent of the total electron density. All s orbitals are spherical. Roughly speaking, the size of an orbital is proportional to  $n^2$ , where  $n$  is the principal quantum number.

**Figure 7.17**

The boundary surface diagrams of the three 2p orbitals. These orbitals are identical in shape and energy, but their orientations are different. The p orbitals of higher principal quantum numbers have a similar shape.



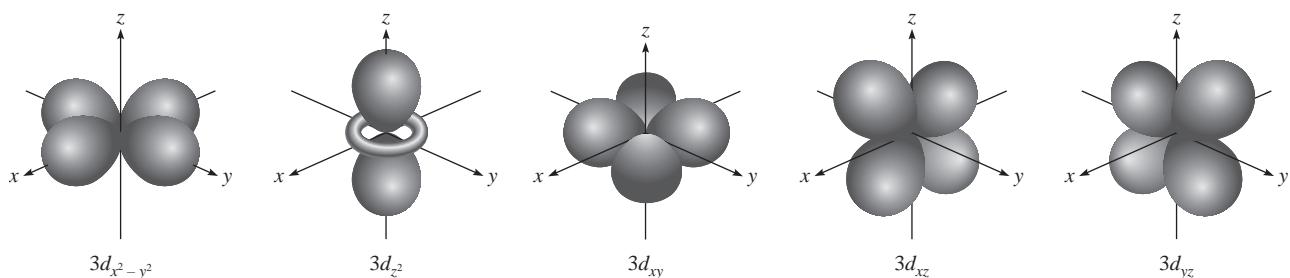
orbitals are identical in size, shape, and energy; they differ from one another only in orientation. Note, however, that there is no simple relation between the values of  $m_\ell$  and the  $x$ ,  $y$ , and  $z$  directions. For our purpose, you need to remember only that because there are three possible values of  $m_\ell$ , there are three  $p$  orbitals with different orientations.

The boundary surface diagrams of  $p$  orbitals in Figure 7.17 show that each  $p$  orbital can be thought of as two lobes on opposite sides of the nucleus. Like  $s$  orbitals,  $p$  orbitals increase in size from  $2p$  to  $3p$  to  $4p$  orbital and so on.

### **d Orbitals and Other Higher-Energy Orbitals**

When  $\ell = 2$ , there are five values of  $m_\ell$ , which correspond to five  $d$  orbitals. The lowest value of  $n$  for a  $d$  orbital is 3. Because  $\ell$  can never be greater than  $n - 1$ , when  $n = 3$  and  $\ell = 2$ , we have five  $3d$  orbitals ( $3d_{xy}$ ,  $3d_{yz}$ ,  $3d_{xz}$ ,  $3d_{x^2-y^2}$ , and  $3d_z^2$ ), as shown in Figure 7.18. As in the case of the  $p$  orbitals, the different orientations of the  $d$  orbitals correspond to the different values of  $m_\ell$ , but again there is no direct correspondence between a given orientation and a particular  $m_\ell$  value. All the  $3d$  orbitals in an atom are identical in energy. The  $d$  orbitals for which  $n$  is greater than 3 ( $4d$ ,  $5d$ , ...) have similar shapes.

Orbitals having higher energy than  $d$  orbitals are labeled  $f$ ,  $g$ , ... and so on. The  $f$  orbitals are important in accounting for the behavior of elements with atomic numbers greater than 57, but their shapes are difficult to represent. In general chemistry we are not concerned with orbitals having  $\ell$  values greater than 3 (the  $g$  orbitals and beyond).

**Figure 7.18**

Boundary surface diagrams of the five  $3d$  orbitals. Although the  $3d_z^2$  orbital looks different, it is equivalent to the other four orbitals in all other respects. The  $d$  orbitals of higher principal quantum numbers have similar shapes.

### Example 7.5

List the values of  $n$ ,  $\ell$ , and  $m_\ell$  for orbitals in the  $4d$  subshell.

**Strategy** What are the relationships among  $n$ ,  $\ell$ , and  $m_\ell$ ? What do “4” and “ $d$ ” represent in  $4d$ ?

**Solution** As we saw earlier, the number given in the designation of the subshell is the principal quantum number, so in this case  $n = 4$ . The letter designates the type of orbital. Because we are dealing with  $d$  orbitals,  $\ell = 2$ . The values of  $m_\ell$  can vary from  $-\ell$  to  $\ell$ . Therefore,  $m_\ell$  can be  $-2$ ,  $-1$ ,  $0$ ,  $1$ , or  $2$ .

**Check** The values of  $n$  and  $\ell$  are fixed for  $4d$ , but  $m_\ell$  can have any one of the five values, which correspond to the five  $d$  orbitals.

**Similar problem:** 7.55.

**Practice Exercise** Give the values of the quantum numbers associated with the orbitals in the  $3p$  subshell.

### Example 7.6

What is the total number of orbitals associated with the principal quantum number  $n = 3$ ?

**Strategy** To calculate the total number of orbitals for a given  $n$  value, we need to first write the possible values of  $\ell$ . We then determine how many  $m_\ell$  values are associated with each value of  $\ell$ . The total number of orbitals is equal to the sum of all the  $m_\ell$  values.

**Solution** For  $n = 3$ , the possible values of  $\ell$  are  $0$ ,  $1$ , and  $2$ . Thus, there is one  $3s$  orbital ( $n = 3$ ,  $\ell = 0$ , and  $m_\ell = 0$ ); there are three  $3p$  orbitals ( $n = 3$ ,  $\ell = 1$ , and  $m_\ell = -1$ ,  $0$ ,  $1$ ); there are five  $3d$  orbitals ( $n = 3$ ,  $\ell = 2$ , and  $m_\ell = -2$ ,  $-1$ ,  $0$ ,  $1$ ,  $2$ ). The total number of orbitals is  $1 + 3 + 5 = 9$ .

**Check** The total number of orbitals for a given value of  $n$  is  $n^2$ . So here we have  $3^2 = 9$ . Can you prove the validity of this relationship?

**Similar problem:** 7.60.

**Practice Exercise** What is the total number of orbitals associated with the principal quantum number  $n = 4$ ?

## The Energies of Orbitals

Now that we have some understanding of the shapes and sizes of atomic orbitals, we are ready to inquire into their relative energies and look at how energy levels affect the actual arrangement of electrons in atoms.

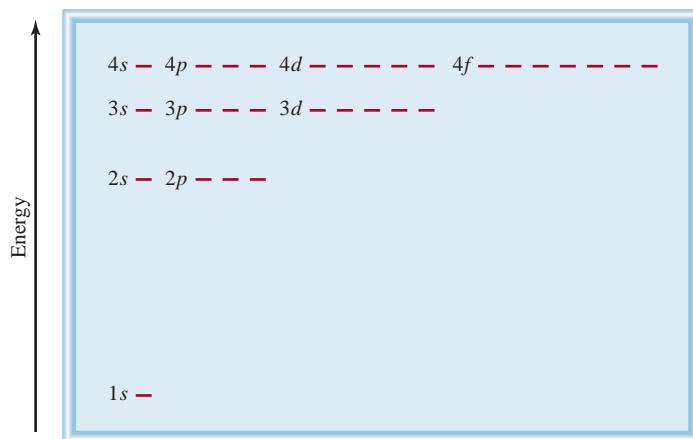
According to Equation (7.4), the energy of an electron in a hydrogen atom is determined solely by its principal quantum number. Thus, the energies of hydrogen orbitals increase as follows (Figure 7.19):

$$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < \dots$$

Although the electron density distributions are different in the  $2s$  and  $2p$  orbitals, hydrogen's electron has the same energy whether it is in the  $2s$  orbital or a  $2p$  orbital. The  $1s$  orbital in a hydrogen atom corresponds to the most stable condition, the ground state. An electron residing in this orbital is most strongly held by the nucleus because it is closest to the nucleus. An electron in the  $2s$ ,  $2p$ , or higher orbitals in a hydrogen atom is in an excited state.

**Figure 7.19**

*Orbital energy levels in the hydrogen atom. Each short horizontal line represents one orbital. Orbitals with the same principal quantum number ( $n$ ) all have the same energy.*



The energy picture is more complex for many-electron atoms than for hydrogen. The energy of an electron in such an atom depends on its angular momentum quantum number as well as on its principal quantum number (Figure 7.20). For many-electron atoms, the  $3d$  energy level is very close to the  $4s$  energy level. The total energy of an atom, however, depends not only on the sum of the orbital energies but also on the energy of repulsion between the electrons in these orbitals (each orbital can accommodate up to two electrons, as we will see in Section 7.8). It turns out that the total energy of an atom is lower when the  $4s$  subshell is filled before a  $3d$  subshell. Figure 7.21 depicts the order in which atomic orbitals are filled in a many-electron atom. We will consider specific examples in Section 7.8.

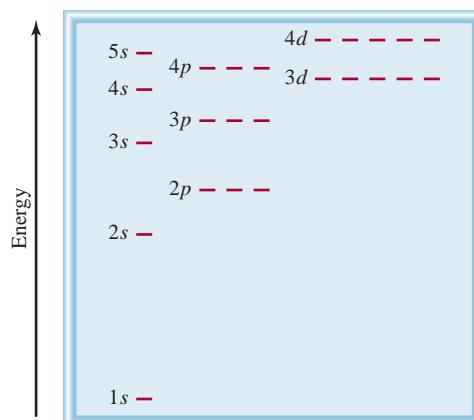
## 7.8 Electron Configuration



**Animation:**  
Electron Configurations  
Online Learning Center,  
Animations

**Figure 7.20**

*Orbital energy levels in a many-electron atom. Note that the energy level depends on both  $n$  and  $\ell$  values.*



so we use the simplified notation  $(n, \ell, m_\ell, m_s)$ . For the preceding example, the quantum numbers are either  $(2, 0, 0, +\frac{1}{2})$  or  $(2, 0, 0, -\frac{1}{2})$ . The value of  $m_s$  has no effect on the energy, size, shape, or orientation of an orbital, but it determines how electrons are arranged in an orbital.

## Example 7.7

Write the four quantum numbers for an electron in a  $3p$  orbital.

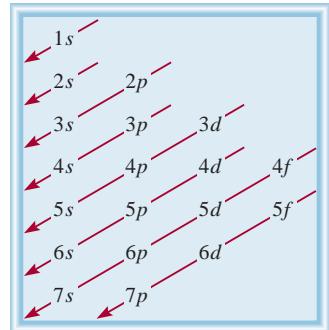
**Strategy** What do the “3” and “ $p$ ” designate in  $3p$ ? How many orbitals (values of  $m_\ell$ ) are there in a  $3p$  subshell? What are the possible values of electron spin quantum number?

**Solution** To start with, we know that the principal quantum number  $n$  is 3 and the angular momentum quantum number  $\ell$  must be 1 (because we are dealing with a  $p$  orbital). For  $\ell = 1$ , there are three values of  $m_\ell$  given by  $-1, 0$ , and  $1$ . Because the electron spin quantum number  $m_s$  can be either  $+\frac{1}{2}$  or  $-\frac{1}{2}$ , we conclude that there are six possible ways to designate the electron using the  $(n, \ell, m_\ell, m_s)$  notation:

$$\begin{array}{ll} (3, 1, -1, +\frac{1}{2}) & (3, 1, -1, -\frac{1}{2}) \\ (3, 1, 0, +\frac{1}{2}) & (3, 1, 0, -\frac{1}{2}) \\ (3, 1, 1, +\frac{1}{2}) & (3, 1, 1, -\frac{1}{2}) \end{array}$$

**Check** In these six designations we see that the values of  $n$  and  $\ell$  are constant, but the values of  $m_\ell$  and  $m_s$  can vary.

**Practice Exercise** Write the four quantum numbers for an electron in a  $4d$  orbital.



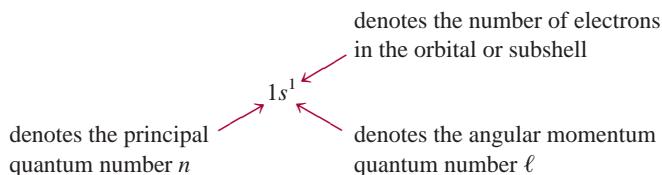
**Figure 7.21**

The order in which atomic subshells are filled in a many-electron atom. Start with the  $1s$  orbital and move downward, following the direction of the arrows. Thus, the order goes as follows:  $1s < 2s < 2p < 3s < 3p < 4s < 3d < \dots$

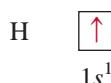
**Similar problem: 7.56.**

The hydrogen atom is a particularly simple system because it contains only one electron. The electron may reside in the 1s orbital (the ground state), or it may be found in some higher-energy orbital (an excited state). For many-electron atoms, however, we must know the ***electron configuration*** of the atom, that is, *how the electrons are distributed among the various atomic orbitals*, in order to understand electronic behavior. We will use the first 10 elements (hydrogen to neon) to illustrate the rules for writing electron configurations for atoms in the *ground state*. (Section 7.9 will describe how these rules can be applied to the remainder of the elements in the periodic table.) For this discussion, recall that the number of electrons in an atom is equal to its atomic number  $Z$ .

Figure 7.19 indicates that the electron in a ground-state hydrogen atom must be in the  $1s$  orbital, so its electron configuration is  $1s^1$ :



The electron configuration can also be represented by an *orbital diagram* that shows the spin of the electron (see Figure 7.14):



**Remember that the direction of electron spin has no effect on the energy of the electron.**

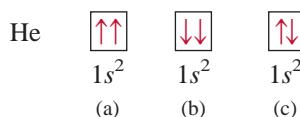
The upward arrow denotes one of the two possible spinning motions of the electron. (Alternatively, we could have represented the electron with a downward arrow.) The box represents an atomic orbital.



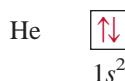
**Interactivity:**  
Pauli Exclusion Principle  
Online Learning Center,  
Interactives

## The Pauli Exclusion Principle

For many-electron atoms we use the **Pauli exclusion principle** (after the Austrian physicist Wolfgang Pauli) to determine electron configurations. This principle states that *no two electrons in an atom can have the same four quantum numbers*. If two electrons in an atom should have the same  $n$ ,  $\ell$ , and  $m_\ell$  values (that is, these two electrons are in the *same* atomic orbital), then they must have different values of  $m_s$ . In other words, only two electrons may occupy the same atomic orbital, and these electrons must have opposite spins. Consider the helium atom, which has two electrons. The three possible ways of placing two electrons in the  $1s$  orbital are as follows:



Diagrams (a) and (b) are ruled out by the Pauli exclusion principle. In (a), both electrons have the same upward spin and would have the quantum numbers  $(1, 0, 0, +\frac{1}{2})$ ; in (b), both electrons have downward spins and would have the quantum numbers  $(1, 0, 0, -\frac{1}{2})$ . Only the configuration in (c) is physically acceptable, because one electron has the quantum numbers  $(1, 0, 0, +\frac{1}{2})$  and the other has  $(1, 0, 0, -\frac{1}{2})$ . Thus, the helium atom has the following configuration:



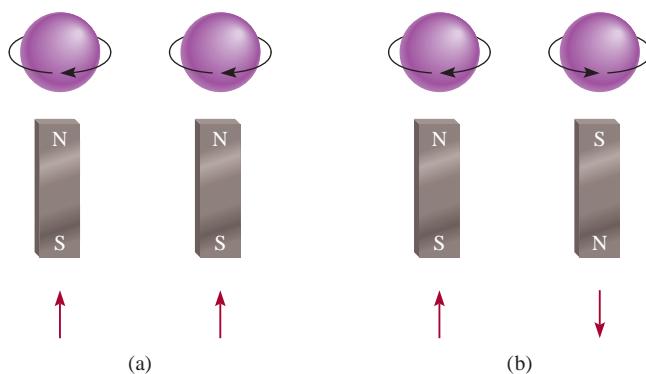
**Electrons that have opposite spins are said to be paired. In helium,  $m_s = +\frac{1}{2}$  for one electron;  $m_s = -\frac{1}{2}$  for the other.**

Note that  $1s^2$  is read “one s two,” not “one s squared.”

## Diamagnetism and Paramagnetism

The Pauli exclusion principle is one of the fundamental principles of quantum mechanics. It can be tested by a simple observation. If the two electrons in the  $1s$  orbital of a helium atom had the same, or parallel, spins ( $\uparrow\uparrow$  or  $\downarrow\downarrow$ ), their net magnetic fields would reinforce each other [Figure 7.22(a)]. Such an arrangement would

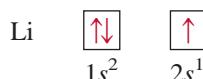
**Figure 7.22**  
The (a) parallel and (b) antiparallel spins of two electrons. In (a) the two magnetic fields reinforce each other. In (b) the two magnetic fields cancel each other.



make the helium gas paramagnetic. **Paramagnetic** substances are those that contain net unpaired spins and are attracted by a magnet. On the other hand, if the electron spins are paired, or antiparallel to each other ( $\uparrow\downarrow$  or  $\downarrow\uparrow$ ), the magnetic effects cancel out [Figure 7.22(b)]. **Diamagnetic** substances do not contain net unpaired spins and are slightly repelled by a magnet.

Measurements of magnetic properties provide the most direct evidence for specific electron configurations of elements. Advances in instrument design during the last 30 years or so enable us to determine the number of unpaired electrons in an atom (Figure 7.23). By experiment we find that the helium atom in its ground state has no net magnetic field. Therefore, the two electrons in the 1s orbital must be paired in accord with the Pauli exclusion principle, and the helium gas is diamagnetic. A useful rule to keep in mind is that any atom with an *odd* number of electrons will always contain one or more unpaired spins because we need an even number of electrons for complete pairing. On the other hand, atoms containing an even number of electrons may or may not contain unpaired spins. We will see the reason for this behavior shortly.

As another example, consider the lithium atom ( $Z = 3$ ) which has three electrons. The third electron cannot go into the 1s orbital because it would inevitably have the same four quantum numbers as one of the first two electrons. Therefore, this electron “enters” the next (energetically) higher orbital, which is the 2s orbital (see Figure 7.20). The electron configuration of lithium is  $1s^22s^1$ , and its orbital diagram is



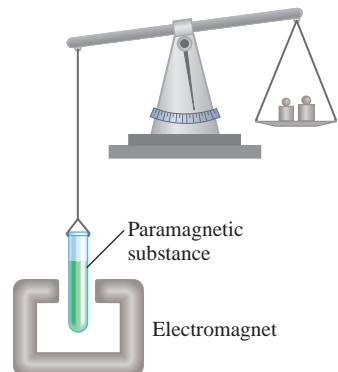
The lithium atom contains one unpaired electron and the lithium metal is therefore paramagnetic.

## The Shielding Effect in Many-Electron Atoms

Experimentally we find that the 2s orbital lies at a lower energy level than the 2p orbital in a many-electron atom. Why? In comparing the electron configurations of  $1s^22s^1$  and  $1s^22p^1$ , we note that, in both cases, the 1s orbital is filled with two electrons. Figure 7.24 shows the radial probability plots for the 1s, 2s, and 2p orbitals. Because the 2s and 2p orbitals are larger than the 1s orbital, an electron in either of these orbitals will spend more time away from the nucleus than an electron in the 1s orbital. Thus, we can speak of a 2s or 2p electron being partly “shielded” from the attractive force of the nucleus by the 1s electrons. The important consequence of the shielding effect is that it *reduces* the electrostatic attraction between the protons in the nucleus and the electron in the 2s or 2p orbital.

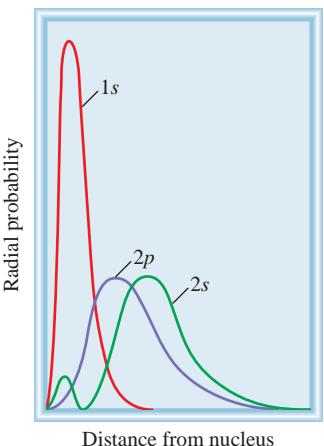
The manner in which the electron density varies as we move from the nucleus outward depends on the type of orbital. Although a 2s electron spends most of its time (on average) slightly farther from the nucleus than a 2p electron, the electron density near the nucleus is actually greater for the 2s electron (see the small maximum for the 2s orbital in Figure 7.24). For this reason, the 2s orbital is said to be more “penetrating” than the 2p orbital. Therefore, a 2s electron is less shielded by the 1s electrons and is more strongly held by the nucleus. In fact, for the same principal quantum number  $n$ , the penetrating power decreases as the angular momentum quantum number  $\ell$  increases, or

$$s > p > d > f > \dots$$



**Figure 7.23**

Initially the paramagnetic substance was weighed on a balance. When the electromagnet is turned on, the balance is offset because the sample tube is drawn into the magnetic field. Knowing the concentration and the additional mass needed to reestablish balance, it is possible to calculate the number of unpaired electrons in the substance.

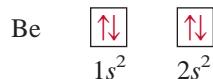


**Figure 7.24**

Radial probability plots for the 1s, 2s, and 2p orbitals. The 1s electrons effectively shield both the 2s and 2p electrons from the nucleus. The 2s orbital is more penetrating than the 2p orbital.

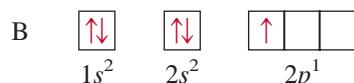
Because the stability of an electron is determined by the strength of its attraction to the nucleus, it follows that a  $2s$  electron will be lower in energy than a  $2p$  electron. To put it another way, less energy is required to remove a  $2p$  electron than a  $2s$  electron because a  $2p$  electron is not held quite as strongly by the nucleus. The hydrogen atom has only one electron and, therefore, is without such a shielding effect.

Continuing our discussion of atoms of the first 10 elements, we go next to beryllium ( $Z = 4$ ). The ground-state electron configuration of beryllium is  $1s^22s^2$ , or



Beryllium is diamagnetic, as we would expect.

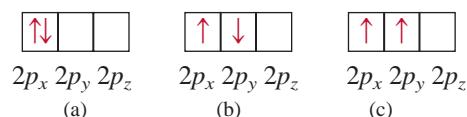
The electron configuration of boron ( $Z = 5$ ) is  $1s^22s^22p^1$ , or



Note that the unpaired electron can be in the  $2p_x$ ,  $2p_y$ , or  $2p_z$  orbital. The choice is completely arbitrary because the three  $p$  orbitals are equivalent in energy. As the diagram shows, boron is paramagnetic.

### Hund's Rule

The electron configuration of carbon ( $Z = 6$ ) is  $1s^22s^22p^2$ . The following are different ways of distributing two electrons among three  $p$  orbitals:



None of the three arrangements violates the Pauli exclusion principle, so we must determine which one will give the greatest stability. The answer is provided by **Hund's rule** (after the German physicist Frederick Hund), which states that *the most stable arrangement of electrons in subshells is the one with the greatest number of parallel spins*. The arrangement shown in (c) satisfies this condition. In both (a) and (b) the two spins cancel each other. Thus, the orbital diagram for carbon is



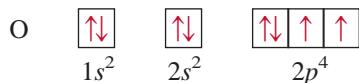
Qualitatively, we can understand why (c) is preferred to (a). In (a), the two electrons are in the same  $2p_x$  orbital, and their proximity results in a greater mutual repulsion than when they occupy two separate orbitals, say  $2p_x$  and  $2p_y$ . The choice of (c) over (b) is more subtle but can be justified on theoretical grounds. The fact that carbon atoms contain two unpaired electrons is in accord with Hund's rule.

The electron configuration of nitrogen ( $Z = 7$ ) is  $1s^22s^22p^3$ :

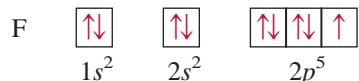


Again, Hund's rule dictates that all three  $2p$  electrons have spins parallel to one another; the nitrogen atom contains three unpaired electrons.

The electron configuration of oxygen ( $Z = 8$ ) is  $1s^22s^22p^4$ . An oxygen atom has two unpaired electrons:

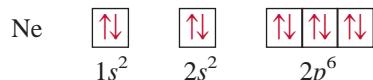


The electron configuration of fluorine ( $Z = 9$ ) is  $1s^22s^22p^5$ . The nine electrons are arranged as follows:



The fluorine atom has one unpaired electron.

In neon ( $Z = 10$ ), the  $2p$  subshell is completely filled. The electron configuration of neon is  $1s^22s^22p^6$ , and *all* the electrons are paired, as follows:



The neon gas should be diamagnetic, and experimental observation bears out this prediction.

## General Rules for Assigning Electrons to Atomic Orbitals

Based on the preceding examples we can formulate some general rules for determining the maximum number of electrons that can be assigned to the various subshells and orbitals for a given value of  $n$ :



**Interactivity:**  
Orbital Filling Rules  
Online Learning Center,  
Interactives

1. Each shell or principal level of quantum number  $n$  contains  $n$  subshells. For example, if  $n = 2$ , then there are two subshells (two values of  $\ell$ ) of angular momentum quantum numbers 0 and 1.
2. Each subshell of quantum number  $\ell$  contains  $(2\ell + 1)$  orbitals. For example, if  $\ell = 1$ , then there are three  $p$  orbitals.
3. No more than two electrons can be placed in each orbital. Therefore, the maximum number of electrons is simply twice the number of orbitals that are employed.
4. A quick way to determine the maximum number of electrons that an atom can have in a principal level  $n$  is to use the formula  $2n^2$ .

### Example 7.8

What is the maximum number of electrons that can be present in the principal level for which  $n = 3$ ?

**Strategy** We are given the principal quantum number ( $n$ ) so we can determine all the possible values of the angular momentum quantum number ( $\ell$ ). The preceding rule shows that the number of orbitals for each value of  $\ell$  is  $(2\ell + 1)$ . Thus, we can determine the total number of orbitals. How many electrons can each orbital accommodate?

(Continued)

**Solution** When  $n = 3$ ,  $\ell = 0, 1$ , and  $2$ . The number of orbitals for each value of  $\ell$  is given by

Value of $\ell$	Number of Orbitals	
		$(2\ell + 1)$
0		1
1		3
2		5

The total number of orbitals is nine. Because each orbital can accommodate two electrons, the maximum number of electrons that can reside in the orbitals is  $2 \times 9$ , or 18.

**Check** If we use the formula  $(n^2)$  in Example 7.6, we find that the total number of orbitals is  $3^2$  and the total number of electrons is  $2(3^2)$  or 18. In general, the number of electrons in a given principal energy level  $n$  is  $2n^2$ .

**Similar problems:** 7.62, 7.63.

**Practice Exercise** Calculate the total number of electrons that can be present in the principal level for which  $n = 4$ .

### Example 7.9

An oxygen atom has a total of eight electrons. Write the four quantum numbers for each of the eight electrons in the ground state.

**Strategy** We start with  $n = 1$  and proceed to fill orbitals in the order shown in Figure 7.21. For each value of  $n$  we determine the possible values of  $\ell$ . For each value of  $\ell$ , we assign the possible values of  $m_\ell$ . We can place electrons in the orbitals according to the Pauli exclusion principle and Hund's rule.

**Solution** We start with  $n = 1$ , so  $\ell = 0$ , a subshell corresponding to the  $1s$  orbital. This orbital can accommodate a total of two electrons. Next,  $n = 2$ , and  $\ell$  may be either 0 or 1. The  $\ell = 0$  subshell contains one  $2s$  orbital, which can accommodate two electrons. The remaining four electrons are placed in the  $\ell = 1$  subshell, which contains three  $2p$  orbitals. The orbital diagram is



The results are summarized in the following table:

Electron	$n$	$\ell$	$m_\ell$	$m_s$	Orbital
1	1	0	0	$+\frac{1}{2}$	$1s$
2	1	0	0	$-\frac{1}{2}$	
3	2	0	0	$+\frac{1}{2}$	$2s$
4	2	0	0	$-\frac{1}{2}$	
5	2	1	-1	$+\frac{1}{2}$	$2p_x, 2p_y, 2p_z$
6	2	1	0	$+\frac{1}{2}$	
7	2	1	1	$+\frac{1}{2}$	
8	2	1	1	$-\frac{1}{2}$	

Of course, the placement of the eighth electron in the orbital labeled  $m_\ell = 1$  is completely arbitrary. It would be equally correct to assign it to  $m_\ell = 0$  or  $m_\ell = -1$ .

**Similar problem:** 7.85.

**Practice Exercise** Write a complete set of quantum numbers for each of the electrons in boron (B).

At this point let's summarize what our examination has revealed about ground-state electron configurations and the properties of electrons in atoms:

- No two electrons in the same atom can have the same four quantum numbers. This is the Pauli exclusion principle.
- Each orbital can be occupied by a maximum of two electrons. They must have opposite spins, or different electron spin quantum numbers.
- The most stable arrangement of electrons in a subshell is the one that has the greatest number of parallel spins. This is Hund's rule.
- Atoms in which one or more electrons are unpaired are paramagnetic. Atoms in which all the electron spins are paired are diamagnetic.
- In a hydrogen atom, the energy of the electron depends only on its principal quantum number  $n$ . In a many-electron atom, the energy of an electron depends on both  $n$  and its angular momentum quantum number  $\ell$ .
- In a many-electron atom the subshells are filled in the order shown in Figure 7.21.
- For electrons of the same principal quantum number, their penetrating power, or proximity to the nucleus, decreases in the order  $s > p > d > f$ . This means that, for example, more energy is required to separate a  $3s$  electron from a many-electron atom than is required to remove a  $3p$  electron.

## 7.9 The Building-Up Principle

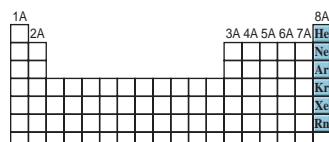
Here we will extend the rules used in writing electron configurations for the first 10 elements to the rest of the elements. This process is based on the Aufbau principle. The **Aufbau principle** dictates that *as protons are added one by one to the nucleus to build up the elements, electrons are similarly added to the atomic orbitals*. Through this process we gain a detailed knowledge of the ground-state electron configurations of the elements. As we will see later, knowledge of electron configurations helps us to understand and predict the properties of the elements; it also explains why the periodic table works so well.

Table 7.3 gives the ground-state electron configurations of elements from H ( $Z = 1$ ) through Rg ( $Z = 111$ ). The electron configurations of all elements except hydrogen and helium are represented by a **noble gas core**, which shows in brackets the noble gas element that most nearly precedes the element being considered, followed by the symbol for the highest filled subshells in the outermost shells. Notice that the electron configurations of the highest filled subshells in the outermost shells for the elements sodium ( $Z = 11$ ) through argon ( $Z = 18$ ) follow a pattern similar to those of lithium ( $Z = 3$ ) through neon ( $Z = 10$ ).

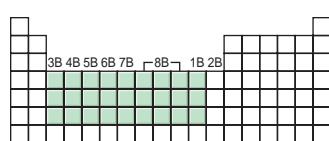
As mentioned in Section 7.7, the  $4s$  subshell is filled before the  $3d$  subshell in a many-electron atom (see Figure 7.21). Thus, the electron configuration of potassium ( $Z = 19$ ) is  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ . Because  $1s^2 2s^2 2p^6 3s^2 3p^6$  is the electron configuration of argon, we can simplify the electron configuration of potassium by writing  $[Ar]4s^1$ , where  $[Ar]$  denotes the “argon core.” Similarly, we can write the electron configuration of calcium ( $Z = 20$ ) as  $[Ar]4s^2$ . The placement of the outermost electron in the  $4s$  orbital (rather than in the  $3d$  orbital) of potassium is strongly supported by experimental evidence. The following comparison also suggests that this is the correct configuration. The chemistry of potassium is very similar to that of lithium and sodium, the first two alkali metals. The outermost electron of both lithium and sodium is in an  $s$  orbital (there is no ambiguity in assigning their electron configurations); therefore, we expect the last electron in potassium to occupy the  $4s$  rather than the  $3d$  orbital.

The elements from scandium ( $Z = 21$ ) to copper ( $Z = 29$ ) are transition metals. **Transition metals** either have incompletely filled  $d$  subshells or readily give rise to

The German word “Aufbau” means “building up.”



The noble gases.



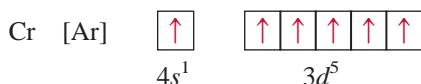
The transition metals.

**TABLE 7.3** The Ground-State Electron Configurations of the Elements\*

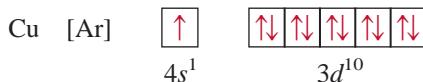
Atomic Number	Symbol	Electron Configuration	Atomic Number	Symbol	Electron Configuration	Atomic Number	Symbol	Electron Configuration
1	H	$1s^1$	38	Sr	$[Kr]5s^2$	75	Re	$[Xe]6s^24f^{14}5d^5$
2	He	$1s^2$	39	Y	$[Kr]5s^24d^1$	76	Os	$[Xe]6s^24f^{14}5d^6$
3	Li	$[He]2s^1$	40	Zr	$[Kr]5s^24d^2$	77	Ir	$[Xe]6s^24f^{14}5d^7$
4	Be	$[He]2s^2$	41	Nb	$[Kr]5s^14d^4$	78	Pt	$[Xe]6s^14f^{14}5d^9$
5	B	$[He]2s^22p^1$	42	Mo	$[Kr]5s^14d^5$	79	Au	$[Xe]6s^14f^{14}5d^{10}$
6	C	$[He]2s^22p^2$	43	Tc	$[Kr]5s^24d^5$	80	Hg	$[Xe]6s^24f^{14}5d^{10}$
7	N	$[He]2s^22p^3$	44	Ru	$[Kr]5s^14d^7$	81	Tl	$[Xe]6s^24f^{14}5d^{10}6p^1$
8	O	$[He]2s^22p^4$	45	Rh	$[Kr]5s^14d^8$	82	Pb	$[Xe]6s^24f^{14}5d^{10}6p^2$
9	F	$[He]2s^22p^5$	46	Pd	$[Kr]4d^{10}$	83	Bi	$[Xe]6s^24f^{14}5d^{10}6p^3$
10	Ne	$[He]2s^22p^6$	47	Ag	$[Kr]5s^14d^{10}$	84	Po	$[Xe]6s^24f^{14}5d^{10}6p^4$
11	Na	$[Ne]3s^1$	48	Cd	$[Kr]5s^24d^{10}$	85	At	$[Xe]6s^24f^{14}5d^{10}6p^5$
12	Mg	$[Ne]3s^2$	49	In	$[Kr]5s^24d^{10}5p^1$	86	Rn	$[Xe]6s^24f^{14}5d^{10}6p^6$
13	Al	$[Ne]3s^23p^1$	50	Sn	$[Kr]5s^24d^{10}5p^2$	87	Fr	$[Rn]7s^1$
14	Si	$[Ne]3s^23p^2$	51	Sb	$[Kr]5s^24d^{10}5p^3$	88	Ra	$[Rn]7s^2$
15	P	$[Ne]3s^23p^3$	52	Te	$[Kr]5s^24d^{10}5p^4$	89	Ac	$[Rn]7s^26d^1$
16	S	$[Ne]3s^23p^4$	53	I	$[Kr]5s^24d^{10}5p^5$	90	Th	$[Rn]7s^26d^2$
17	Cl	$[Ne]3s^23p^5$	54	Xe	$[Kr]5s^24d^{10}5p^6$	91	Pa	$[Rn]7s^25f^26d^1$
18	Ar	$[Ne]3s^23p^6$	55	Cs	$[Xe]6s^1$	92	U	$[Rn]7s^25f^36d^1$
19	K	$[Ar]4s^1$	56	Ba	$[Xe]6s^2$	93	Np	$[Rn]7s^25f^46d^1$
20	Ca	$[Ar]4s^2$	57	La	$[Xe]6s^25d^1$	94	Pu	$[Rn]7s^25f^6$
21	Sc	$[Ar]4s^23d^1$	58	Ce	$[Xe]6s^24f^15d^1$	95	Am	$[Rn]7s^25f^7$
22	Ti	$[Ar]4s^23d^2$	59	Pr	$[Xe]6s^24f^3$	96	Cm	$[Rn]7s^25f^76d^1$
23	V	$[Ar]4s^23d^3$	60	Nd	$[Xe]6s^24f^4$	97	Bk	$[Rn]7s^25f^9$
24	Cr	$[Ar]4s^13d^5$	61	Pm	$[Xe]6s^24f^5$	98	Cf	$[Rn]7s^25f^{10}$
25	Mn	$[Ar]4s^23d^5$	62	Sm	$[Xe]6s^24f^6$	99	Es	$[Rn]7s^25f^{11}$
26	Fe	$[Ar]4s^23d^6$	63	Eu	$[Xe]6s^24f^7$	100	Fm	$[Rn]7s^25f^{12}$
27	Co	$[Ar]4s^23d^7$	64	Gd	$[Xe]6s^24f^75d^1$	101	Md	$[Rn]7s^25f^{13}$
28	Ni	$[Ar]4s^23d^8$	65	Tb	$[Xe]6s^24f^9$	102	No	$[Rn]7s^25f^{14}$
29	Cu	$[Ar]4s^13d^{10}$	66	Dy	$[Xe]6s^24f^{10}$	103	Lr	$[Rn]7s^25f^{14}6d^1$
30	Zn	$[Ar]4s^23d^{10}$	67	Ho	$[Xe]6s^24f^{11}$	104	Rf	$[Rn]7s^25f^{14}6d^2$
31	Ga	$[Ar]4s^23d^{10}4p^1$	68	Er	$[Xe]6s^24f^{12}$	105	Db	$[Rn]7s^25f^{14}6d^3$
32	Ge	$[Ar]4s^23d^{10}4p^2$	69	Tm	$[Xe]6s^24f^{13}$	106	Sg	$[Rn]7s^25f^{14}6d^4$
33	As	$[Ar]4s^23d^{10}4p^3$	70	Yb	$[Xe]6s^24f^{14}$	107	Bh	$[Rn]7s^25f^{14}6d^5$
34	Se	$[Ar]4s^23d^{10}4p^4$	71	Lu	$[Xe]6s^24f^{14}5d^1$	108	Hs	$[Rn]7s^25f^{14}6d^6$
35	Br	$[Ar]4s^23d^{10}4p^5$	72	Hf	$[Xe]6s^24f^{14}5d^2$	109	Mt	$[Rn]7s^25f^{14}6d^7$
36	Kr	$[Ar]4s^23d^{10}4p^6$	73	Ta	$[Xe]6s^24f^{14}5d^3$	110	Ds	$[Rn]7s^25f^{14}6d^8$
37	Rb	$[Kr]5s^1$	74	W	$[Xe]6s^24f^{14}5d^4$	111	Rg	$[Rn]7s^25f^{14}6d^9$

\*The symbol [He] is called the helium core and represents  $1s^2$ . [Ne] is called the neon core and represents  $1s^22s^22p^6$ . [Ar] is called the argon core and represents  $[Ne]3s^23p^6$ . [Kr] is called the krypton core and represents  $[Ar]4s^23d^{10}4p^6$ . [Xe] is called the xenon core and represents  $[Kr]5s^24d^{10}5p^6$ . [Rn] is called the radon core and represents  $[Xe]6s^24f^{14}5d^{10}6p^6$ .

cations that have incompletely filled d subshells. Consider the first transition metal series, from scandium through copper. In this series additional electrons are placed in the 3d orbitals, according to Hund's rule. However, there are two irregularities. The electron configuration of chromium ( $Z = 24$ ) is  $[Ar]4s^13d^5$  and not  $[Ar]4s^23d^4$ , as we might expect. A similar break in the pattern is observed for copper, whose electron configuration is  $[Ar]4s^13d^{10}$  rather than  $[Ar]4s^23d^9$ . The reason for these irregularities is that a slightly greater stability is associated with the half-filled ( $3d^5$ ) and completely filled ( $3d^{10}$ ) subshells. Electrons in the same subshell (in this case, the d orbitals) have equal energy but different spatial distributions. Consequently, their shielding of one another is relatively small, and the electrons are more strongly attracted by the nucleus when they have the  $3d^5$  configuration. According to Hund's rule, the orbital diagram for Cr is



Thus, Cr has a total of six unpaired electrons. The orbital diagram for copper is



Again, extra stability is gained in this case by having the 3d subshell completely filled.

For elements Zn ( $Z = 30$ ) through Kr ( $Z = 36$ ), the 4s and 4p subshells fill in a straightforward manner. With rubidium ( $Z = 37$ ), electrons begin to enter the  $n = 5$  energy level.

The electron configurations in the second transition metal series [yttrium ( $Z = 39$ ) to silver ( $Z = 47$ )] are also irregular, but we will not be concerned with the details here.

The sixth period of the periodic table begins with cesium ( $Z = 55$ ) and barium ( $Z = 56$ ), whose electron configurations are  $[Xe]6s^1$  and  $[Xe]6s^2$ , respectively. Next we come to lanthanum ( $Z = 57$ ). From Figure 7.21 we would expect that after filling the 6s orbital we would place the additional electrons in 4f orbitals. In reality, the energies of the 5d and 4f orbitals are very close; in fact, for lanthanum 4f is slightly higher in energy than 5d. Thus, lanthanum's electron configuration is  $[Xe]6s^25d^1$  and not  $[Xe]6s^24f^1$ .

Following lanthanum are the 14 elements known as the *lanthanides*, or *rare earth series* [cerium ( $Z = 58$ ) to lutetium ( $Z = 71$ )]. The rare earth metals *have incompletely filled 4f subshells or readily give rise to cations that have incompletely filled 4f subshells*. In this series, the added electrons are placed in 4f orbitals. After the 4f subshell is completely filled, the next electron enters the 5d subshell of lutetium. Note that the electron configuration of gadolinium ( $Z = 64$ ) is  $[Xe]6s^24f^75d^1$  rather than  $[Xe]6s^24f^8$ . Like chromium, gadolinium gains extra stability by having a half-filled subshell ( $4f^7$ ).

The third transition metal series, including lanthanum and hafnium ( $Z = 72$ ) and extending through gold ( $Z = 79$ ), is characterized by the filling of the 5d subshell. With Hg ( $Z = 80$ ), both the 6s and 5d orbitals are now filled. The 6p subshell is filled next, which takes us to radon ( $Z = 86$ ).

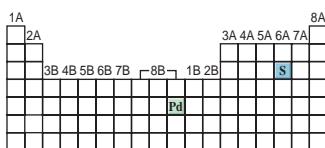
The *last row of elements* is the *actinide series*, which starts at thorium ( $Z = 90$ ). *Most of these elements are not found in nature but have been synthesized.*

With few exceptions, you should be able to write the electron configuration of any element, using Figure 7.21 as a guide. Elements that require particular care are the transition metals, the lanthanides, and the actinides. As we noted earlier, at larger values of the principal quantum number  $n$ , the order of subshell filling may reverse from one element to the next. Figure 7.25 groups the elements according to the type of subshell in which the outermost electrons are placed.

**Figure 7.25**

*Classification of groups of elements in the periodic table according to the type of subshell being filled with electrons.*

1s			1s
2s			2p
3s			3p
4s	3d		4p
5s	4d		5p
6s	5d		6p
7s	6d		7p
		4f	
		5f	



### Example 7.10

Write the ground-state electron configurations for (a) sulfur (S) and (b) palladium (Pd), which is diamagnetic.

**(a) Strategy** How many electrons are in the S ( $Z = 16$ ) atom? We start with  $n = 1$  and proceed to fill orbitals in the order shown in Figure 7.21. For each value of  $\ell$ , we assign the possible values of  $m_\ell$ . We can place electrons in the orbitals according to the Pauli exclusion principle and Hund's rule and then write the electron configuration. The task is simplified if we use the noble-gas core preceding S for the inner electrons.

**Solution** Sulfur has 16 electrons. The noble gas core in this case is [Ne]. (Ne is the noble gas in the period preceding sulfur.) [Ne] represents  $1s^22s^22p^6$ . This leaves us 6 electrons to fill the  $3s$  subshell and partially fill the  $3p$  subshell. Thus, the electron configuration of S is  $1s^22s^22p^63s^23p^4$  or  $[Ne]3s^23p^4$ .

**(b) Strategy** We use the same approach as that in (a). What does it mean to say that Pd is a diamagnetic element?

**Solution** Palladium has 46 electrons. The noble-gas core in this case is [Kr]. (Kr is the noble gas in the period preceding palladium.) [Kr] represents

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$

The remaining 10 electrons are distributed among the  $4d$  and  $5s$  orbitals. The three choices are (1)  $4d^{10}$ , (2)  $4d^95s^1$ , and (3)  $4d^85s^2$ . Because palladium is diamagnetic, all the electrons are paired and its electron configuration must be

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 4d^{10}$

or simply [Kr]4d<sup>10</sup>. The configurations in (2) and (3) both represent paramagnetic elements.

**Check** To confirm the answer, write the orbital diagrams for (1), (2), and (3).

**Practice Exercise** Write the ground-state electron configuration for phosphorus (P).

## KEY EQUATIONS

$$u = \lambda\nu \quad (7.1)$$

$$E = h\nu \quad (7.2)$$

$$E = h\frac{c}{\lambda} \quad (7.3)$$

$$E_n = -R_H \left( \frac{1}{n^2} \right) \quad (7.4)$$

$$\Delta E = h\nu = R_H \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \quad (7.5)$$

$$\lambda = \frac{h}{mu} \quad (7.7)$$

Relating speed of a wave to its wavelength and frequency.

Relating energy of a quantum (and of a photon) to the frequency.

Relating energy of a quantum (and of a photon) to the wavelength.

Energy of an electron in the  $n$ th state in a hydrogen atom.

Energy of a photon emitted (or absorbed) as the electron undergoes a transition from the  $n_i$  level to the  $n_f$  level.

Relating wavelength of a particle to its mass  $m$  and velocity  $u$ .

## SUMMARY OF FACTS AND CONCEPTS

1. The quantum theory developed by Planck successfully explains the emission of radiation by heated solids. The quantum theory states that radiant energy is emitted by atoms and molecules in small discrete amounts (quanta), rather than over a continuous range. This behavior is governed by the relationship  $E = h\nu$ , where  $E$  is the energy of the radiation,  $h$  is Planck's constant, and  $\nu$  is the frequency of the radiation. Energy is always emitted in whole-number multiples of  $h\nu$  ( $1 h\nu$ ,  $2 h\nu$ ,  $3 h\nu$ , ...).
2. Using quantum theory, Einstein solved another mystery of physics—the photoelectric effect. Einstein proposed that light can behave like a stream of particles (photons).
3. The line spectrum of hydrogen, yet another mystery to nineteenth-century physicists, was also explained by applying the quantum theory. Bohr developed a model of the hydrogen atom in which the energy of its single electron is quantized—limited to certain energy values determined by an integer, the principal quantum number.
4. An electron in its most stable energy state is said to be in the ground state, and an electron at an energy level higher than its most stable state is said to be in an excited state. In the Bohr model, an electron emits a photon when it drops from a higher-energy state (an excited state) to a lower-energy state (the ground state or another, less excited state). The release of specific amounts of energy in the form of photons accounts for the lines in the hydrogen emission spectrum.
5. De Broglie extended Einstein's wave-particle description of light to all matter in motion. The wavelength of a moving particle of mass  $m$  and velocity  $u$  is given by the de Broglie equation  $\lambda = h/mu$ .
6. The Schrödinger equation describes the motions and energies of submicroscopic particles. This equation launched quantum mechanics and a new era in physics.
7. The Schrödinger equation tells us the possible energy states of the electron in a hydrogen atom and the probability of its location in a particular region surrounding the nucleus. These results can be applied with reasonable accuracy to many-electron atoms.
8. An atomic orbital is a function ( $\psi$ ) that defines the distribution of electron density ( $\psi^2$ ) in space. Orbitals are represented by electron density diagrams or boundary surface diagrams.
9. Four quantum numbers characterize each electron in an atom: the principal quantum number  $n$  identifies the main energy level, or shell, of the orbital; the angular momentum quantum number  $\ell$  indicates the shape of the orbital; the magnetic quantum number  $m_\ell$  specifies the orientation of the orbital in space; and the electron spin quantum number  $m_s$  indicates the direction of the electron's spin on its own axis.
10. The single  $s$  orbital for each energy level is spherical and centered on the nucleus. The three  $p$  orbitals present

- at  $n = 2$  and higher; each has two lobes, and the pairs of lobes are arranged at right angles to one another. Starting with  $n = 3$ , there are five  $d$  orbitals, with more complex shapes and orientations.
- The energy of the electron in a hydrogen atom is determined solely by its principal quantum number. In many-electron atoms, the principal quantum number and the angular momentum quantum number together determine the energy of an electron.
  - No two electrons in the same atom can have the same four quantum numbers (the Pauli exclusion principle).
  - The most stable arrangement of electrons in a subshell is the one that has the greatest number of parallel spins (Hund's rule). Atoms with one or more unpaired electron spins are paramagnetic. Atoms in which all electrons are paired are diamagnetic.
  - The Aufbau principle provides the guideline for building up the elements. The periodic table classifies the elements according to their atomic numbers and thus also by the electronic configurations of their atoms.

## KEY WORDS

Actinide series, p. 235	Electromagnetic wave, p. 208	Hund's rule, p. 230	Photoelectric effect, p. 211
Amplitude, p. 207	Electron configuration, p. 227	Lanthanide (rare earth) series, p. 235	Photon, p. 211
Atomic orbital, p. 220	Electron density, p. 220	Line spectrum, p. 213	Quantum, p. 210
Aufbau principle, p. 233	Emission spectrum, p. 212	Many-electron atom, p. 220	Quantum numbers, p. 221
Boundary surface diagram, p. 223	Excited level (or state), p. 214	Noble gas core, p. 233	Rare earth series, p. 235
Diamagnetic, p. 229	Frequency ( $\nu$ ), p. 207	Node, p. 217	Transition metals, p. 233
Electromagnetic radiation, p. 208	Ground level (or state), p. 214	Paramagnetic, p. 229	Wave, p. 207
	Heisenberg uncertainty principle, p. 219	Pauli exclusion principle, p. 228	Wavelength ( $\lambda$ ), p. 207

## QUESTIONS AND PROBLEMS

### Quantum Theory and Electromagnetic Radiation

#### Review Questions

- What is a wave? Explain the following terms associated with waves: wavelength, frequency, amplitude.
- What are the units for wavelength and frequency of electromagnetic waves? What is the speed of light in meters per second and miles per hour?
- List the types of electromagnetic radiation, starting with the radiation having the longest wavelength and ending with the radiation having the shortest wavelength.
- Give the high and low wavelength values that define the visible region of the electromagnetic spectrum.
- Briefly explain Planck's quantum theory and explain what a quantum is. What are the units for Planck's constant?
- Give two everyday examples that illustrate the concept of quantization.

#### Problems

- (a) What is the wavelength (in nanometers) of light having a frequency of  $8.6 \times 10^{13}$  Hz? (b) What is the frequency (in Hz) of light having a wavelength of 566 nm?
- (a) What is the frequency of light having a wavelength of 456 nm? (b) What is the wavelength (in nanometers) of radiation having a frequency of  $2.45 \times 10^9$  Hz? (This is the type of radiation used in microwave ovens.)
- The average distance between Mars and Earth is about  $1.3 \times 10^8$  miles. How long would it take TV pictures transmitted from the *Viking* space vehicle on Mars' surface to reach Earth? (1 mile = 1.61 km.)
- How many minutes would it take a radio wave to travel from the planet Venus to Earth? (Average distance from Venus to Earth = 28 million miles.)
- The SI unit of time is the second, which is defined as 9,192,631,770 cycles of radiation associated with a certain emission process in the cesium atom. Calculate

the wavelength of this radiation (to three significant figures). In which region of the electromagnetic spectrum is this wavelength found?

- 7.12** The SI unit of length is the meter, which is defined as the length equal to 1,650,763.73 wavelengths of the light emitted by a particular energy transition in krypton atoms. Calculate the frequency of the light to three significant figures.

## The Photoelectric Effect

### Review Questions

- 7.13 Explain what is meant by the photoelectric effect.  
 7.14 What are photons? What role did Einstein's explanation of the photoelectric effect play in the development of the particle-wave interpretation of the nature of electromagnetic radiation?

### Problems

- 7.15 A photon has a wavelength of 624 nm. Calculate the energy of the photon in joules.  
**7.16** The blue color of the sky results from the scattering of sunlight by air molecules. The blue light has a frequency of about  $7.5 \times 10^{14}$  Hz. (a) Calculate the wavelength, in nm, associated with this radiation, and (b) calculate the energy, in joules, of a single photon associated with this frequency.  
 7.17 A photon has a frequency of  $6.0 \times 10^{14}$  Hz. (a) Convert this frequency into wavelength (nm). Does this frequency fall in the visible region? (b) Calculate the energy (in joules) of this photon. (c) Calculate the energy (in joules) of 1 mole of photons all with this frequency.  
**7.18** What is the wavelength, in nm, of radiation that has an energy content of  $1.0 \times 10^3$  kJ/mol? In which region of the electromagnetic spectrum is this radiation found?  
 7.19 When copper is bombarded with high-energy electrons, X rays are emitted. Calculate the energy (in joules) associated with the photons if the wavelength of the X rays is 0.154 nm.  
**7.20** A particular form of electromagnetic radiation has a frequency of  $8.11 \times 10^{14}$  Hz. (a) What is its wavelength in nanometers? In meters? (b) To what region of the electromagnetic spectrum would you assign it? (c) What is the energy (in joules) of one quantum of this radiation?

## Bohr's Theory of the Hydrogen Atom

### Review Questions

- 7.21 What are emission spectra? How do line spectra differ from continuous spectra?

- 7.22 What is an energy level? Explain the difference between ground state and excited state.  
 7.23 Briefly describe Bohr's theory of the hydrogen atom and how it explains the appearance of an emission spectrum. How does Bohr's theory differ from concepts of classical physics?  
 7.24 Explain the meaning of the negative sign in Equation (7.4).

### Problems

- 7.25 Explain why elements produce their own characteristic colors when they emit photons.  
**7.26** Some copper compounds emit green light when they are heated in a flame. How would you determine whether the light is of one wavelength or a mixture of two or more wavelengths?  
 7.27 Is it possible for a fluorescent material to emit radiation in the ultraviolet region after absorbing visible light? Explain your answer.  
**7.28** Explain how astronomers are able to tell which elements are present in distant stars by analyzing the electromagnetic radiation emitted by the stars.  
 7.29 Consider the following energy levels of a hypothetical atom:  
 $E_4$  \_\_\_\_\_  $-1.0 \times 10^{-19}$  J  
 $E_3$  \_\_\_\_\_  $-5.0 \times 10^{-19}$  J  
 $E_2$  \_\_\_\_\_  $-10 \times 10^{-19}$  J  
 $E_1$  \_\_\_\_\_  $-15 \times 10^{-19}$  J  
 (a) What is the wavelength of the photon needed to excite an electron from  $E_1$  to  $E_4$ ? (b) What is the energy (in joules) a photon must have in order to excite an electron from  $E_2$  to  $E_3$ ? (c) When an electron drops from the  $E_3$  level to the  $E_1$  level, the atom is said to undergo emission. Calculate the wavelength of the photon emitted in this process.  
**7.30** The first line of the Balmer series occurs at a wavelength of 656.3 nm. What is the energy difference between the two energy levels involved in the emission that results in this spectral line?  
 7.31 Calculate the wavelength (in nanometers) of a photon emitted by a hydrogen atom when its electron drops from the  $n = 5$  state to the  $n = 3$  state.  
**7.32** Calculate the frequency (Hz) and wavelength (nm) of the emitted photon when an electron drops from the  $n = 4$  to the  $n = 2$  level in a hydrogen atom.  
 7.33 Careful spectral analysis shows that the familiar yellow light of sodium lamps (such as street lamps) is made up of photons of two wavelengths, 589.0 nm and 589.6 nm. What is the difference in energy (in joules) between photons with these wavelengths?  
**7.34** An electron in the hydrogen atom makes a transition from an energy state of principal quantum numbers

$n_i$  to the  $n = 2$  state. If the photon emitted has a wavelength of 434 nm, what is the value of  $n_i$ ?

## Particle-Wave Duality

### Review Questions

- 7.35 Explain the statement, Matter and radiation have a “dual nature.”
- 7.36 How does de Broglie’s hypothesis account for the fact that the energies of the electron in a hydrogen atom are quantized?
- 7.37 Why is Equation (7.7) meaningful only for submicroscopic particles, such as electrons and atoms, and not for macroscopic objects?
- 7.38 Does a baseball in flight possess wave properties? If so, why can we not determine its wave properties?

### Problems

- 7.39 Thermal neutrons are neutrons that move at speeds comparable to those of air molecules at room temperature. These neutrons are most effective in initiating a nuclear chain reaction among  $^{235}\text{U}$  isotopes. Calculate the wavelength (in nm) associated with a beam of neutrons moving at  $7.00 \times 10^2$  m/s. (Mass of a neutron =  $1.675 \times 10^{-27}$  kg.)
- 7.40 Protons can be accelerated to speeds near that of light in particle accelerators. Estimate the wavelength (in nm) of such a proton moving at  $2.90 \times 10^8$  m/s. (Mass of a proton =  $1.673 \times 10^{-27}$  kg.)
- 7.41 What is the de Broglie wavelength, in cm, of a 12.4-g hummingbird flying at  $1.20 \times 10^2$  mph? (1 mile = 1.61 km.)
- 7.42 What is the de Broglie wavelength (in nm) associated with a 2.5-g Ping-Pong ball traveling 35 mph?

## Quantum Mechanics

### Review Questions

- 7.43 What are the inadequacies of Bohr’s theory?
- 7.44 What is the Heisenberg uncertainty principle? What is the Schrödinger equation?
- 7.45 What is the physical significance of the wave function?
- 7.46 How is the concept of electron density used to describe the position of an electron in the quantum mechanical treatment of an atom?
- 7.47 What is an atomic orbital? How does an atomic orbital differ from an orbit?
- 7.48 Describe the characteristics of an  $s$  orbital, a  $p$  orbital, and a  $d$  orbital. Which of the following orbitals do not exist:  $1p$ ,  $2s$ ,  $2d$ ,  $3p$ ,  $3d$ ,  $3f$ ,  $4g$ ?
- 7.49 Why is a boundary surface diagram useful in representing an atomic orbital?

- 7.50 Describe the four quantum numbers used to characterize an electron in an atom.
- 7.51 Which quantum number defines a shell? Which quantum numbers define a subshell?
- 7.52 Which of the four quantum numbers ( $n$ ,  $\ell$ ,  $m_\ell$ ,  $m_s$ ) determine (a) the energy of an electron in a hydrogen atom and in a many-electron atom, (b) the size of an orbital, (c) the shape of an orbital, (d) the orientation of an orbital in space?

### Problems

- 7.53 An electron in a certain atom is in the  $n = 2$  quantum level. List the possible values of  $\ell$  and  $m_\ell$  that it can have.
- 7.54 An electron in an atom is in the  $n = 3$  quantum level. List the possible values of  $\ell$  and  $m_\ell$  that it can have.
- 7.55 Give the values of the quantum numbers associated with the following orbitals: (a)  $2p$ , (b)  $3s$ , (c)  $5d$ .
- 7.56 Give the values of the four quantum numbers of an electron in the following orbitals: (a)  $3s$ , (b)  $4p$ , (c)  $3d$ .
- 7.57 Discuss the similarities and differences between a  $1s$  and a  $2s$  orbital.
- 7.58 What is the difference between a  $2p_x$  and a  $2p_y$  orbital?
- 7.59 List all the possible subshells and orbitals associated with the principal quantum number  $n$ , if  $n = 5$ .
- 7.60 List all the possible subshells and orbitals associated with the principal quantum number  $n$ , if  $n = 6$ .
- 7.61 Calculate the total number of electrons that can occupy (a) one  $s$  orbital, (b) three  $p$  orbitals, (c) five  $d$  orbitals, (d) seven  $f$  orbitals.
- 7.62 What is the total number of electrons that can be held in all orbitals having the same principal quantum number  $n$ ?
- 7.63 Determine the maximum number of electrons that can be found in each of the following subshells:  $3s$ ,  $3d$ ,  $4p$ ,  $4f$ ,  $5f$ .
- 7.64 Indicate the total number of (a)  $p$  electrons in N ( $Z = 7$ ); (b)  $s$  electrons in Si ( $Z = 14$ ); and (c)  $3d$  electrons in S ( $Z = 16$ ).
- 7.65 Make a chart of all allowable orbitals in the first four principal energy levels of the hydrogen atom. Designate each by type (for example,  $s$ ,  $p$ ) and indicate how many orbitals of each type there are.
- 7.66 Why do the  $3s$ ,  $3p$ , and  $3d$  orbitals have the same energy in a hydrogen atom but different energies in a many-electron atom?
- 7.67 For each of the following pairs of hydrogen orbitals, indicate which is higher in energy: (a)  $1s$ ,  $2s$ ; (b)  $2p$ ,  $3p$ ; (c)  $3d_{xy}$ ,  $3d_{yz}$ ; (d)  $3s$ ,  $3d$ ; (e)  $4f$ ,  $5s$ .
- 7.68 Which orbital in each of the following pairs is lower in energy in a many-electron atom? (a)  $2s$ ,  $2p$ ; (b)  $3p$ ,  $3d$ ; (c)  $3s$ ,  $4s$ ; (d)  $4d$ ,  $5f$ .

## Atomic Orbitals

### Review Questions

- 7.69 Describe the shapes of *s*, *p*, and *d* orbitals. How are these orbitals related to the quantum numbers *n*, *l*, and *m<sub>l</sub>*?
- 7.70 List the hydrogen orbitals in increasing order of energy.

## Electron Configuration

### Review Questions

- 7.71 What is electron configuration? Describe the roles that the Pauli exclusion principle and Hund's rule play in writing the electron configuration of elements.
- 7.72 Explain the meaning of the symbol  $4d^6$ .
- 7.73 Explain the meaning of diamagnetic and paramagnetic. Give an example of an element that is diamagnetic and one that is paramagnetic. What does it mean when we say that electrons are paired?
- 7.74 What is meant by the term "shielding of electrons" in an atom? Using the Li atom as an example, describe the effect of shielding on the energy of electrons in an atom.
- 7.75 Define the following terms and give an example of each: transition metals, lanthanides, actinides.
- 7.76 Explain why the ground-state electron configurations of Cr and Cu are different from what we might expect.
- 7.77 Explain what is meant by a noble gas core. Write the electron configuration of a xenon core.
- 7.78 Comment on the correctness of the following statement: The probability of finding two electrons with the same four quantum numbers in an atom is zero.

### Problems

- 7.79 Indicate which of the following sets of quantum numbers in an atom are unacceptable and explain why: (a)  $(1, 0, \frac{1}{2}, \frac{1}{2})$ , (b)  $(3, 0, 0, +\frac{1}{2})$ , (c)  $(2, 2, 1, +\frac{1}{2})$ , (d)  $(4, 3, -2, +\frac{1}{2})$ , (e)  $(3, 2, 1, 1)$ .
- 7.80** The ground-state electron configurations listed here are incorrect. Explain what mistakes have been made in each and write the correct electron configurations.  
 A:  $1s^2 2s^2 2p^4 3s^2 3p^3$   
 B:  $1s^2 2s^2 2p^5$   
 F:  $1s^2 2s^2 2p^6$
- 7.81 The atomic number of an element is 73. Is this element diamagnetic or paramagnetic?

**7.82** Indicate the number of unpaired electrons present in each of the following atoms: B, Ne, P, Sc, Mn, Se, Kr, Fe, Cd, I, Pb.

**7.83** Write the ground-state electron configurations for the following elements: B, V, Ni, As, I, Au.

**7.84** Write the ground-state electron configurations for the following elements: Ge, Fe, Zn, Ni, W, Tl.

**7.85** The electron configuration of a neutral atom is  $1s^2 2s^2 2p^6 3s^2$ . Write a complete set of quantum numbers for each of the electrons. Name the element.

**7.86** Which of the following species has the most unpaired electrons? S<sup>+</sup>, S, or S<sup>-</sup>. Explain how you arrive at your answer.

## The Aufbau Principle

### Review Questions

- 7.87 State the Aufbau principle and explain the role it plays in classifying the elements in the periodic table.
- 7.88 Describe the characteristics of the following groups of elements: transition metals, lanthanides, actinides.
- 7.89 What is the noble gas core? How does it simplify the writing of electron configurations?
- 7.90 What are the group and period of the element osmium?

### Problems

- 7.91 Use the Aufbau principle to obtain the ground-state electron configuration of selenium.
- 7.92** Use the Aufbau principle to obtain the ground-state electron configuration of technetium.

## Additional Problems

7.93 When a compound containing cesium ion is heated in a Bunsen burner flame, photons with an energy of  $4.30 \times 10^{-19}$  J are emitted. What color is the cesium flame?

**7.94** What is the maximum number of electrons in an atom that can have the following quantum numbers? Specify the orbitals in which the electrons would be found. (a)  $n = 2, m_s = +\frac{1}{2}$ ; (b)  $n = 4, m_e = +1$ ; (c)  $n = 3, l = 2$ ; (d)  $n = 2, l = 0, m_s = -\frac{1}{2}$ ; (e)  $n = 4, l = 3, m_e = -2$ .

7.95 Identify the following individuals and their contributions to the development of quantum theory: Bohr, de Broglie, Einstein, Planck, Heisenberg, Schrödinger.

**7.96** What properties of electrons are used in the operation of an electron microscope?

7.97 How many photons at 660 nm must be absorbed to melt  $5.0 \times 10^2$  g of ice? On average, how many H<sub>2</sub>O molecules does one photon convert from ice to water? (*Hint:* It takes 334 J to melt 1 g of ice at 0°C.)

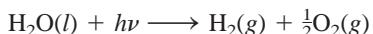
7.98 A certain pitcher's fastballs have been clocked at about 100 mph. (a) Calculate the wavelength of a 0.141-kg baseball (in nm) at this speed. (b) What is the wavelength of a hydrogen atom at the same speed? (1 mile = 1609 m.)

7.99 Considering only the ground-state electron configuration, are there more diamagnetic or paramagnetic elements? Explain.

7.100 A ruby laser produces radiation of wavelength 633 nm in pulses whose duration is  $1.00 \times 10^{-9}$  s. (a) If the laser produces 0.376 J of energy per pulse, how many photons are produced in each pulse? (b) Calculate the power (in watts) delivered by the laser per pulse. (1 W = 1 J/s.)

7.101 A 368-g sample of water absorbs infrared radiation at  $1.06 \times 10^4$  nm from a carbon dioxide laser. Suppose all the absorbed radiation is converted to heat. Calculate the number of photons at this wavelength required to raise the temperature of the water by 5.00°C.

### 7.102 Photodissociation of water



has been suggested as a source of hydrogen. The  $\Delta H_{rxn}^\circ$  for the reaction, calculated from thermochemical data, is 285.8 kJ per mole of water decomposed. Calculate the maximum wavelength (in nm) that would provide the necessary energy. In principle, is it feasible to use sunlight as a source of energy for this process?

7.103 Spectral lines of the Lyman and Balmer series do not overlap. Verify this statement by calculating the longest wavelength associated with the Lyman series and the shortest wavelength associated with the Balmer series (in nm).

7.104 Only a fraction of the electrical energy supplied to a tungsten lightbulb is converted to visible light. The rest of the energy shows up as infrared radiation (that is, heat). A 75-W lightbulb converts 15.0 percent of the energy supplied to it into visible light (assume the wavelength to be 550 nm). How many photons are emitted by the lightbulb per second? (1 W = 1 J/s.)

7.105 A microwave oven operating at  $1.22 \times 10^8$  nm is used to heat 150 mL of water (roughly the volume of a tea cup) from 20°C to 100°C. Calculate the number of photons needed if 92.0 percent of microwave energy is converted to the thermal energy of water.

7.106 The He<sup>+</sup> ion contains only one electron and is therefore a hydrogen-like ion. Calculate the wavelengths, in increasing order, of the first four transitions in the Balmer series of the He<sup>+</sup> ion. Compare these wavelengths with the same transitions in a H atom. Comment on the differences. (The Rydberg constant for He<sup>+</sup> is  $8.72 \times 10^{-18}$  J.)

7.107 Ozone (O<sub>3</sub>) in the stratosphere absorbs the harmful radiation from the sun by undergoing decomposition: O<sub>3</sub> → O + O<sub>2</sub>. (a) Referring to Table 6.4, calculate the  $\Delta H^\circ$  for this process. (b) Calculate the maximum wavelength of photons (in nm) that possess this energy to cause the decomposition of ozone photochemically.

7.108 The retina of a human eye can detect light when radiant energy incident on it is at least  $4.0 \times 10^{-17}$  J. For light of 600-nm wavelength, how many photons does this correspond to?

7.109 An electron in an excited state in a hydrogen atom can return to the ground state in two different ways: (a) via a direct transition in which a photon of wavelength  $\lambda_1$  is emitted and (b) via an intermediate excited state reached by the emission of a photon of wavelength  $\lambda_2$ . This intermediate excited state then decays to the ground state by emitting another photon of wavelength  $\lambda_3$ . Derive an equation that relates  $\lambda_1$  to  $\lambda_2$  and  $\lambda_3$ .

7.110 A photoelectric experiment was performed by separately shining a laser at 450 nm (blue light) and a laser at 560 nm (yellow light) on a clean metal surface and measuring the number and kinetic energy of the ejected electrons. Which light would generate more electrons? Which light would eject electrons with greater kinetic energy? Assume that the same amount of energy is delivered to the metal surface by each laser and that the frequencies of the laser lights exceed the threshold frequency.

7.111 The UV light that is responsible for tanning the skin falls in the 320- to 400-nm region. Calculate the total energy (in joules) absorbed by a person exposed to this radiation for 2.0 h, given that there are  $2.0 \times 10^{16}$  photons hitting Earth's surface per square centimeter per second over a 80-nm (320 nm to 400 nm) range and that the exposed body area is 0.45 m<sup>2</sup>. Assume that only half of the radiation is absorbed and the other half is reflected by the body. (*Hint:* Use an average wavelength of 360 nm in calculating the energy of a photon.)

7.112 Calculate the wavelength of a helium atom whose speed is equal to the root-mean-square speed at 20°C.

7.113 The sun is surrounded by a white circle of gaseous material called the corona, which becomes visible during a total eclipse of the sun. The temperature

of the corona is in the millions of degrees Celsius, which is high enough to break up molecules and remove some or all of the electrons from atoms. One way astronomers have been able to estimate the temperature of the corona is by studying the emission lines of ions of certain elements. For example, the emission spectrum of  $\text{Fe}^{14+}$  ions has been recorded and analyzed. Knowing that it takes

$3.5 \times 10^4 \text{ kJ/mol}$  to convert  $\text{Fe}^{13+}$  to  $\text{Fe}^{14+}$ , estimate the temperature of the sun's corona. (*Hint:* The average kinetic energy of one mole of a gas is  $\frac{3}{2}RT$ .)

- 7.114** The radioactive Co-60 isotope is used in nuclear medicine to treat certain types of cancer. Calculate the wavelength and frequency of an emitted gamma particle having the energy of  $1.29 \times 10^{11} \text{ J/mol}$ .

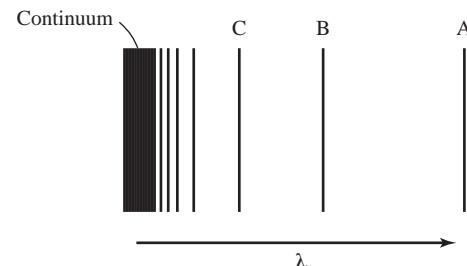
## SPECIAL PROBLEMS

- 7.115** An electron in a hydrogen atom is excited from the ground state to the  $n = 4$  state. Comment on the correctness of the following statements (true or false).

- $n = 4$  is the first excited state.
- It takes more energy to ionize (remove) the electron from  $n = 4$  than from the ground state.
- The electron is farther from the nucleus (on average) in  $n = 4$  than from the ground state.
- The wavelength of light emitted when the electron drops from  $n = 4$  to  $n = 1$  is longer than that from  $n = 4$  to  $n = 2$ .
- The wavelength the atom absorbs in going from  $n = 1$  to  $n = 4$  is the same as that emitted as it goes from  $n = 4$  to  $n = 1$ .

- 7.116** When an electron makes a transition between energy levels of a hydrogen atom, there are no restrictions on the initial and final values of the principal quantum number  $n$ . However, there is a quantum mechanical rule that restricts the initial and final values of the orbital angular momentum  $\ell$ . This is the *selection rule*, which states that  $\Delta\ell = \pm 1$ , that is, in a transition, the value of  $\ell$  can only increase or decrease by one. According to this rule, which of the following transitions are allowed: (a)  $1s \rightarrow 2s$ , (b)  $2p \rightarrow 1s$ , (c)  $1s \rightarrow 3d$ , (d)  $3d \rightarrow 4f$ , (e)  $4d \rightarrow 3s$ ?

- 7.117** For hydrogen-like ions, that is, ions containing only one electron, Equation (7.4) is modified as follows:  $E_n = -R_H Z^2(1/n^2)$ , where  $Z$  is the atomic number of the parent atom. The figure here represents the emission spectrum of such a hydrogen-like ion in the gas phase. All the lines result from the electronic transitions from the excited states to the  $n = 2$  state. (a) What electronic transitions correspond to lines B and C? (b) If the wavelength of line C is 27.1 nm, calculate the wavelengths of lines A and B. (c) Calculate the energy needed to remove the electron from the ion in the  $n = 4$  state. (d) What is the physical significance of the continuum?



- 7.118** Calculate the energies needed to remove an electron from the  $n = 1$  state and the  $n = 5$  state in the  $\text{Li}^{2+}$  ion. What is the wavelength (in nm) of the emitted photon in a transition from  $n = 5$  to  $n = 1$ ? The Rydberg constant for hydrogen-like ions is  $(2.18 \times 10^{-18} \text{ J})Z^2$ , where  $Z$  is the atomic number.

- 7.119** According to Einstein's special theory of relativity, the mass of a moving particle,  $m_{\text{moving}}$ , is related to its mass at rest,  $m_{\text{rest}}$ , by the following equation

$$m_{\text{moving}} = \frac{m_{\text{rest}}}{\sqrt{1 - \left(\frac{u}{c}\right)^2}}$$

where  $u$  and  $c$  are the speeds of the particle and light, respectively. (a) In particle accelerators, protons, electrons, and other charged particles are often accelerated to speeds close to the speed of light. Calculate the wavelength (in nm) of a proton moving at 50.0 percent the speed of light. The mass of a proton is  $1.673 \times 10^{-27} \text{ kg}$ . (b) Calculate the mass of a  $6.0 \times 10^{-2} \text{ kg}$  tennis ball moving at 63 m/s. Comment on your results.

- 7.120** The mathematical equation for studying the photoelectric effect is

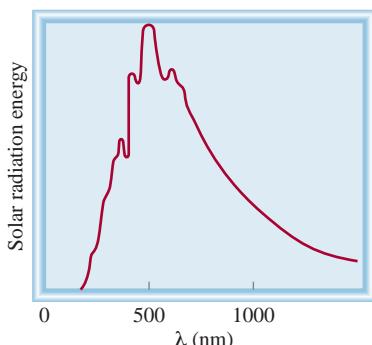
$$h\nu = W + \frac{1}{2}m_e u^2$$

where  $\nu$  is the frequency of light shining on the metal,  $W$  is the work function (see p. 211),  $m_e$  and  $u$  are the mass and speed of the ejected electron. In an experiment, a student found that a maximum

wavelength of 351 nm is needed to just dislodge electrons from a zinc metal surface. Calculate the velocity (in m/s) of an ejected electron when she employed light with a wavelength of 313 nm.

- 7.121 Blackbody radiation is the term used to describe the dependence of the radiation energy emitted by an object on wavelength at a certain temperature. Planck proposed the quantum theory to account for this dependence. Shown in the figure is a plot of the radiation energy emitted by our sun versus wavelength. This curve is characteristic of objects at about 6000 K, which is the temperature at the surface of the sun. At a higher temperature, the curve has a similar shape but the maximum will shift to a shorter wavelength. (a) What does this curve reveal about two consequences of great biological signifi-

cance on Earth? (b) How are astronomers able to determine the temperature at the surface of stars in general?



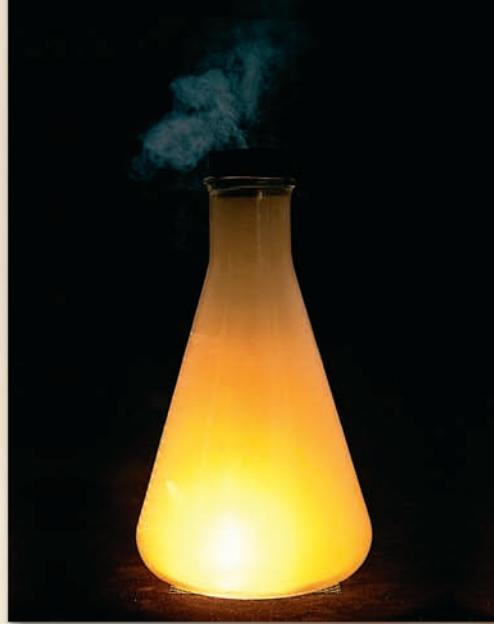
## ANSWERS TO PRACTICE EXERCISES

**7.1** 8.24 m. **7.2**  $3.39 \times 10^3$  nm. **7.3**  $2.63 \times 10^3$  nm.

**7.4** 56.6 nm. **7.5**  $n = 3$ ,  $\ell = 1$ ,  $m_\ell = -1, 0, 1$ . **7.6** 16.

**7.7**  $(4, 2, -2, +\frac{1}{2})$ ,  $(4, 2, -1, +\frac{1}{2})$ ,  $(4, 2, 0, +\frac{1}{2})$ ,  $(4, 2, 1, +\frac{1}{2})$ ,  $(4, 2, 2, +\frac{1}{2})$ . Five more with  $m_s = -\frac{1}{2}$ . **7.8** 32.

**7.9**  $(1, 0, 0, +\frac{1}{2})$ ,  $(1, 0, 0, -\frac{1}{2})$ ,  $(2, 0, 0, +\frac{1}{2})$ ,  $(2, 0, 0, -\frac{1}{2})$ ,  $(2, 1, -1, +\frac{1}{2})$ . There are five other acceptable ways to write the quantum numbers for the last electron. **7.10** [Ne]3s<sup>2</sup>3p<sup>3</sup>.



## The Periodic Table

### CHAPTER OUTLINE

- 8.1 Development of the Periodic Table 246
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  - General Trends in Chemical Properties • Properties of Oxides Across a Period

### ESSENTIAL CONCEPTS

**Development of the Periodic Table** In the nineteenth century, chemists noticed a regular, periodic recurrence of chemical and physical properties of elements. In particular, the periodic table drawn up by Mendeleev grouped the elements accurately and was able to predict the properties of several elements that had not yet been discovered.

**Periodic Classification of the Elements** Elements are grouped according to their outer-shell electron configurations, which account for their similar chemical behavior. Special names are assigned to these various groups.

**Periodic Variation in Properties** Overall, physical properties such as atomic and ionic radii of the elements vary in a regular and periodic fashion. Similar variation is also noted in their chemical properties. Chemical properties of special importance are ionization energy, which measures the tendency of an atom of an element to lose an electron, and electron affinity, which measures the tendency of an atom to accept an electron. Ionization energy and electron affinity form the basis for understanding chemical bond formation.

### Interactive Activity Summary

- 1. Interactivity: Attraction of Nucleus (8.3)
- 2. Animation: Atomic and Ionic Radius (8.3)
- 3. Interactivity: Atomic Radii (8.3)
- 4. Interactivity: Ionic Radii (8.3)
- 5. Interactivity: Ionization Energy (8.4)

## 8.1 Development of the Periodic Table

In the nineteenth century, when chemists had only a vague idea of atoms and molecules and did not know of the existence of electrons and protons, they devised the periodic table using their knowledge of atomic masses. Accurate measurements of the atomic masses of many elements had already been made. Arranging elements according to their atomic masses in a periodic table seemed logical to chemists, who felt that chemical behavior should somehow be related to atomic mass.

In 1864 the English chemist John Newlands noticed that when the known elements were arranged in order of atomic mass, every eighth element had similar properties. Newlands referred to this peculiar relationship as the *law of octaves*. However, this “law” turned out to be inadequate for elements beyond calcium, and Newlands’s work was not accepted by the scientific community.

Five years later the Russian chemist Dmitri Mendeleev and the German chemist Lothar Meyer independently proposed a much more extensive tabulation of the elements, based on the regular, periodic recurrence of properties. Mendeleev’s classification was a great improvement over Newlands’s for two reasons. First, it grouped the elements together more accurately, according to their properties. Equally important, it made possible the prediction of the properties of several elements that had not yet been discovered. For example, Mendeleev proposed the existence of an unknown element that he called eka-aluminum. (*Eka* is a Sanskrit word meaning “first”; thus, eka-aluminum would be the first element under aluminum in the same group.) When gallium was discovered 4 years later, its properties closely matched the predicted properties of eka-aluminum as shown here.



Gallium melts in a person’s hand (body temperature is about 37°C).

	Eka-Aluminum (Ea)	Gallium (Ga)
Atomic mass	68 amu	69.9 amu
Melting point	Low	29.78°C
Density	5.9 g/cm <sup>3</sup>	5.94 g/cm <sup>3</sup>
Formula of oxide	Ea <sub>2</sub> O <sub>3</sub>	Ga <sub>2</sub> O <sub>3</sub>

Nevertheless, the early versions of the periodic table had some glaring inconsistencies. For example, the atomic mass of argon (39.95 amu) is greater than that of potassium (39.10 amu). If elements were arranged solely according to increasing atomic mass, argon would appear in the position occupied by potassium in our modern periodic table (see the inside front cover). But no chemist would place argon, an inert gas, in the same group as lithium and sodium, two very reactive metals. This and other discrepancies suggested that some fundamental property other than atomic mass is the basis of the observed periodicity. This property turned out to be associated with atomic number.

Using data from  $\alpha$ -scattering experiments (see Section 2.2), Rutherford was able to estimate the number of positive charges in the nucleus of a few elements, but until 1913 there was no general procedure for determining atomic numbers. In that year a young English physicist, Henry Moseley, discovered a correlation between atomic number and the frequency of X rays generated by the bombardment of the element under study with high-energy electrons. With a few exceptions, Moseley found that the order of increasing atomic number is the same as the order of increasing atomic mass. For example, calcium is the twentieth element in increasing order of atomic mass, and it has an atomic number of 20. The discrepancies that bothered scientists now made sense. The atomic number of argon is 18 and that of potassium is 19, so potassium should follow argon in the periodic table.

A modern periodic table usually shows the atomic number along with the element symbol. As you already know, the atomic number also indicates the number of electrons in the atoms of an element. Electron configurations of elements help explain the recurrence of physical and chemical properties. The importance and usefulness of the periodic table lie in the fact that we can use our understanding of the general properties and trends within a group or a period to predict with considerable accuracy the properties of any element, even though that element may be unfamiliar to us.

**Appendix 4 explains the names and symbols of the elements.**

## 8.2 Periodic Classification of the Elements

Figure 8.1 shows the periodic table together with the outermost ground-state electron configurations of the elements. (The electron configurations of the elements are also given in Table 7.3.) Starting with hydrogen, we see that the subshells are filled in the order shown in Figure 7.21. According to the type of subshell being filled, the elements can be divided into categories—the representative elements, the noble gases, the transition elements (or transition metals), the lanthanides, and the actinides. Referring to Figure 8.1, the **representative elements** (also called *main group elements*) are the *elements in Groups 1A through 7A, all of which have incompletely filled s or p subshells of the highest principal quantum number*. With the exception of helium, the **noble gases** (the Group 8A elements) all have a completely filled p subshell. (The electron configurations are  $1s^2$  for helium and  $ns^2np^6$  for the other noble gases, in

1 1A 1 H $1s^1$	2 2A 2 Be $2s^2$	3 3B 3 Li $2s^1$	4 4B 4 Be $2s^2$	5 5B 5 Na $3s^1$	6 6B 6 Mg $3s^2$	7 7B 7 F $2s^1$	8 8B 8 O $2s^2$	13 3A 13 Al $3s^23p^1$	14 4A 14 Si $3s^23p^2$	15 5A 15 P $3s^23p^3$	16 6A 16 S $3s^23p^4$	17 7A 17 Cl $3s^23p^5$	18 8A 18 Ar $3s^23p^6$
19 K $4s^1$	20 Ca $4s^2$	21 Sc $4s^23d^1$	22 Ti $4s^23d^2$	23 V $4s^23d^3$	24 Cr $4s^13d^5$	25 Mn $4s^23d^6$	26 Fe $4s^23d^6$	27 Co $4s^23d^7$	28 Ni $4s^23d^8$	29 Cu $4s^13d^{10}$	30 Zn $4s^23d^{10}$	31 Ga $4s^24p^1$	32 Ge $4s^24p^2$
37 Rb $5s^1$	38 Sr $5s^2$	39 Y $5s^24d^1$	40 Zr $5s^24d^2$	41 Nb $5s^14d^4$	42 Mo $5s^14d^5$	43 Tc $5s^14d^5$	44 Ru $5s^14d^7$	45 Rh $5s^14d^8$	46 Pd $4d^{10}$	47 Ag $5s^14d^{10}$	48 Cd $5s^24d^{10}$	49 In $5s^25p^1$	50 Sn $5s^25p^2$
55 Cs $6s^1$	56 Ba $6s^2$	57 La $6s^25d^1$	72 Hf $6s^25d^2$	73 Ta $6s^25d^3$	74 W $6s^25d^4$	75 Re $6s^25d^5$	76 Os $6s^25d^6$	77 Ir $6s^25d^7$	78 Pt $6s^15d^9$	79 Au $6s^15d^{10}$	80 Hg $6s^25d^{10}$	81 Tl $6s^26p^1$	82 Pb $6s^26p^2$
87 Fr $7s^1$	88 Ra $7s^2$	89 Ac $7s^26d^1$	104 Rf $7s^26d^2$	105 Db $7s^26d^3$	106 Sg $7s^26d^4$	107 Bh $7s^26d^5$	108 Mt $7s^26d^6$	109 Ds $7s^26d^7$	110 Rg $7s^26d^8$	111 Nh $7s^26d^9$	112 (113) $7s^26d^{10}$	(114) $7s^27p^2$	(115) $7s^27p^4$
58 Ce $6s^24f^15d^1$	59 Pr $6s^24f^3$	60 Nd $6s^24f^4$	61 Pm $6s^24f^5$	62 Sm $6s^24f^6$	63 Eu $6s^24f^7$	64 Gd $6s^24f^5d^1$	65 Tb $6s^24f^9$	66 Dy $6s^24f^{10}$	67 Ho $6s^24f^{11}$	68 Er $6s^24f^{12}$	69 Tm $6s^24f^{13}$	70 Yb $6s^24f^{14}$	71 Lu $6s^24f^{14}5d^1$
90 Th $7s^26d^2$	91 Pa $7s^25f^26d^1$	92 U $7s^25f^36d^1$	93 Np $7s^25f^46d^1$	94 Pu $7s^25f^6$	95 Am $7s^25f^7$	96 Cm $7s^25f^6d^1$	97 Bk $7s^25f^9$	98 Cf $7s^25f^{10}$	99 No $7s^25f^{11}$	100 Fm $7s^25f^{12}$	101 Md $7s^25f^{13}$	102 No $7s^25f^{14}$	103 Lr $7s^25f^{14}6d^1$

**Figure 8.1**

The ground-state electron configurations of the elements. For simplicity, only the configurations of the outer electrons are shown.

**TABLE 8.1**
**Electron Configurations of Group 1A and Group 2A Elements**

Group 1A	Group 2A
Li [He]2s <sup>1</sup>	Be [He]2s <sup>2</sup>
Na [Ne]3s <sup>1</sup>	Mg [Ne]3s <sup>2</sup>
K [Ar]4s <sup>1</sup>	Ca [Ar]4s <sup>2</sup>
Rb [Kr]5s <sup>1</sup>	Sr [Kr]5s <sup>2</sup>
Cs [Xe]6s <sup>1</sup>	Ba [Xe]6s <sup>2</sup>
Fr [Rn]7s <sup>1</sup>	Ra [Rn]7s <sup>2</sup>

For the representative elements, the valence electrons are simply those electrons at the highest principal energy level  $n$ .

which  $n$  is the principal quantum number for the outermost shell.) The transition metals are the elements in Groups 1B and 3B through 8B, which have incompletely filled  $d$  subshells or readily produce cations with incompletely filled  $d$  subshells. (These metals are sometimes referred to as the  $d$ -block transition elements.) The Group 2B elements are Zn, Cd, and Hg, which are neither representative elements nor transition metals. The lanthanides and actinides are sometimes called  $f$ -block transition elements because they have incompletely filled  $f$  subshells.

A clear pattern emerges when we examine the electron configurations of the elements in a particular group. The electron configurations for Groups 1A and 2A elements are shown in Table 8.1. We see that all members of the Group 1A alkali metals have similar outer electron configurations; each has a noble gas core and an  $ns^1$  configuration of the outer electron. Similarly, the Group 2A alkaline earth metals have a noble gas core and an  $ns^2$  configuration of the outer electrons. *The outer electrons of an atom, which are those involved in chemical bonding*, are often called the **valence electrons**. Having the same number of valence electrons accounts for similarities in chemical behavior among the elements within each of these groups. This observation holds true also for the halogens (the Group 7A elements), which have outer electron configurations of  $ns^2np^5$  and exhibit very similar properties. We must be careful, however, in predicting properties for Groups 3A through 6A. For example, the elements in Group 4A all have the same outer electron configuration,  $ns^2np^4$ , but there is much variation in chemical properties among these elements: Carbon is a nonmetal, silicon and germanium are metalloids, and tin and lead are metals.

As a group, the noble gases behave very similarly. With the exception of krypton and xenon, these elements are totally inert chemically. The reason is that these elements all have completely filled outer  $ns^2np^6$  subshells, a condition that represents great stability. Although the outer electron configuration of the transition metals is not always the same within a group and there is no regular pattern in the change of the electron configuration from one metal to the next in the same period, all transition metals share many characteristics that set them apart from other elements. The reason is that these metals all have an incompletely filled  $d$  subshell. Likewise, the lanthanide (and the actinide) elements resemble one another within the series because they have incompletely filled  $f$  subshells. Figure 8.2 distinguishes the groups of elements discussed here.

### Example 8.1

An atom of a certain element has 15 electrons. Without consulting a periodic table, answer the following questions: (a) What is the ground-state electron configuration of the element? (b) How should the element be classified? (c) Is the element diamagnetic or paramagnetic?

**Strategy** (a) We refer to the building-up principle discussed in Section 7.9 and start writing the electron configuration with principal quantum number  $n = 1$  and continuing upward until all the electrons are accounted for. (b) What are the electron configuration characteristics of representative elements? transition elements? noble gases? (c) Examine the pairing scheme of the electrons in the outermost shell. What determines whether an element is diamagnetic or paramagnetic?

**Solution** (a) We know that for  $n = 1$  we have a  $1s$  orbital (2 electrons); for  $n = 2$  we have a  $2s$  orbital (2 electrons) and three  $2p$  orbitals (6 electrons); for  $n = 3$  we have a  $3s$  orbital (2 electrons). The number of electrons left is  $15 - 12 = 3$  and these three electrons are placed in the  $3p$  orbitals. The electron configuration is  $1s^22s^22p^63s^23p^3$ .

(Continued)

**Figure 8.2**

*Classification of the elements. Note that the Group 2B elements are often classified as transition metals even though they do not exhibit the characteristics of the transition metals.*

- (b) Because the  $3p$  subshell is not completely filled, this is a representative element. Based on the information given, we cannot say whether it is a metal, a nonmetal, or a metalloid.
  - (c) According to Hund's rule, the three electrons in the  $3p$  orbitals have parallel spins (three unpaired electrons). Therefore, the element is paramagnetic.

**Check** For (b), note that a transition metal possesses an incompletely filled  $d$  subshell and a noble gas has a completely filled outer shell. For (c), recall that if the atoms of an element contain an odd number of electrons, then the element must be paramagnetic.

**Similar problem: 8.16.**

**Practice Exercise** An atom of a certain element has 20 electrons. (a) Write the ground-state electron configuration of the element, (b) classify the element, (c) determine whether the element is diamagnetic or paramagnetic.

## Electron Configurations of Cations and Anions

Because many ionic compounds are made up of monatomic anions and/or cations, it is helpful to know how to write the electron configurations of these ionic species. The procedure for writing the electron configurations of ions requires only a slight extension

of the method used for neutral atoms. We will group the ions in two categories for discussion.

### Ions Derived from Representative Elements

In the formation of a cation from the neutral atom of a representative element, one or more electrons are removed from the highest occupied  $n$  shell. Here are the electron configurations of some neutral atoms and their corresponding cations:

Na: [Ne]3s <sup>1</sup>	Na <sup>+</sup> : [Ne]
Ca: [Ar]4s <sup>2</sup>	Ca <sup>2+</sup> : [Ar]
Al: [Ne]3s <sup>2</sup> 3p <sup>1</sup>	Al <sup>3+</sup> : [Ne]

Note that each ion has a stable noble gas configuration.

In the formation of an anion, one or more electrons are added to the highest partially filled  $n$  shell. Consider these examples:

H: 1s <sup>1</sup>	H <sup>-</sup> : 1s <sup>2</sup> or [He]
F: 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>5</sup>	F <sup>-</sup> : 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> or [Ne]
O: 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>4</sup>	O <sup>2-</sup> : 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> or [Ne]
N: 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>3</sup>	N <sup>3-</sup> : 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> or [Ne]

Again, all the anions have stable noble gas configurations. Thus, a characteristic of most representative elements is that ions derived from their neutral atoms have the noble gas outer electron configuration  $ns^2np^6$ . *Ions, or atoms and ions, that have the same number of electrons, and hence the same ground-state electron configuration, are said to be isoelectronic.* Thus, H<sup>-</sup> and He are isoelectronic; F<sup>-</sup>, Na<sup>+</sup>, and Ne are isoelectronic; and so on.

### Cations Derived from Transition Metals

In Section 7.9 we saw that in the first-row transition metals (Sc to Cu), the 4s orbital is always filled before the 3d orbitals. Consider manganese, whose electron configuration is [Ar]4s<sup>2</sup>3d<sup>5</sup>. When the Mn<sup>2+</sup> ion is formed, we might expect the two electrons to be removed from the 3d orbitals to yield [Ar]4s<sup>2</sup>3d<sup>3</sup>. In fact, the electron configuration of Mn<sup>2+</sup> is [Ar]3d<sup>5</sup>! The reason is that the electron-electron and electron-nucleus interactions in a neutral atom can be quite different from those in its ion. Thus, whereas the 4s orbital is always filled before the 3d orbital in Mn, electrons are removed from the 4s orbital in forming Mn<sup>2+</sup> because the 3d orbital is more stable than the 4s orbital in transition metal ions. Therefore, when a cation is formed from an atom of a transition metal, electrons are always removed first from the  $ns$  orbital and then from the  $(n - 1)d$  orbitals.

Keep in mind that most transition metals can form more than one cation and that frequently the cations are not isoelectronic with the preceding noble gases.

Bear in mind that the order of electron filling does not determine or predict the order of electron removal for transition metals.

## 8.3 Periodic Variation in Physical Properties

As we have seen, the electron configurations of the elements show a periodic variation with increasing atomic number. Consequently, there are also periodic variations in physical and chemical behavior. In this section and Sections 8.4 and 8.5, we will examine some physical properties of elements that are in the same group or period and additional properties that influence the chemical behavior of the elements. First,

let's look at the concept of effective nuclear charge, which has a direct bearing on atomic size and on the tendency for ionization.

## Effective Nuclear Charge

In Chapter 7, we discussed the shielding effect that electrons close to the nucleus have on outer-shell electrons in many-electron atoms. The presence of shielding electrons reduces the electrostatic attraction between the positively charged protons in the nucleus and the outer electrons. Moreover, the repulsive forces between electrons in a many-electron atom further offset the attractive force exerted by the nucleus. The concept of effective nuclear charge enables us to account for the effects of shielding on periodic properties.

Consider, for example, the helium atom, which has the ground-state electron configuration  $1s^2$ . Helium's two protons give the nucleus a charge of +2, but the full attractive force of this charge on the two  $1s$  electrons is partially offset by electron-electron repulsion. Consequently we say that the  $1s$  electrons shield each other from the nucleus. The effective nuclear charge ( $Z_{\text{eff}}$ ), which is the charge felt by an electron, is given by

$$Z_{\text{eff}} = Z - \sigma$$

where  $Z$  is the actual nuclear charge (that is, the atomic number of the element) and  $\sigma$  (sigma) is called the *shielding constant* (also called the *screening constant*). The shielding constant is greater than zero but smaller than  $Z$ .

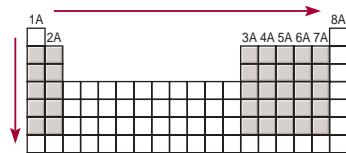
One way to illustrate electron shielding is to consider the amounts of energy required to remove the two electrons from a helium atom. Measurements show that it takes 2373 kJ of energy to remove the first electron from 1 mole of He atoms and 5251 kJ of energy to remove the remaining electron from 1 mole of  $\text{He}^+$  ions. The reason it takes so much more energy to remove the second electron is that with only one electron present, there is no shielding, and the electron feels the full effect of the +2 nuclear charge.

For atoms with three or more electrons, the electrons in a given shell are shielded by electrons in inner shells (that is, shells closer to the nucleus) but not by electrons in outer shells. Thus, in a lithium atom, whose electron configuration is  $1s^22s^1$ , the  $2s$  electron is shielded by the two  $1s$  electrons, but the  $2s$  electron does not have a shielding effect on the  $1s$  electrons. In addition, filled inner shells shield outer electrons more effectively than electrons in the same subshell shield each other.

## Atomic Radius

A number of physical properties, including density, melting point, and boiling point, are related to the sizes of atoms, but atomic size is difficult to define. As we saw in Chapter 7, the electron density in an atom extends far beyond the nucleus, but we normally think of atomic size as the volume containing about 90 percent of the total electron density around the nucleus. When we must be even more specific, we define the size of an atom in terms of its **atomic radius**, which is *one-half the distance between the two nuclei in two adjacent metal atoms*.

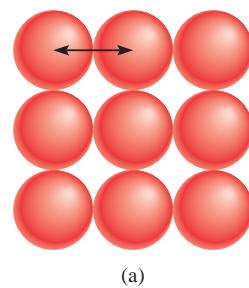
For atoms linked together to form an extensive three-dimensional network, atomic radius is simply one-half the distance between the nuclei in two neighboring atoms [Figure 8.3(a)]. For elements that exist as simple diatomic molecules, the atomic radius is one-half the distance between the nuclei of the two atoms in a particular molecule [Figure 8.3(b)].



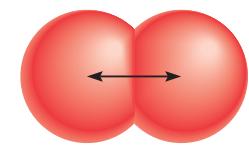
The increase in effective nuclear charge from left to right across a period and from top to bottom in a group for representative elements.



See Figure 7.24 for radial probability plots of  $1s$  and  $2s$  orbitals.



(a)

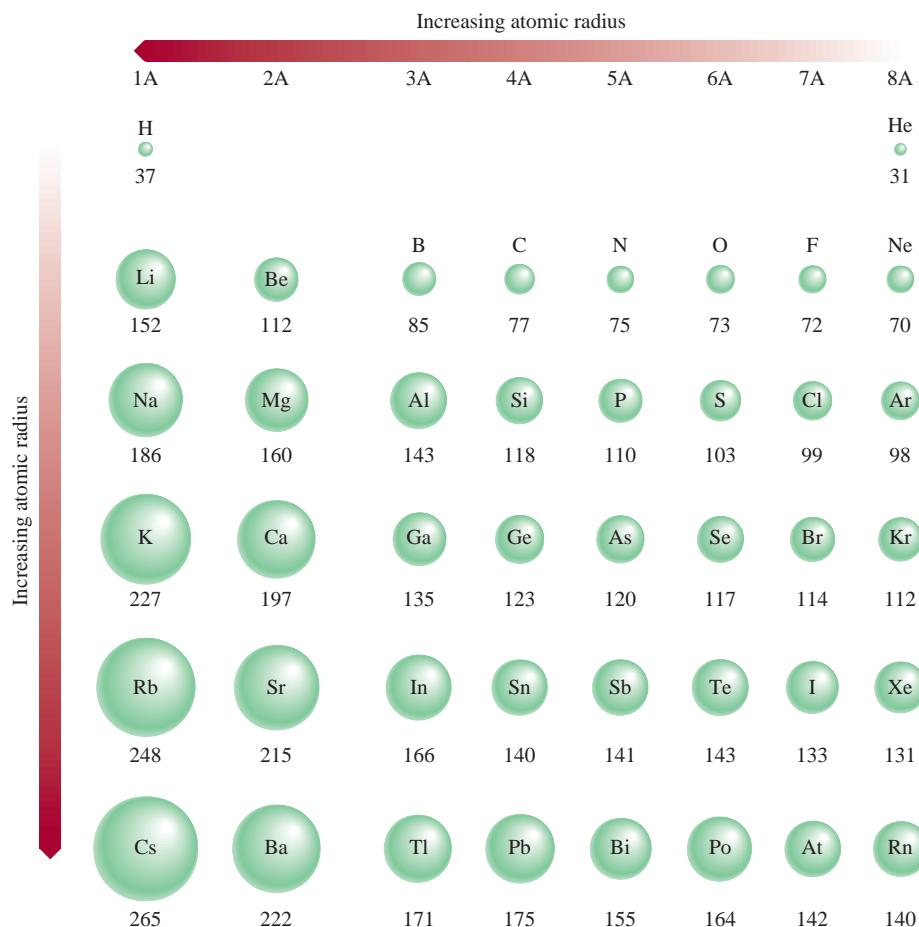


(b)

**Figure 8.3**  
 (a) In metals such as beryllium, the atomic radius is defined as one-half the distance between the centers of two adjacent atoms. (b) For elements that exist as diatomic molecules, such as iodine, the radius of the atom is defined as one-half the distance between the centers of the atoms in the molecule.

**Figure 8.4**

Atomic radii (in picometers) of representative elements according to their positions in the periodic table. Note that there is no general agreement on the size of atomic radii. We focus only on the trends in atomic radii, not on their precise values.



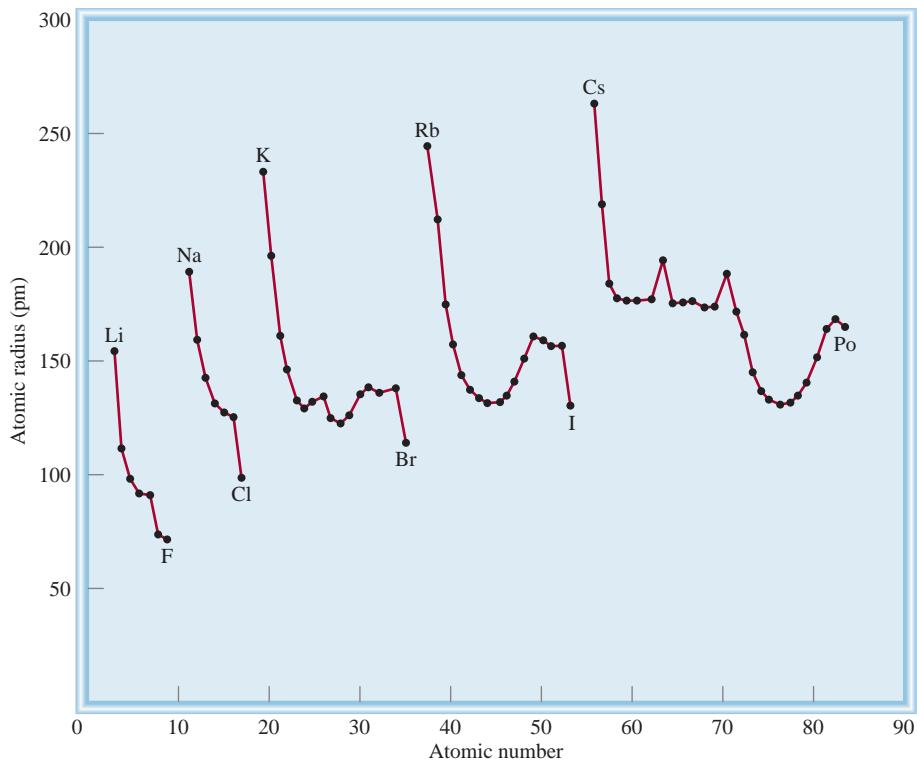
**Animation:**  
Atomic and Ionic Radius  
ARIS, Animations



**Interactivity:**  
Atomic Radii  
ARIS, Interactives

Figure 8.4 shows the atomic radii of many elements according to their positions in the periodic table, and Figure 8.5 plots the atomic radii of these elements against their atomic numbers. Periodic trends are clearly evident. In studying the trends, bear in mind that the atomic radius is determined to a large extent by the strength of the attraction between the nucleus and the outer-shell electrons. The larger the effective nuclear charge, the stronger the hold of the nucleus on these electrons, and the smaller the atomic radius. Consider the second-period elements from Li to F, for example. Moving from left to right, we find that the number of electrons in the inner shell ( $1s^2$ ) remains constant while the nuclear charge increases. The electrons that are added to counterbalance the increasing nuclear charge are ineffective in shielding one another. Consequently, the effective nuclear charge increases steadily while the principal quantum number remains constant ( $n = 2$ ). For example, the outer  $2s$  electron in lithium is shielded from the nucleus (which has three protons) by the two  $1s$  electrons. As an approximation, we assume that the shielding effect of the two  $1s$  electrons is to cancel two positive charges in the nucleus. Thus, the  $2s$  electron only feels the attraction of one proton in the nucleus; the effective nuclear charge is +1. In beryllium ( $1s^22s^2$ ), each of the  $2s$  electrons is shielded by the inner two  $1s$  electrons, which cancel two of the four positive charges in the nucleus. Because the  $2s$  electrons do not shield each other as effectively, the net result is that the effective nuclear charge of each  $2s$  electron is greater than +1. Thus, as the effective nuclear charge increases, the atomic radius decreases steadily from lithium to fluorine.

Within a group of elements we find that atomic radius increases with increasing atomic number. For the alkali metals in Group 1A, the outermost electron resides in

**Figure 8.5**

Plot of atomic radii (in picometers) of elements against their atomic numbers.

the  $ns$  orbital. Because orbital size increases with the increasing principal quantum number  $n$ , the size of the metal atoms increases from Li to Cs even though the effective nuclear charge also increases. We can apply the same reasoning to the elements in other groups.

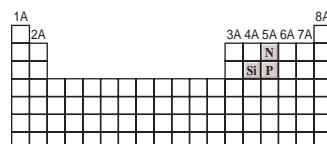
### Example 8.2

Referring to a periodic table, arrange the following atoms in order of increasing atomic radius: P, Si, N.

**Strategy** What are the trends in atomic radii in a periodic group and in a particular period? Which of the preceding elements are in the same group? in the same period?

**Solution** From Figure 8.2 we see that N and P are in the same group (Group 5A). Therefore, the radius of N is smaller than that of P (atomic radius increases as we go down a group). Both Si and P are in the third period, and Si is to the left of P. Therefore, the radius of P is smaller than that of Si (atomic radius decreases as we move from left to right across a period). Thus, the order of increasing radius is  $N < P < Si$ .

**Practice Exercise** Arrange the following atoms in order of decreasing radius: C, Li, Be.



Similar problems: 8.37, 8.38.

### Ionic Radius

**Ionic radius** is the radius of a cation or an anion. Ionic radius affects the physical and chemical properties of an ionic compound. For example, the three-dimensional structure of an ionic compound depends on the relative sizes of its cations and anions.

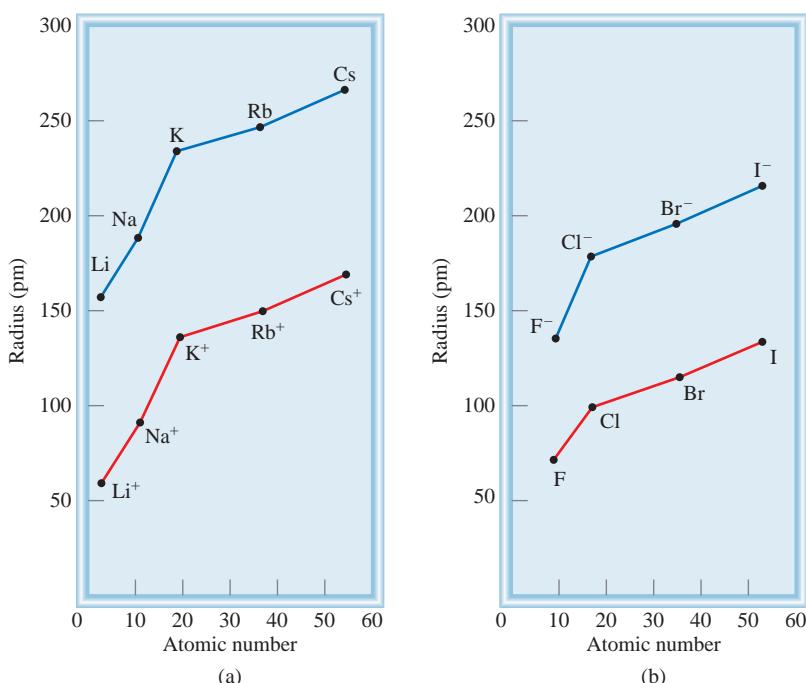
When a neutral atom is converted to an ion, we expect a change in size. If the atom forms an anion, its size (or radius) increases, because the nuclear charge remains the same but the repulsion resulting from the additional electron(s) enlarges the domain of the electron cloud. On the other hand, removing one or more electrons



**Interactivity:**  
Ionic Radii  
ARIS, Interactives

**Figure 8.6**

*Comparison of atomic radii with ionic radii. (a) Alkali metals and alkali metal cations. (b) Halogens and halide ions.*



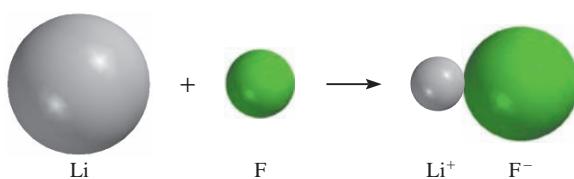
from an atom reduces electron-electron repulsion but the nuclear charge remains the same, so the electron cloud shrinks, and the cation is smaller than the atom. Figure 8.6 shows the changes in size that result when alkali metals are converted to cations and halogens are converted to anions; Figure 8.7 shows the changes in size that occur when a lithium atom reacts with a fluorine atom to form a LiF unit.

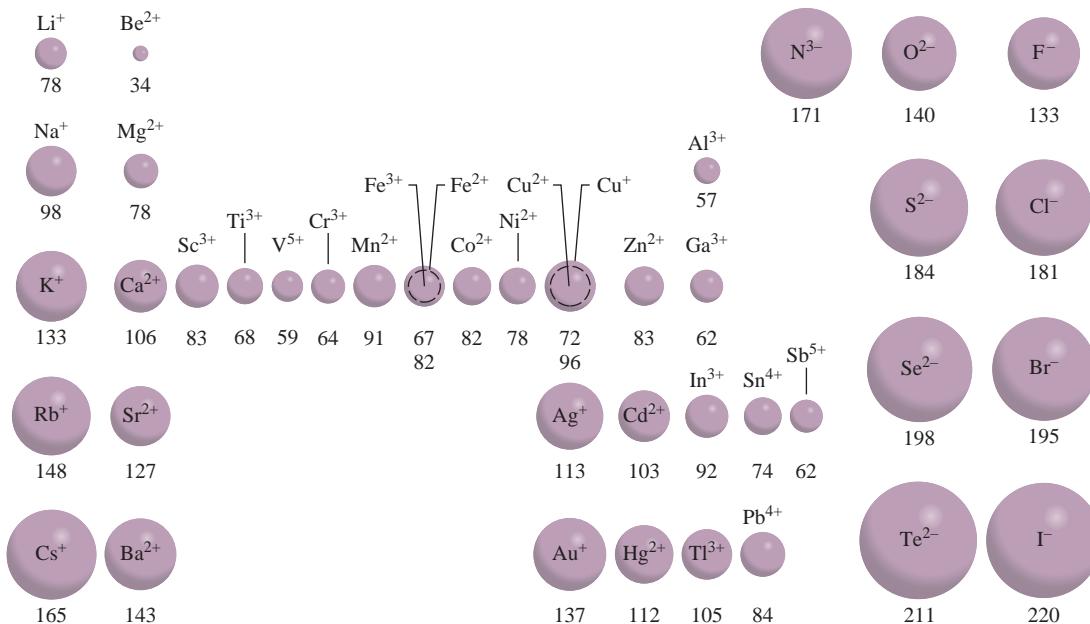
Figure 8.8 shows the radii of ions derived from the familiar elements, arranged according to elements' positions in the periodic table. We can see parallel trends between atomic radii and ionic radii. For example, from top to bottom both the atomic radius and the ionic radius increase within a group. For ions derived from elements in different groups, a size comparison is meaningful only if the ions are isoelectronic. If we examine isoelectronic ions, we find that cations are smaller than anions. For example,  $\text{Na}^+$  is smaller than  $\text{F}^-$ . Both ions have the same number of electrons, but  $\text{Na}$  ( $Z = 11$ ) has more protons than  $\text{F}$  ( $Z = 9$ ). The larger effective nuclear charge of  $\text{Na}^+$  results in a smaller radius.

Focusing on isoelectronic cations, we see that the radii of *tripositive ions* (ions that bear three positive charges) are smaller than those of *dipositive ions* (ions that bear two positive charges), which in turn are smaller than *unipositive ions* (ions that bear one positive charge). This trend is nicely illustrated by the sizes of three isoelectronic ions in the third period:  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$  (see Figure 8.8). The  $\text{Al}^{3+}$  ion has the same number of electrons as  $\text{Mg}^{2+}$ , but it has one more proton. Thus, the electron cloud in  $\text{Al}^{3+}$  is pulled inward more than that in  $\text{Mg}^{2+}$ . The smaller radius of  $\text{Mg}^{2+}$  compared with that of  $\text{Na}^{2+}$  can be similarly explained. Turning to isoelectronic

**Figure 8.7**

*Changes in the sizes of Li and F when they react to form LiF.*





**Figure 8.8**

The radii (in picometers) of ions of familiar elements arranged according to the elements' positions in the periodic table.

anions, we find that the radius increases as we go from ions with uninegative charge ( $-$ ) to those with dinegative charge ( $2-$ ), and so on. Thus, the oxide ion is larger than the fluoride ion because oxygen has one fewer proton than fluorine; the electron cloud is spread out more in  $O^{2-}$ .

### Example 8.3

For each of the following pairs, indicate which one of the two species is larger:

- (a)  $\text{N}^{3-}$  or  $\text{F}^-$ ; (b)  $\text{Mg}^{2+}$  or  $\text{Ca}^{2+}$ ; (c)  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ .

**Strategy** In comparing ionic radii, it is useful to classify the ions into three categories: (1) isoelectronic ions, (2) ions that carry the same charges and are generated from atoms of the same periodic group, and (3) ions carry different charges but are generated from the same atom. In case (1), ions carrying a greater negative charge are always larger; in case (2), ions from atoms having a greater atomic number are always larger; in case (3), ions having a smaller positive charge are always larger.

**Solution** (a)  $\text{N}^{3-}$  and  $\text{F}^-$  are isoelectronic anions, both containing 10 electrons.

Because  $\text{N}^{3-}$  has only seven protons and  $\text{F}^-$  has nine, the smaller attraction exerted by the nucleus on the electrons results in a larger  $\text{N}^{3-}$  ion.

- (b) Both Mg and Ca belong to Group 2A (the alkaline earth metals). Thus, the  $\text{Ca}^{2+}$  ion is larger than  $\text{Mg}^{2+}$  because Ca's valence electrons are in a larger shell ( $n = 4$ ) than are Mg's ( $n = 3$ ).

(c) Both ions have the same nuclear charge, but  $\text{Fe}^{2+}$  has one more electron (24 electrons compared to 23 electrons for  $\text{Fe}^{3+}$ ) and hence greater electron-electron repulsion. The radius of  $\text{Fe}^{2+}$  is larger.

**Practice Exercise** Select the smaller ion in each of the following pairs: (a)  $\text{K}^+$ ,  $\text{Li}^+$ ; (b)  $\text{Au}^+$ ,  $\text{Au}^{3+}$ ; (c)  $\text{P}^{3-}$ ,  $\text{N}^{3-}$ .

**Similar problems:** 8.43, 8.45.

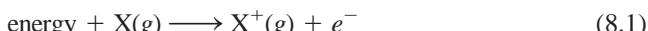


**Interactivity:**  
Ionization Energy  
ARIS, Interactives

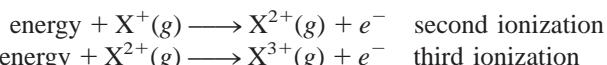
## 8.4 Ionization Energy

As we will see throughout this book, the chemical properties of any atom are determined by the configuration of the atom's valence electrons. The stability of these outermost electrons is reflected directly in the atom's ionization energies. **Ionization energy** is the minimum energy (in kJ/mol) required to remove an electron from a gaseous atom in its ground state. In other words, ionization energy is the amount of energy in kilojoules needed to strip 1 mole of electrons from 1 mole of gaseous atoms. Gaseous atoms are specified in this definition because an atom in the gas phase is virtually uninfluenced by its neighbors and so there are no intermolecular forces (that is, forces between molecules) to take into account when measuring ionization energy.

The magnitude of ionization energy is a measure of how "tightly" the electron is held in the atom. The higher the ionization energy, the more difficult it is to remove the electron. For a many-electron atom, the amount of energy required to remove the first electron from the atom in its ground state,



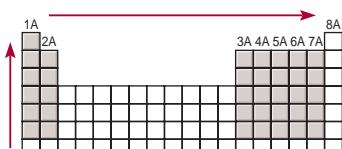
is called the *first ionization energy* ( $I_1$ ). In Equation (8.1), X represents an atom of any element and  $e^-$  is an electron. The second ionization energy ( $I_2$ ) and the third ionization energy ( $I_3$ ) are shown in the following equations:



The pattern continues for the removal of subsequent electrons.

When an electron is removed from an atom, the repulsion among the remaining electrons decreases. Because the nuclear charge remains constant, more energy is needed to remove another electron from the positively charged ion. Thus, ionization energies always increase in the following order:

$$I_1 < I_2 < I_3 < \dots$$



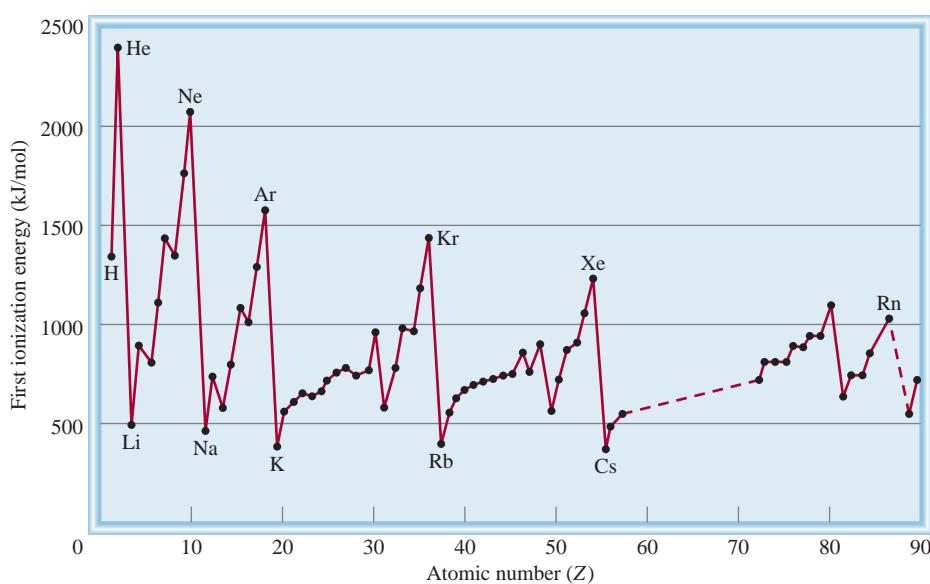
The increase in first ionization energy from left to right across a period and from bottom to top in a group for representative elements.

Table 8.2 lists the ionization energies of the first 20 elements. Ionization is always an endothermic process. By convention, energy absorbed by atoms (or ions) in the ionization process has a positive value. Thus, ionization energies are all positive quantities. Figure 8.9 shows the variation of the first ionization energy with atomic number. The plot clearly exhibits the periodicity in the stability of the most loosely held electron. Note that, apart from small irregularities, the first ionization energies of elements in a period increase with increasing atomic number. This trend is due to the increase in effective nuclear charge from left to right (as in the case of atomic radii variation). A larger effective nuclear charge means a more tightly held outer electron, and hence a higher first ionization energy. A notable feature of Figure 8.9 is the peaks, which correspond to the noble gases. The high ionization energies of the noble gases, stemming from their stable ground-state electron configurations, account for the fact that most of them are chemically unreactive. In fact, helium ( $1s^2$ ) has the highest first ionization energy of all the elements.

At the bottom of the graph in Figure 8.9 are the Group 1A elements (the alkali metals), which have the lowest first ionization energies. Each of these metals has one valence electron (the outermost electron configuration is  $ns^1$ ), which is effectively shielded by the completely filled inner shells. Consequently, it is energetically easy to remove an electron from the atom of an alkali metal to form a unipositive ion ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , ...). Significantly, the electron configurations of these cations are isoelectronic with those noble gases just preceding them in the periodic table.

**TABLE 8.2** The Ionization Energies (kJ/mol) of the First 20 Elements

Z	Element	First	Second	Third	Fourth	Fifth	Sixth
1	H	1,312					
2	He	2,373	5,251				
3	Li	520	7,300	11,815			
4	Be	899	1,757	14,850	21,005		
5	B	801	2,430	3,660	25,000	32,820	
6	C	1,086	2,350	4,620	6,220	38,000	47,261
7	N	1,400	2,860	4,580	7,500	9,400	53,000
8	O	1,314	3,390	5,300	7,470	11,000	13,000
9	F	1,680	3,370	6,050	8,400	11,000	15,200
10	Ne	2,080	3,950	6,120	9,370	12,200	15,000
11	Na	495.9	4,560	6,900	9,540	13,400	16,600
12	Mg	738.1	1,450	7,730	10,500	13,600	18,000
13	Al	577.9	1,820	2,750	11,600	14,800	18,400
14	Si	786.3	1,580	3,230	4,360	16,000	20,000
15	P	1,012	1,904	2,910	4,960	6,240	21,000
16	S	999.5	2,250	3,360	4,660	6,990	8,500
17	Cl	1,251	2,297	3,820	5,160	6,540	9,300
18	Ar	1,521	2,666	3,900	5,770	7,240	8,800
19	K	418.7	3,052	4,410	5,900	8,000	9,600
20	Ca	589.5	1,145	4,900	6,500	8,100	11,000

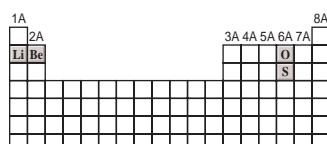
**Figure 8.9**

Variation of the first ionization energy with atomic number. Note that the noble gases have high ionization energies, whereas the alkali metals and alkaline earth metals have low ionization energies.

The Group 2A elements (the alkaline earth metals) have higher first ionization energies than the alkali metals do. The alkaline earth metals have two valence electrons (the outermost electron configuration is  $ns^2$ ). Because these two  $s$  electrons do not shield each other well, the effective nuclear charge for an alkaline earth metal atom is larger than that for the preceding alkali metal. Most alkaline earth compounds contain dipositive ions ( $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ ). The  $Be^{2+}$  ion is isoelectronic with  $Li^+$  and with  $He$ ,  $Mg^{2+}$ , is isoelectronic with  $Na^+$  and with  $Ne$ , and so on.

As Figure 8.9 shows, metals have relatively low ionization energies compared to nonmetals. The ionization energies of the metalloids generally fall between those of metals and nonmetals. The difference in ionization energies suggests why metals always form cations and nonmetals form anions in ionic compounds. (The only important nonmetallic cation is the ammonium ion,  $NH_4^+$ .) For a given group, ionization energy decreases with increasing atomic number (that is, as we move down the group). Elements in the same group have similar outer electron configurations. However, as the principal quantum number  $n$  increases, so does the average distance of a valence electron from the nucleus. A greater separation between the electron and the nucleus means a weaker attraction, so that it becomes increasingly easier to remove the first electron as we go from element to element down a group. Thus, the metallic character of the elements within a group increases from top to bottom. This trend is particularly noticeable for elements in Groups 3A to 7A. For example, in Group 4A, carbon is a nonmetal, silicon and germanium are metalloids, and tin and lead are metals.

Although the general trend in the periodic table is for first ionization energies to increase from left to right, some irregularities do exist. The first exception occurs between Group 2A and 3A elements in the same period (for example, between Be and B and between Mg and Al). The Group 3A elements have lower first ionization energies than 2A elements because they all have a single electron in the outermost  $p$  subshell ( $ns^2np^1$ ), which is well shielded by the inner electrons and the  $ns^2$  electrons. Therefore, less energy is needed to remove a single  $p$  electron than to remove a paired  $s$  electron from the same principal energy level. The second irregularity occurs between Groups 5A and 6A (for example, between N and O and between P and S). In the Group 5A elements ( $ns^2np^3$ ) the  $p$  electrons are in three separate orbitals according to Hund's rule. In Group 6A ( $ns^2np^4$ ) the additional electron must be paired with one of the three  $p$  electrons. The proximity of two electrons in the same orbital results in greater electrostatic repulsion, which makes it easier to ionize an atom of the Group 6A element, even though the nuclear charge has increased by one unit. Thus, the ionization energies for Group 6A elements are lower than those for Group 5A elements in the same period.



### Example 8.4

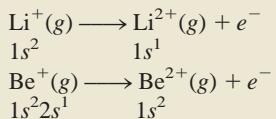
- Which atom should have a smaller first ionization energy: oxygen or sulfur?
- Which atom should have a higher second ionization energy: lithium or beryllium?

**Strategy** (a) First ionization energy decreases as we go down a group because the outermost electron is farther away from the nucleus and feels less attraction. (b) Removal of the outermost electron requires less energy if it is shielded by a filled inner shell.

**Solution** (a) Oxygen and sulfur are members of Group 6A. They have the same valence electron configuration ( $ns^2np^4$ ), but the  $3p$  electron in sulfur is farther from the nucleus and experiences less nuclear attraction than the  $2p$  electron in oxygen. Thus, we predict that sulfur should have a smaller first ionization energy.

(Continued)

(b) The electron configurations of Li and Be are  $1s^22s^1$  and  $1s^22s^2$ , respectively. The second ionization energy is the minimum energy required to remove an electron from a gaseous unipositive ion in its ground state. For the second ionization process we write



Because  $1s$  electrons shield  $2s$  electrons much more effectively than they shield each other, we predict that it should be easier to remove a  $2s$  electron from  $\text{Be}^+$  than to remove a  $1s$  electron from  $\text{Li}^+$ .

**Check** Compare your result with the data shown in Table 8.2. In (a), is your prediction consistent with the fact that the metallic character of the elements increases as we move down a periodic group? In (b), does your prediction account for the fact that alkali metals form  $+1$  ions while alkaline earth metals form  $+2$  ions?

**Similar problem:** 8.53.

**Practice Exercise** (a) Which of the following atoms should have a larger first ionization energy: N or P? (b) Which of the following atoms should have a smaller second ionization energy: Na or Mg?

## 8.5 Electron Affinity

Another property that greatly influences the chemical behavior of atoms is their ability to accept one or more electrons. This property is called **electron affinity**, which is *the negative of the energy change that occurs when an electron is accepted by an atom in the gaseous state to form an anion*.



Consider the process in which a gaseous fluorine atom accepts an electron:



The electron affinity of fluorine is therefore assigned a value of  $+328$  kJ/mol. The more positive is the electron affinity of an element, the greater is the affinity of an atom of the element to accept an electron. Another way of viewing electron affinity is to think of it as the energy that must be supplied to remove an electron from the anion. For fluorine, we write



Thus, a large positive electron affinity means that the negative ion is very stable (that is, the atom has a great tendency to accept an electron), just as a high ionization energy of an atom means that the electron in the atom is very stable.

Experimentally, electron affinity is determined by removing the additional electron from an anion. In contrast to ionization energies, however, electron affinities are difficult to measure because the anions of many elements are unstable. Table 8.3 shows the electron affinities of some representative elements and the noble gases. The overall trend is an increase in the tendency to accept electrons (electron affinity values become more positive) from left to right across a period. The electron affinities of metals are generally lower than those of nonmetals. The values vary little within a given group. The

**TABLE 8.3** Electron Affinities (kJ/mol) of Some Representative Elements and the Noble Gases\*

1A	2A	3A	4A	5A	6A	7A	8A
H							He
73							< 0
Li	Be	B	C	N	O	F	Ne
60	≤ 0	27	122	0	141	328	< 0
Na	Mg	Al	Si	P	S	Cl	Ar
53	≤ 0	44	134	72	200	349	< 0
K	Ca	Ga	Ge	As	Se	Br	Kr
48	2.4	29	118	77	195	325	< 0
Rb	Sr	In	Sn	Sb	Te	I	Xe
47	4.7	29	121	101	190	295	< 0
Cs	Ba	Tl	Pb	Bi	Po	At	Rn
45	14	30	110	110	?	?	< 0

\*The electron affinities of the noble gases, Be, and Mg have not been determined experimentally, but are believed to be close to zero or negative.

halogens (Group 7A) have the highest electron affinity values. This is not surprising when we realize that by accepting an electron, each halogen atom assumes the stable electron configuration of the noble gas immediately to its right. For example, the electron configuration of  $\text{F}^-$  is  $1s^22s^22p^6$ , or [Ne]; for  $\text{Cl}^-$  it is [Ne]3s $^2$ 3p $^6$  or [Ar]; and so on. Calculations show that the noble gases all have electron affinities of less than zero. Thus, the anions of these gases, if formed, would be inherently unstable.

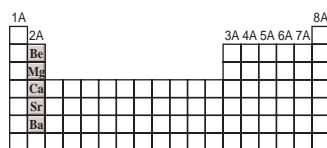
The electron affinity of oxygen has a positive value (141 kJ/mol), which means that the process



is favorable (exothermic). On the other hand, the electron affinity of the  $\text{O}^-$  ion is highly negative ( $-780 \text{ kJ/mol}$ ), which means the process



is endothermic even though the  $\text{O}^{2-}$  ion is isoelectronic with the noble gas Ne. This process is unfavorable in the gas phase because the resulting increase in electron-electron repulsion outweighs the stability gained by achieving a noble gas configuration. However, note that  $\text{O}^{2-}$  is common in ionic compounds (for example,  $\text{Li}_2\text{O}$  and  $\text{MgO}$ ); in solids, the  $\text{O}^{2-}$  ion is stabilized by the neighboring cations.



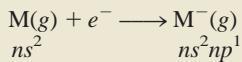
### Example 8.5

Why are the electron affinities of the alkaline earth metals, shown in Table 8.3, either negative or small positive values?

**Strategy** What are the electron configurations of alkaline earth metals? Would the added electron to such an atom be held strongly by the nucleus?

(Continued)

**Solution** The valence electron configuration of the alkaline earth metals is  $ns^2$ , where  $n$  is the highest principal quantum number. For the process



where M denotes a member of the Group 2A family, the extra electron must enter the  $np$  subshell, which is effectively shielded by the two  $ns$  electrons (the  $ns$  electrons are more penetrating than the  $np$  electrons) and the inner electrons. Consequently, alkaline earth metals have little tendency to pick up an extra electron.

**Similar problem:** 8.62.

**Practice Exercise** Is it likely that Ar will form the anion  $\text{Ar}^-$ ?

## 8.6 Variation in Chemical Properties of the Representative Elements

Ionization energy and electron affinity help chemists understand the types of reactions that elements undergo and the nature of the elements' compounds. On a conceptual level, these two measures are related in a simple way: Ionization energy indexes the attraction of an atom for its own electrons, whereas electron affinity expresses the attraction of an atom for an additional electron from some other source. Together they give us insight into the general attraction of an atom for electrons. With these concepts we can survey the chemical behavior of the elements systematically, paying particular attention to the relationship between chemical properties and electron configuration.

We have seen that the metallic character of the elements *decreases* from left to right across a period and *increases* from top to bottom within a group. On the basis of these trends and the knowledge that metals usually have low ionization energies while nonmetals usually have high electron affinities, we can frequently predict the outcome of a reaction involving some of these elements.

### General Trends in Chemical Properties

Before we study the elements in individual groups, let us look at some overall trends. We have said that elements in the same group resemble one another in chemical behavior because they have similar outer electron configurations. This statement, although correct in the general sense, must be applied with caution. Chemists have long known that the first member of each group (the element in the second period from lithium to fluorine) differs from the rest of the members of the same group. Lithium, for example, exhibits many, but not all, of the properties characteristic of the alkali metals. Similarly, beryllium is a somewhat atypical member of Group 2A, and so on. The difference can be attributed to the unusually small size of the first element in each group (see Figure 8.4).

Another trend in the chemical behavior of the representative elements is the diagonal relationship. **Diagonal relationships** are *similarities between pairs of elements in different groups and periods of the periodic table*. Specifically, the first three members of the second period (Li, Be, and B) exhibit many similarities to those elements located diagonally below them in the periodic table (Figure 8.10). The reason for this phenomenon is the closeness of the charge densities of their cations. (Charge density is the charge of an ion divided by its volume.) Cations with comparable charge densities react similarly with anions and therefore form the same type of compounds. Thus, the

1A	2A	3A	4A
Li	Be	B	C
Na	Mg	Al	Si

**Figure 8.10**  
*Diagonal relationships in the periodic table.*

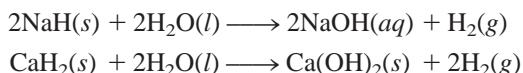
chemistry of lithium resembles that of magnesium in some ways; the same holds for beryllium and aluminum and for boron and silicon. Each of these pairs is said to exhibit a diagonal relationship. We will see a number of examples of this relationship later.

Bear in mind that a comparison of the properties of elements in the same group is most valid if we are dealing with elements of the same type with respect to their metallic character. This guideline applies to the elements in Groups 1A and 2A, which are all metals, and to the elements in Groups 7A and 8A, which are all nonmetals. In Groups 3A through 6A, where the elements change either from nonmetals to metals or from nonmetals to metalloids, it is natural to expect greater variation in chemical properties even though the members of the same group have similar outer electron configurations.

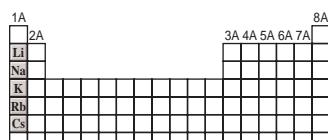
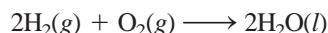
Now let us take a closer look at the chemical properties of the representative elements and the noble gases. (We will consider the chemistry of the transition metals in Chapter 20.)

### **Hydrogen ( $1s^1$ )**

There is no totally suitable position for hydrogen in the periodic table. Traditionally hydrogen is shown in Group 1A, but it really could be a class by itself. Like the alkali metals, it has a single  $s$  valence electron and forms a unipositive ion ( $H^+$ ), which is hydrated in solution. On the other hand, hydrogen also forms the hydride ion ( $H^-$ ) in ionic compounds such as  $\text{NaH}$  and  $\text{CaH}_2$ . In this respect, hydrogen resembles the halogens, all of which form uninegative ions ( $F^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $I^-$ ) in ionic compounds. Ionic hydrides react with water to produce hydrogen gas and the corresponding metal hydroxides:

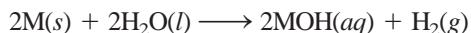


Of course, the most important compound of hydrogen is water, which forms when hydrogen burns in air:

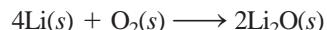


### **Group 1A Elements ( $ns^1$ , $n \geq 2$ )**

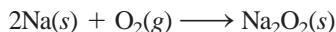
Figure 8.11 shows the Group 1A elements, the alkali metals. All of these elements have low ionization energies and therefore a great tendency to lose the single valence electron. In fact, in the vast majority of their compounds they are unipositive ions. These metals are so reactive that they are never found in the pure state in nature. They react with water to produce hydrogen gas and the corresponding metal hydroxide:



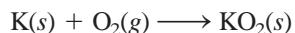
where M denotes an alkali metal. When exposed to air, they gradually lose their shiny appearance as they combine with oxygen gas to form oxides. Lithium forms lithium oxide (containing the  $\text{O}^{2-}$  ion):



The other alkali metals all form oxides and *peroxides* (containing the  $\text{O}_2^{2-}$  ion). For example,



Potassium, rubidium, and cesium also form *superoxides* (containing the  $\text{O}_2^-$  ion):

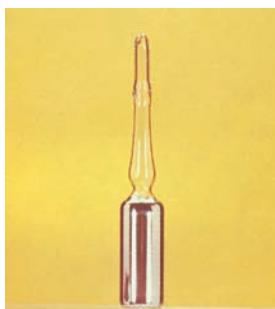




## Lithium (Li)



### Sodium (Na)



### Potassium (K)



## Rubidium (Rb)



## Cesium (Cs)

**Figure 8.11**

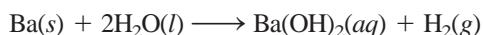
*The Group 1A elements: the alkali metals. Francium (not shown) is radioactive.*

The reason that different types of oxides are formed when alkali metals react with oxygen has to do with the stability of the oxides in the solid state. Because these oxides are all ionic compounds, their stability depends on how strongly the cations and anions attract one another. Lithium tends to form predominantly lithium oxide because this compound is more stable than lithium peroxide. The formation of other alkali metal oxides can be explained similarly.

## **Group 2A Elements ( $ns^2$ , $n \geq 2$ )**

Figure 8.12 shows the Group 2A elements. As a group, the alkaline earth metals are somewhat less reactive than the alkali metals. Both the first and the second ionization energies decrease from beryllium to barium. Thus, the tendency is to form  $M^{2+}$  ions (where M denotes an alkaline earth metal atom), and hence the metallic character increases from top to bottom. Most beryllium compounds ( $BeH_2$  and beryllium halides, such as  $BeCl_2$ ) and some magnesium compounds ( $MgH_2$ , for example) are molecular rather than ionic in nature.

The reactivities of alkaline earth metals with water vary quite markedly. Beryllium does not react with water; magnesium reacts slowly with steam; calcium, strontium, and barium are reactive enough to attack cold water:



The reactivities of the alkaline earth metals toward oxygen also increase from Be to Ba. Beryllium and magnesium form oxides ( $\text{BeO}$  and  $\text{MgO}$ ) only at elevated temperatures, whereas  $\text{CaO}$ ,  $\text{SrO}$ , and  $\text{BaO}$  form at room temperature.



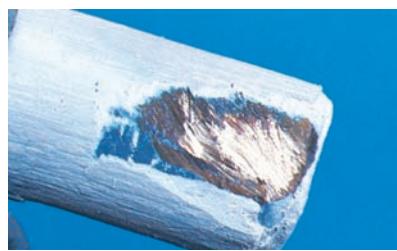
### Beryllium (Be)



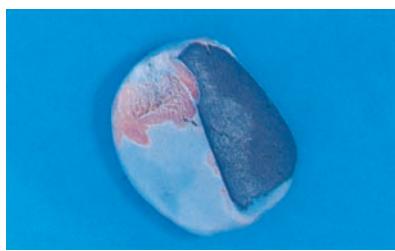
### Magnesium (Mg)



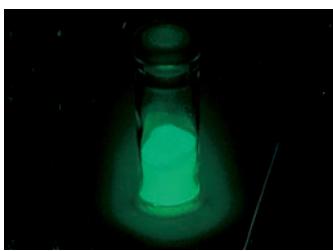
### Calcium (Ca)



### Strontium (Sr)



### Barium (Ba)



### Radium (Ra)

**Figure 8.12**

### *The Group 2A elements: the alkaline earth metals.*

Magnesium reacts with acids in aqueous solution, liberating hydrogen gas:

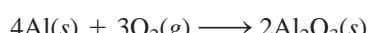


Calcium, strontium, and barium also react with aqueous acid solutions to produce hydrogen gas. However, because these metals also attack water, two different reactions will occur simultaneously.

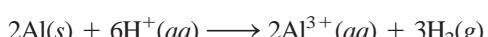
The chemical properties of calcium and strontium provide an interesting example of periodic group similarity. Strontium-90, a radioactive isotope, is a major product of an atomic bomb explosion. If an atomic bomb is exploded in the atmosphere, the strontium-90 formed will eventually settle on land and water, and it will reach our bodies via a relatively short food chain. For example, if cows eat contaminated grass and drink contaminated water, they will pass along strontium-90 in their milk. Because calcium and strontium are chemically similar,  $\text{Sr}^{2+}$  ions can replace  $\text{Ca}^{2+}$  ions in our bones. Constant exposure of the body to the high-energy radiation emitted by the strontium-90 isotopes can lead to anemia, leukemia, and other chronic illnesses.

### Group 3A Elements ( $ns^2 np^1$ , $n \geq 2$ )

The first member of Group 3A, boron, is a metalloid; the rest are metals (Figure 8.13). Boron does not form binary ionic compounds and is unreactive toward oxygen gas and water. The next element, aluminum, readily forms aluminum oxide when exposed to air.



Aluminum that has a protective coating of aluminum oxide is less reactive than elemental aluminum. Aluminum forms only tripositive ions. It reacts with hydrochloric acid as follows:





Boron (B)



Aluminum (Al)



Gallium (Ga)



Indium (In)

**Figure 8.13**

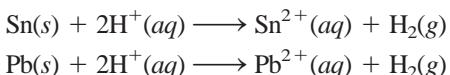
*The Group 3A elements. The low melting point of gallium ( $29.8^{\circ}\text{C}$ ) causes it to melt when held in hand.*

The other Group 3A metallic elements form both unipositive and tripositive ions. Moving down the group, we find that the unipositive ion becomes more stable than the tripositive ion.

The metallic elements in Group 3A also form many molecular compounds. For example, aluminum reacts with hydrogen to form  $\text{AlH}_3$ , which resembles  $\text{BeH}_2$  in its properties. (Here is an example of the diagonal relationship.) Thus, from left to right across the periodic table, we are seeing a gradual shift from metallic to nonmetallic character in the representative elements.

**Group 4A Elements ( $ns^2np^2$ ,  $n \geq 2$ )**

The first member of Group 4A, carbon, is a nonmetal, and the next two members, silicon and germanium, are metalloids (Figure 8.14). The metallic elements of this group, tin and lead, do not react with water, but they do react with acids (hydrochloric acid, for example) to liberate hydrogen gas:



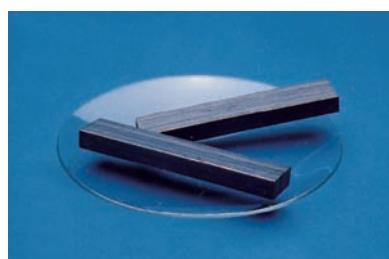
The Group 4A elements form compounds in both the +2 and +4 oxidation states. For carbon and silicon, the +4 oxidation state is the more stable one. For example,  $\text{CO}_2$  is more stable than  $\text{CO}$ , and  $\text{SiO}_2$  is a stable compound, but  $\text{SiO}$  does not exist under normal conditions. As we move down the group, however, the trend in stability is reversed. In tin compounds, the +4 oxidation state is only slightly more stable than the +2 oxidation state. In lead compounds, the +2 oxidation state is unquestionably the more stable one. The outer electron configuration of lead is  $6s^26p^2$ , and lead tends to lose only the  $6p$  electrons (to form  $\text{Pb}^{2+}$ ) rather than both the  $6p$  and  $6s$  electrons (to form  $\text{Pb}^{4+}$ ).

**Group 5A Elements ( $ns^2np^3$ ,  $n \geq 2$ )**

In Group 5A, nitrogen and phosphorus are nonmetals, arsenic and antimony are metalloids, and bismuth is a metal (Figure 8.15). Thus, we expect a greater variation in properties within the group.

1A	2A	3A	4A	5A	6A	7A	8A
		C					
		Si					
		Ge					
		Sn					
		Pb					

1A	2A	3A	4A	5A	6A	7A	8A
		N					
		P					
		As					
		Sb					
		Bi					



Carbon (graphite)



Carbon (diamond)



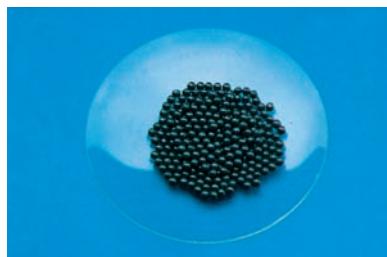
Silicon (Si)



Germanium (Ge)



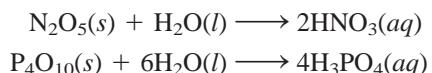
Tin (Sn)



Lead (Pb)

**Figure 8.14**  
The Group 4A elements.

Elemental nitrogen is a diatomic gas ( $N_2$ ). It forms a number of oxides ( $NO$ ,  $N_2O$ ,  $NO_2$ ,  $N_2O_4$ , and  $N_2O_5$ ), of which only  $N_2O_5$  is a solid; the others are gases. Nitrogen has a tendency to accept three electrons to form the nitride ion,  $N^{3-}$  (thus, achieving the electron configuration  $1s^22s^22p^6$ , which is isoelectronic with neon). Most metallic nitrides ( $Li_3N$  and  $Mg_3N_2$ , for example) are ionic compounds. Phosphorus exists as  $P_4$  molecules. It forms two solid oxides with the formulas  $P_4O_6$  and  $P_4O_{10}$ . The important oxoacids  $HNO_3$  and  $H_3PO_4$  are formed when the following oxides react with water:

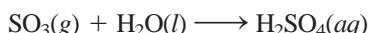


Arsenic, antimony, and bismuth have extensive three-dimensional structures. Bismuth is a far less reactive metal than those in the preceding groups.

1A	2A	3A	4A	5A	6A	7A	8A
			O				
			S				
			Se				
			Te				
			Po				

### Group 6A Elements ( $ns^2np^4$ , $n \geq 2$ )

The first three members of Group 6A (oxygen, sulfur, and selenium) are nonmetals, and the last two (tellurium and polonium) are metalloids (Figure 8.16). Oxygen is a diatomic gas; elemental sulfur and selenium have the molecular formulas  $S_8$  and  $Se_8$ , respectively; tellurium and polonium have more extensive three-dimensional structures. (Polonium is a radioactive element that is difficult to study in the laboratory.) Oxygen has a tendency to accept two electrons to form the oxide ion ( $O^{2-}$ ) in many ionic compounds. Sulfur, selenium, and tellurium also form dinegative anions ( $S^{2-}$ ,  $Se^{2-}$ , and  $Te^{2-}$ ). The elements in this group (especially oxygen) form a large number of molecular compounds with nonmetals. The important compounds of sulfur are  $SO_2$ ,  $SO_3$ , and  $H_2S$ . Sulfuric acid is formed when sulfur trioxide reacts with water:



Nitrogen ( $N_2$ )

White and red phosphorus (P)



Arsenic (As)



Antimony (Sb)



Bismuth (Bi)

**Figure 8.15**  
The Group 5A elements. Molecular nitrogen is a colorless, odorless gas.

Sulfur ( $S_8$ )Selenium ( $Se_8$ )

Tellurium (Te)

**Figure 8.16**  
The Group 6A elements sulfur, selenium, and tellurium. Molecular oxygen is a colorless, odorless gas. Polonium (not shown) is radioactive.

**Figure 8.17**

The Group 7A elements chlorine, bromine, and iodine. Fluorine is a greenish-yellow gas that attacks ordinary glassware. Astatine is radioactive.



1A	2A						8A
		3A	4A	5A	6A	7A	
				F			
					Cl		
						Br	
						I	
							Au

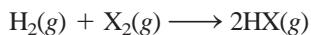
### Group 7A Elements ( $ns^2np^5$ , $n \geq 2$ )

All the halogens are nonmetals with the general formula  $X_2$ , where X denotes a halogen element (Figure 8.17). Because of their great reactivity, the halogens are never found in the elemental form in nature. (The last member of Group 7A, astatine, is a radioactive element. Little is known about its properties.) Fluorine is so reactive that it attacks water to generate oxygen:



Actually the reaction between molecular fluorine and water is quite complex; the products formed depend on reaction conditions. The reaction just shown is one of several possible changes.

The halogens have high ionization energies and large positive electron affinities. Anions derived from the halogens ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ ) are called *halides*. They are isoelectronic with the noble gases immediately to their right in the periodic table. For example,  $\text{F}^-$  is isoelectronic with Ne,  $\text{Cl}^-$  with Ar, and so on. The vast majority of the alkali metal halides and alkaline earth metal halides are ionic compounds. The halogens also form many molecular compounds among themselves (such as  $\text{ICl}$  and  $\text{BrF}_3$ ) and with nonmetallic elements in other groups (such as  $\text{NF}_3$ ,  $\text{PCl}_5$ , and  $\text{SF}_6$ ). The halogens react with hydrogen to form hydrogen halides:

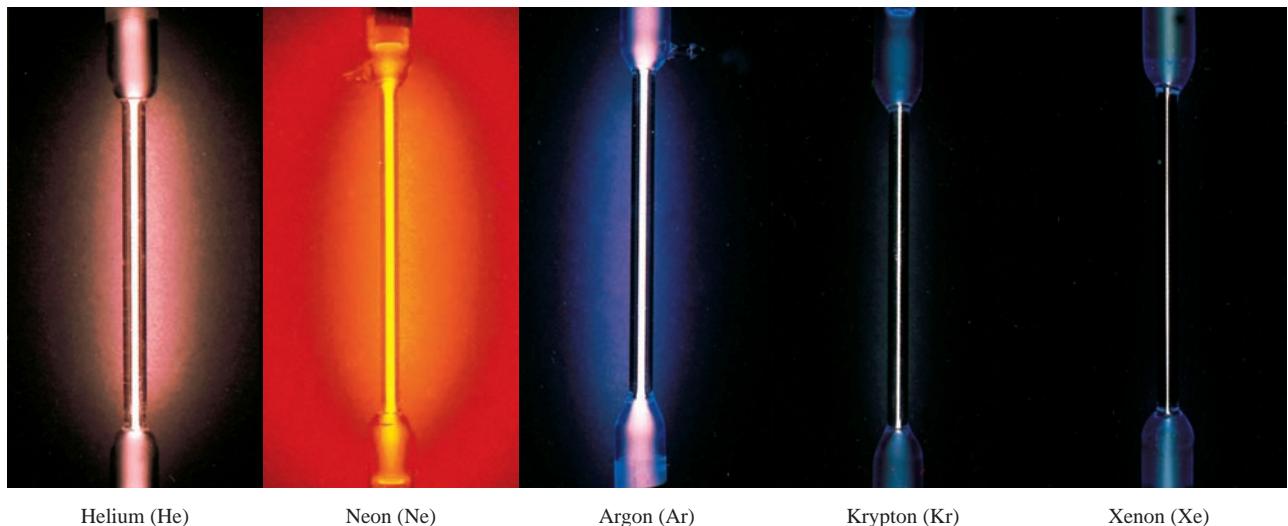


When this reaction involves fluorine, it is explosive, but it becomes less and less violent as we substitute chlorine, bromine, and iodine. The hydrogen halides dissolve in water to form hydrohalic acids. Hydrofluoric acid (HF) is a weak acid (that is, it is a weak electrolyte), but the other hydrohalic acids (HCl, HBr, and HI) are all strong acids (strong electrolytes).

1A	2A						8A
		3A	4A	5A	6A	7A	
						He	
						Ne	
						Ar	
						Kr	
						Xe	
						Rn	

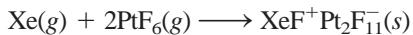
### Group 8A Elements ( $ns^2np^6$ , $n \geq 2$ )

All noble gases exist as monatomic species (Figure 8.18). Their atoms have completely filled outer  $ns$  and  $np$  subshells, which give them great stability. (Helium is  $1s^2$ .) The Group 8A ionization energies are among the highest of all elements, and these gases have no tendency to accept extra electrons. For years these elements were called inert gases, and rightly so. Until 1962 no one had been able to prepare a compound containing any of these elements. The British chemist Neil Bartlett

**Figure 8.18**

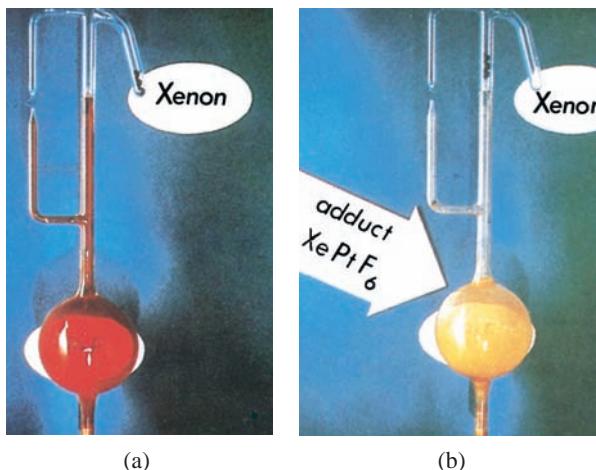
All noble gases are colorless and odorless. These pictures show the colors emitted by the gases from a discharge tube.

shattered chemists' long-held views of these elements when he exposed xenon to platinum hexafluoride, a strong oxidizing agent, and brought about the following reaction (Figure 8.19):

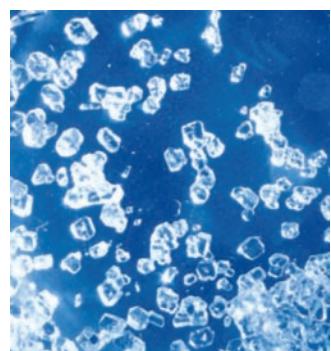


Since then, a number of xenon compounds ( $\text{XeF}_4$ ,  $\text{XeO}_3$ ,  $\text{XeO}_4$ ,  $\text{XeOF}_4$ ) and a few krypton compounds ( $\text{KrF}_2$ , for example) have been prepared (Figure 8.20). Despite the immense interest in the chemistry of the noble gases, however, their compounds do not have any large-scale commercial applications, and they are not involved in natural biological processes. No compounds of helium and neon are known.

In 2000, chemists prepared a compound containing argon (HArF), which is stable only at very low temperatures.

**Figure 8.19**

(a) Xenon gas (colorless) and  $\text{PtF}_6$  (red gas) separated from each other. (b) When the two gases are allowed to mix, a yellow-orange solid compound is formed. Note that the product was initially erroneously given the formula  $\text{XePtF}_6$ .

**Figure 8.20**

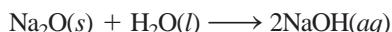
Crystals of xenon tetrafluoride ( $\text{XeF}_4$ ).

1A	2A	3A	4A	5A	6A	7A	8A
Na	Mg	Al	Si	P	S	Cl	

## Properties of Oxides Across a Period

One way to compare the properties of the representative elements across a period is to examine the properties of a series of similar compounds. Because oxygen combines with almost all elements, we will compare the properties of oxides of the third-period elements to see how metals differ from metalloids and nonmetals. Some elements in the third period (P, S, and Cl) form several types of oxides, but for simplicity we will consider only those oxides in which the elements have the highest oxidation number. Table 8.4 lists a few general characteristics of these oxides. We observed earlier that oxygen has a tendency to form the oxide ion. This tendency is greatly favored when oxygen combines with metals that have low ionization energies, namely, those in Groups 1A and 2A, plus aluminum. Thus, Na<sub>2</sub>O, MgO, and Al<sub>2</sub>O<sub>3</sub> are ionic compounds, as indicated by their high melting points and boiling points. They have extensive three-dimensional structures in which each cation is surrounded by a specific number of anions, and vice versa. As the ionization energies of the elements increase from left to right, so does the molecular nature of the oxides that are formed. Silicon is a metalloid; its oxide (SiO<sub>2</sub>) also has a huge three-dimensional network, although no ions are present. The oxides of phosphorus, sulfur, and chlorine are molecular compounds composed of small discrete units. The weak attractions among these molecules result in relatively low melting points and boiling points.

Most oxides can be classified as acidic or basic depending on whether they produce acids or bases when dissolved in water or react as acids or bases in certain processes. Some oxides are *amphoteric*, which means that they *display both acidic and basic properties*. The first two oxides of the third period, Na<sub>2</sub>O and MgO, are basic oxides. For example, Na<sub>2</sub>O reacts with water to form the base sodium hydroxide:



Magnesium oxide is quite insoluble; it does not react with water to any appreciable extent. However, it does react with acids in a manner that resembles an acid-base reaction:



Note that the products of this reaction are a salt (MgCl<sub>2</sub>) and water, the usual products of an acid-base neutralization.

Aluminum oxide is even less soluble than magnesium oxide; it too does not react with water. However, it shows basic properties by reacting with acids:



**TABLE 8.4** Some Properties of Oxides of the Third-Period Elements

	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>4</sub> O <sub>10</sub>	SO <sub>3</sub>	Cl <sub>2</sub> O <sub>7</sub>
Type of compound	← Ionic →	← Molecular →					
Structure	← Extensive three-dimensional →	← Discrete → molecular units					
Melting point (°C)	1275	2800	2045	1610	580	16.8	-91.5
Boiling point (°C)	?	3600	2980	2230	?	44.8	82
Acid-base nature	Basic	Basic	Amphoteric	← Acidic →			

It also exhibits acidic properties by reacting with bases:



Note that this acid-base neutralization produces a salt but no water.

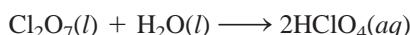
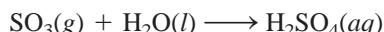
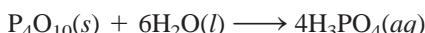
Thus,  $\text{Al}_2\text{O}_3$  is classified as an amphoteric oxide because it has properties of both acids and bases. Other amphoteric oxides are  $\text{ZnO}$ ,  $\text{BeO}$ , and  $\text{Bi}_2\text{O}_3$ .

Silicon dioxide is insoluble and does not react with water. It has acidic properties, however, because it reacts with very concentrated bases:



For this reason, concentrated aqueous, strong bases such as  $\text{NaOH}(aq)$  should not be stored in Pyrex glassware, which is made of  $\text{SiO}_2$ .

The remaining third-period oxides are acidic. They react with water to form phosphoric acid ( $\text{H}_3\text{PO}_4$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), and perchloric acid ( $\text{HClO}_4$ ):



Certain oxides such as  $\text{CO}$  and  $\text{NO}$  are neutral; that is, they do not react with water to produce an acidic or basic solution. In general, oxides containing nonmetallic elements are not basic.

This brief examination of oxides of the third-period elements shows that as the metallic character of the elements decreases from left to right across the period, their oxides change from basic to amphoteric to acidic. Metallic oxides are usually basic, and most oxides of nonmetals are acidic. The intermediate properties of the oxides (as shown by the amphoteric oxides) are exhibited by elements whose positions are intermediate within the period. Note also that because the metallic character of the elements increases from top to bottom within a group of representative elements, we would expect oxides of elements with higher atomic numbers to be more basic than the lighter elements. This is indeed the case.

### Example 8.6

Classify the following oxides as acidic, basic, or amphoteric: (a)  $\text{Rb}_2\text{O}$ , (b)  $\text{BeO}$ , (c)  $\text{As}_2\text{O}_5$ .

**Strategy** What type of elements form acidic oxides? basic oxides? amphoteric oxides?

**Solution** (a) Because rubidium is an alkali metal, we would expect  $\text{Rb}_2\text{O}$  to be a basic oxide.

(b) Beryllium is an alkaline earth metal. However, because it is the first member of Group 2A, we expect that it may differ somewhat from the other members of the group. In the text we saw that  $\text{Al}_2\text{O}_3$  is amphoteric. Because beryllium and aluminum exhibit a diagonal relationship,  $\text{BeO}$  may resemble  $\text{Al}_2\text{O}_3$  in properties. It turns out that  $\text{BeO}$  is also an amphoteric oxide.

(c) Because arsenic is a nonmetal, we expect  $\text{As}_2\text{O}_5$  to be an acidic oxide.

**Practice Exercise** Classify the following oxides as acidic, basic, or amphoteric:

- (a)  $\text{ZnO}$ , (b)  $\text{P}_4\text{O}_{10}$ , (c)  $\text{CaO}$ .

1A	2A						8A
	Be						As
Rb							

**Similar problem: 8.70.**

## SUMMARY OF FACTS AND CONCEPTS

- Nineteenth-century chemists developed the periodic table by arranging elements in the increasing order of their atomic masses. Discrepancies in early versions of the periodic table were resolved by arranging the elements in order of their atomic numbers.
- Electron configuration determines the properties of an element. The modern periodic table classifies the elements according to their atomic numbers, and thus also by their electron configurations. The configuration of the valence electrons directly affects the properties of the atoms of the representative elements.
- Periodic variations in the physical properties of the elements reflect differences in atomic structure. The metallic character of elements decreases across a period from metals through the metalloids to nonmetals and increases from top to bottom within a particular group of representative elements.
- Atomic radius varies periodically with the arrangement of the elements in the periodic table. It decreases from left to right and increases from top to bottom.
- Ionization energy is a measure of the tendency of an atom to resist the loss of an electron. The higher the ionization energy, the stronger the attraction between the nucleus and an electron. Electron affinity is a measure of the tendency of an atom to gain an electron. The more positive the electron affinity, the greater the tendency for the atom to gain an electron. Metals usually have low ionization energies, and nonmetals usually have high electron affinities.
- Noble gases are very stable because their outer  $ns$  and  $np$  subshells are completely filled. The metals among the representative elements (in Groups 1A, 2A, and 3A) tend to lose electrons until their cations become isoelectronic with the noble gases that precede them in the periodic table. The nonmetals in Groups 5A, 6A, and 7A tend to accept electrons until their anions become isoelectronic with the noble gases that follow them in the periodic table.

## KEY WORDS

Amphoteric oxide, p. 270  
 Atomic radius, p. 251  
 Diagonal relationship, p. 261

Electron affinity, p. 259  
 Ionic radius, p. 253  
 Ionization energy, p. 256

Isoelectronic, p. 250  
 Representative elements, p. 247

Valence electrons, p. 248

## QUESTIONS AND PROBLEMS

### Development of the Periodic Table

#### *Review Questions*

- Briefly describe the significance of Mendeleev's periodic table.
- What is Moseley's contribution to the modern periodic table?
- Describe the general layout of a modern periodic table.
- What is the most important relationship among elements in the same group in the periodic table?

### Periodic Classification of the Elements

#### *Review Questions*

- Which of these elements are metals, nonmetals, and metalloids: As, Xe, Fe, Li, B, Cl, Ba, P, I, Si?

- Compare the physical and chemical properties of metals and nonmetals.
- Draw a rough sketch of a periodic table (no details are required). Indicate where metals, nonmetals, and metalloids are located.
- What is a representative element? Give names and symbols of four representative elements.
- Without referring to a periodic table, write the name and symbol for an element in each of these groups: 1A, 2A, 3A, 4A, 5A, 6A, 7A, 8A, transition metals.
- Indicate whether these elements exist as atomic species, molecular species, or extensive three-dimensional structures in their most stable state at 25°C and 1 atm, and write the molecular or empirical formula for the elements: phosphorus, iodine, magnesium, neon, arsenic, sulfur, carbon, selenium, and oxygen.

- 8.11 You are given a dark shiny solid and asked to determine whether it is iodine or a metallic element. Suggest a nondestructive test that would enable you to arrive at the correct answer.
- 8.12 Define valence electrons. For representative elements, the number of valence electrons of an element is equal to its group number. Show that this is true for the following elements: Al, Sr, K, Br, P, S, C.
- 8.13 Write the outer electron configurations for (a) the alkali metals, (b) the alkaline earth metals, (c) the halogens, (d) the noble gases.
- 8.14 Use the first-row transition metals (Sc to Cu) as an example to illustrate the characteristics of the electron configurations of transition metals.

### Problems

- 8.15 In the periodic table, the element hydrogen is sometimes grouped with the alkali metals (as in this book) and sometimes with the halogens. Explain why hydrogen can resemble the Group 1A and the Group 7A elements.
- 8.16** A neutral atom of a certain element has 17 electrons. Without consulting a periodic table, (a) write the ground-state electron configuration of the element, (b) classify the element, (c) determine whether the atoms of this element are diamagnetic or paramagnetic.
- 8.17 Group these electron configurations in pairs that would represent similar chemical properties of their atoms:
- $1s^2 2s^2 2p^6 3s^2$
  - $1s^2 2s^2 2p^3$
  - $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$
  - $1s^2 2s^2$
  - $1s^2 2s^2 2p^6$
  - $1s^2 2s^2 2p^6 3s^2 3p^3$
- 8.18** Group these electron configurations in pairs that would represent similar chemical properties of their atoms:
- $1s^2 2s^2 2p^5$
  - $1s^2 2s^1$
  - $1s^2 2s^2 2p^6$
  - $1s^2 2s^2 2p^6 3s^2 3p^5$
  - $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
  - $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$
- 8.19 Without referring to a periodic table, write the electron configurations of elements with these atomic numbers: (a) 9, (b) 20, (c) 26, (d) 33. Classify the elements.
- 8.20** Specify in what group of the periodic table each of these elements is found: (a)  $[\text{Ne}]3s^1$ , (b)  $[\text{Ne}]3s^2 3p^3$ , (c)  $[\text{Ne}]3s^2 3p^6$ , (d)  $[\text{Ar}]4s^2 3d^8$ .

8.21 An ion  $M^{2+}$  derived from a metal in the first transition metal series has four and only four electrons in the  $3d$  subshell. What element might M be?

**8.22** A metal ion with a net +3 charge has five electrons in the  $3d$  subshell. Identify the metal.

### Electron Configurations of Ions

#### Review Questions

- 8.23 What is the characteristic of the electron configuration of stable ions derived from representative elements?
- 8.24 What do we mean when we say that two ions or an atom and an ion are isoelectronic?
- 8.25 What is wrong with the statement “The atoms of element X are isoelectronic with the atoms of element Y”?
- 8.26 Give three examples of first-row transition metal (Sc to Cu) ions whose electron configurations are represented by the argon core.

### Problems

- 8.27 Write ground-state electron configurations for these ions: (a)  $\text{Li}^+$ , (b)  $\text{H}^-$ , (c)  $\text{N}^{3-}$ , (d)  $\text{F}^-$ , (e)  $\text{S}^{2-}$ , (f)  $\text{Al}^{3+}$ , (g)  $\text{Se}^{2-}$ , (h)  $\text{Br}^-$ , (i)  $\text{Rb}^+$ , (j)  $\text{Sr}^{2+}$ , (k)  $\text{Sn}^{2+}$ .
- 8.28** Write ground-state electron configurations for these ions, which play important roles in biochemical processes in our bodies: (a)  $\text{Na}^+$ , (b)  $\text{Mg}^{2+}$ , (c)  $\text{Cl}^-$ , (d)  $\text{K}^+$ , (e)  $\text{Ca}^{2+}$ , (f)  $\text{Fe}^{2+}$ , (g)  $\text{Cu}^{2+}$ , (h)  $\text{Zn}^{2+}$ .
- 8.29 Write ground-state electron configurations for these transition metal ions: (a)  $\text{Sc}^{3+}$ , (b)  $\text{Ti}^{4+}$ , (c)  $\text{V}^{5+}$ , (d)  $\text{Cr}^{3+}$ , (e)  $\text{Mn}^{2+}$ , (f)  $\text{Fe}^{2+}$ , (g)  $\text{Fe}^{3+}$ , (h)  $\text{Co}^{2+}$ , (i)  $\text{Ni}^{2+}$ , (j)  $\text{Cu}^+$ , (k)  $\text{Cu}^{2+}$ , (l)  $\text{Ag}^+$ , (m)  $\text{Au}^+$ , (n)  $\text{Au}^{3+}$ , (o)  $\text{Pt}^{2+}$ .
- 8.30** Name the ions with +3 charges that have these electron configurations: (a)  $[\text{Ar}]3d^3$ , (b)  $[\text{Ar}]$ , (c)  $[\text{Kr}]4d^6$ , (d)  $[\text{Xe}]4f^{14}5d^6$ .
- 8.31 Which of these species are isoelectronic with each other: C,  $\text{Cl}^-$ ,  $\text{Mn}^{2+}$ ,  $\text{B}^-$ , Ar, Zn,  $\text{Fe}^{3+}$ ,  $\text{Ge}^{2+}$ ?
- 8.32** Group the species that are isoelectronic:  $\text{Be}^{2+}$ ,  $\text{F}^-$ ,  $\text{Fe}^{2+}$ ,  $\text{N}^{3-}$ , He,  $\text{S}^{2-}$ ,  $\text{Co}^{3+}$ , Ar.

### Periodic Variation in Physical Properties

#### Review Questions

- 8.33 Define atomic radius. Does the size of an atom have a precise meaning?
- 8.34 How does atomic radius change as we move (a) from left to right across the period and (b) from top to bottom in a group?
- 8.35 Define ionic radius. How does the size change when an atom is converted to (a) an anion and (b) a cation?
- 8.36 Explain why, for isoelectronic ions, the anions are larger than the cations.

**Problems**

- 8.37** On the basis of their positions in the periodic table, select the atom with the larger atomic radius in each of these pairs: (a) Na, Cs; (b) Be, Ba; (c) N, Sb; (d) F, Br; (e) Ne, Xe.
- 8.38** Arrange the following atoms in order of decreasing atomic radius: Na, Al, P, Cl, Mg.
- 8.39** Which is the largest atom in Group 4A?
- 8.40** Which is the smallest atom in Group 7A?
- 8.41** Why is the radius of the lithium atom considerably larger than the radius of the hydrogen atom?
- 8.42** Use the second period of the periodic table as an example to show that the sizes of atoms decrease as we move from left to right. Explain the trend.
- 8.43** In each of the following pairs, indicate which one of the two species is smaller: (a) Cl or  $\text{Cl}^-$ , (b) Na or  $\text{Na}^+$ , (c)  $\text{O}^{2-}$  or  $\text{S}^{2-}$ , (d)  $\text{Mg}^{2+}$  or  $\text{Al}^{3+}$ , (e)  $\text{Au}^+$  or  $\text{Au}^{3+}$ .
- 8.44** List these ions in order of increasing ionic radius:  $\text{N}^{3-}$ ,  $\text{Na}^+$ ,  $\text{F}^-$ ,  $\text{Mg}^{2+}$ ,  $\text{O}^{2-}$ .
- 8.45** Explain which of these ions is larger, and why:  $\text{Cu}^+$  or  $\text{Cu}^{2+}$ .
- 8.46** Explain which of these anions is larger, and why:  $\text{Se}^{2-}$  or  $\text{Te}^{2-}$ .
- 8.47** Give the physical states (gas, liquid, or solid) of the representative elements in the fourth period at 1 atm and 25°C: K, Ca, Ga, Ge, As, Se, Br.
- 8.48** The boiling points of neon and krypton are  $-245.9^\circ\text{C}$  and  $-152.9^\circ\text{C}$ , respectively. Using these data, estimate the boiling point of argon. (*Hint:* The properties of argon are intermediate between those of neon and krypton.)

**Ionization Energy****Review Questions**

- 8.49** Define ionization energy. Ionization energy is usually measured in the gaseous state. Why? Why is the second ionization energy always greater than the first ionization energy for any element?
- 8.50** Sketch an outline of the periodic table and show group and period trends in the first ionization energy of the elements. What types of elements have the highest ionization energies and what types the lowest ionization energies?

**Problems**

- 8.51** Use the third period of the periodic table as an example to illustrate the change in first ionization energies of the elements as we move from left to right. Explain the trend.
- 8.52** Ionization energy usually increases from left to right across a given period. Aluminum, however,

has a lower ionization energy than magnesium. Explain.

- 8.53** The first and second ionization energies of K are 419 kJ/mol and 3052 kJ/mol, and those of Ca are 590 kJ/mol and 1145 kJ/mol, respectively. Compare their values and comment on the differences.
- 8.54** Two atoms have the electron configurations  $1s^22s^22p^6$  and  $1s^22s^22p^63s^1$ . The first ionization energy of one is 2080 kJ/mol, and that of the other is 496 kJ/mol. Pair each ionization energy with one of the given electron configurations. Justify your choice.
- 8.55** A hydrogen-like ion is an ion containing only one electron. The energies of the electron in a hydrogen-like ion are given by
- $$E_n = -(2.18 \times 10^{-18} \text{ J})Z^2 \left( \frac{1}{n^2} \right)$$
- in which  $n$  is the principal quantum number and  $Z$  is the atomic number of the element. Calculate the ionization energy (in kilojoules per mole) of the  $\text{He}^+$  ion.
- 8.56** Plasma is a state of matter in which a gaseous system consists of positive ions and electrons. In the plasma state, a mercury atom would be stripped of its 80 electrons and exist as  $\text{Hg}^{80+}$ . Use the equation in Problem 8.55 to calculate the energy required for the last step of ionization; that is,
- $$\text{Hg}^{79+}(g) \longrightarrow \text{Hg}^{80+}(g) + e^-$$

**Electron Affinity****Review Questions**

- 8.57** (a) Define electron affinity. Electron affinity is usually measured with atoms in the gaseous state. Why? (b) Ionization energy is always a positive quantity, whereas electron affinity may be either positive or negative. Explain.
- 8.58** Explain the trends in electron affinity from aluminum to chlorine (see Table 8.3).

**Problems**

- 8.59** Arrange the elements in each of these groups in order of increasing electron affinity: (a) Li, Na, K; (b) F, Cl, Br, I.
- 8.60** Which of these elements would you expect to have the greatest electron affinity? He, K, Co, S, Cl.
- 8.61** From the electron-affinity values for the alkali metals, do you think it is possible for these metals to form an anion like  $\text{M}^-$ , where M represents an alkali metal?
- 8.62** Explain why alkali metals have a greater affinity for electrons than alkaline earth metals do.

## Variation in Chemical Properties

### Review Questions

- 8.63 Explain what is meant by the diagonal relationship. List two pairs of elements that show this relationship.
- 8.64 Which elements are more likely to form acidic oxides? basic oxides? amphoteric oxides?

### Problems

- 8.65 Use the alkali metals and alkaline earth metals as examples to show how we can predict the chemical properties of elements simply from their electron configurations.
- 8.66** Based on your knowledge of the chemistry of the alkali metals, predict some of the chemical properties of francium, the last member of the group.
- 8.67 As a group, the noble gases are very stable chemically (only Kr and Xe are known to form some compounds). Why?
- 8.68** Why are the Group 1B elements more stable than the Group 1A elements even though they seem to have the same outer electron configuration  $ns^1$  in which  $n$  is the principal quantum number of the outermost shell?
- 8.69 How do the chemical properties of oxides change as we move across a period from left to right? as we move down a particular group?
- 8.70** Predict (and give balanced equations for) the reactions between each of these oxides and water: (a) Li<sub>2</sub>O, (b) CaO, (c) CO<sub>2</sub>.
- 8.71 Write formulas and give names for the binary hydrogen compounds of the second-period elements (Li to F). Describe the changes in physical and chemical properties of these compounds as we move across the period from left to right.
- 8.72** Which oxide is more basic, MgO or BaO? Why?

### Additional Problems

- 8.73 State whether each of these properties of the representative elements generally increases or decreases (a) from left to right across a period and (b) from top to bottom in a group: metallic character, atomic size, ionization energy, acidity of oxides.
- 8.74** With reference to the periodic table, name (a) a halogen element in the fourth period, (b) an element similar to phosphorus in chemical properties, (c) the most reactive metal in the fifth period, (d) an element that has an atomic number smaller than 20 and is similar to strontium.
- 8.75 Why do elements that have high ionization energies usually have more positive electron affinities?
- 8.76** Arrange the following isoelectronic species in order of (a) increasing ionic radius and (b) increasing ionization energy: O<sup>2-</sup>, F<sup>-</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>.
- 8.77 Write the empirical (or molecular) formulas of compounds that the elements in the third period (sodium to chlorine) are expected to form with (a) molecular oxygen and (b) molecular chlorine. In each case indicate whether you expect the compound to be ionic or molecular.
- 8.78** Element M is a shiny and highly reactive metal (melting point 63°C), and element X is a highly reactive nonmetal (melting point -7.2°C). They react to form a compound with the empirical formula MX, a colorless, brittle solid that melts at 734°C. When dissolved in water or when molten, the substance conducts electricity. When chlorine gas is bubbled through an aqueous solution containing MX, a reddish-brown liquid appears and Cl<sup>-</sup> ions are formed. From these observations, identify M and X. (You may need to consult a handbook of chemistry for the melting-point values.)
- 8.79 Match each of the elements on the right with its description on the left:
- |  |                            |
|--|----------------------------|
| (a) A dark-red liquid                        | Calcium (Ca)               |
| (b) A colorless gas that burns in oxygen gas | Gold (Au)                  |
| (c) A reactive metal that attacks water      | Hydrogen (H <sub>2</sub> ) |
|  | Neon (Ne)                  |
|  | Bromine (Br <sub>2</sub> ) |
| (d) A shiny metal that is used in jewelry    |                            |
| (e) A totally inert gas                      |                            |
- 8.80** Arrange these species in isoelectronic pairs: O<sup>+</sup>, Ar, S<sup>2-</sup>, Ne, Zn, Cs<sup>+</sup>, N<sup>3-</sup>, As<sup>3+</sup>, N, Xe.
- 8.81 In which of these are the species written in decreasing radius? (a) Be, Mg, Ba, (b) N<sup>3-</sup>, O<sup>2-</sup>, F<sup>-</sup>, (c) Ti<sup>3+</sup>, Ti<sup>2+</sup>, Ti<sup>+</sup>.
- 8.82** Which of these properties show a clear periodic variation? (a) first ionization energy, (b) molar mass of the elements, (c) number of isotopes of an element, (d) atomic radius.
- 8.83 When carbon dioxide is bubbled through a clear calcium hydroxide solution, the solution becomes milky. Write an equation for the reaction and explain how this reaction illustrates that CO<sub>2</sub> is an acidic oxide.
- 8.84** You are given four substances: a fuming red liquid, a dark metallic-looking solid, a pale-yellow gas, and a yellow-green gas that attacks glass. You are told that these substances are the first four members of Group 7A, the halogens. Name each one.
- 8.85 For each pair of elements listed here, give three properties that show their chemical similarity:

(a) sodium and potassium and (b) chlorine and bromine.

**8.86** Name the element that forms compounds, under appropriate conditions, with every other element in the periodic table except He and Ne.

**8.87** Explain why the first electron affinity of sulfur is 200 kJ/mol but the second electron affinity is  $-649$  kJ/mol.

**8.88** The  $\text{H}^-$  ion and the He atom have two  $1s$  electrons each. Which of the two species is larger? Explain.

**8.89** Acidic oxides are those that react with water to produce acid solutions, whereas the reactions of basic oxides with water produce basic solutions. Non-metallic oxides are usually acidic, whereas those of metals are basic. Predict the products of the reactions of these oxides with water:  $\text{Na}_2\text{O}$ ,  $\text{BaO}$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}_5$ ,  $\text{P}_4\text{O}_{10}$ ,  $\text{SO}_3$ . Write an equation for each of the reactions.

**8.90** Write the formulas and names of the oxides of the second-period elements (Li to N). Identify the oxides as acidic, basic, or amphoteric.

**8.91** State whether each of the elements listed here is a gas, a liquid, or a solid under atmospheric conditions. Also state whether it exists in the elemental form as atoms, as molecules, or as a three-dimensional network: Mg, Cl, Si, Kr, O, I, Hg, Br.

**8.92** What factors account for the unique nature of hydrogen?

**8.93** The formula for calculating the energies of an electron in a hydrogen-like ion is

$$E_n = -(2.18 \times 10^{-18} \text{ J})Z^2 \left( \frac{1}{n^2} \right)$$

This equation cannot be applied to many-electron atoms. One way to modify it for the more complex atoms is to replace  $Z$  with  $(Z - \sigma)$ , in which  $Z$  is the atomic number and  $\sigma$  is a positive dimensionless quantity called the shielding constant. Consider the helium atom as an example. The physical significance of  $\sigma$  is that it represents the extent of shielding that the two  $1s$  electrons exert on each other. Thus, the quantity  $(Z - \sigma)$  is appropriately called the “effective nuclear charge.” Calculate the value of  $\sigma$  if the first ionization energy of helium is  $3.94 \times 10^{-18}$  J per atom. (Ignore the minus sign in the given equation in your calculation.)

**8.94** A technique called photoelectron spectroscopy is used to measure the ionization energy of atoms. A sample is irradiated with ultraviolet (UV) light, and electrons are ejected from the valence shell. The kinetic energies of the ejected electrons are measured. Because the energy of the UV photon and the kinetic energy of the

ejected electron are known, we can write

$$h\nu = \text{IE} + \frac{1}{2}mu^2$$

in which  $\nu$  is the frequency of the UV light, and  $m$  and  $u$  are the mass and velocity of the electron, respectively. In one experiment the kinetic energy of the ejected electron from potassium is found to be  $5.34 \times 10^{-19}$  J using a UV source of wavelength 162 nm. Calculate the ionization energy of potassium. How can you be sure that this ionization energy corresponds to the electron in the valence shell (that is, the most loosely held electron)?

**8.95** A student is given samples of three elements, X, Y, and Z, which could be an alkali metal, a member of Group 4A, and a member of Group 5A. She makes the following observations: Element X has a metallic luster and conducts electricity. It reacts slowly with hydrochloric acid to produce hydrogen gas. Element Y is a light-yellow solid that does not conduct electricity. Element Z has a metallic luster and conducts electricity. When exposed to air, it slowly forms a white powder. A solution of the white powder in water is basic. What can you conclude about the elements from these observations?

**8.96** Using these melting-point data, estimate the melting point of francium, which is a radioactive element:

Metal	Li	Na	K	Rb	Cs
melting point (°C)	180.5	97.8	63.3	38.9	28.4

(Hint: Plot melting point versus atomic number.)

**8.97** Experimentally, the electron affinity of an element can be determined by using a laser light to ionize the anion of the element in the gas phase:



Referring to Table 8.3, calculate the photon wavelength (in nanometers) corresponding to the electron affinity for chlorine. In what region of the electromagnetic spectrum does this wavelength fall?

**8.98** Name an element in Group 1A or Group 2A that is an important constituent of each of these substances: (a) remedy for acid indigestion, (b) coolant in nuclear reactors, (c) Epsom salt, (d) baking powder, (e) gunpowder, (f) a light alloy, (g) fertilizer that also neutralizes acid rain, (h) cement, and (i) grit for icy roads. You may need to ask your instructor about some of the items.

**8.99** Explain why the electron affinity of nitrogen is approximately zero, although the elements on either side, carbon and oxygen, have substantial positive electron affinities.

**8.100** Little is known of the chemistry of astatine, the last member of Group 7A. Describe the physical characteristics that you would expect this halogen to have. Predict the products of the reaction between sodium

astatide ( $\text{NaAt}$ ) and sulfuric acid. (*Hint:* Sulfuric acid is an oxidizing agent.)

- 8.101 The ionization energies of sodium (in  $\text{kJ/mol}$ ), starting with the first and ending with the eleventh, are 495.9, 4560, 6900, 9540, 13,400, 16,600, 20,120, 25,490, 28,930, 141,360, 170,000. Plot the log of ionization energy ( $y$  axis) versus the number of ionization ( $x$  axis); for example,  $\log 495.9$  is plotted versus 1 (labeled  $I_1$ , the first ionization energy),  $\log 4560$  is plotted versus 2 (labeled  $I_2$ , the second ionization energy), and so on. (a) Label  $I_1$  through  $I_{11}$  with the electrons in orbitals such as  $1s$ ,  $2s$ ,  $2p$ , and  $3s$ . (b) What can you deduce about electron shells from the breaks in the curve?
- 8.102 Calculate the maximum wavelength of light (in nanometers) required to ionize a single sodium atom.
- 8.103 The first four ionization energies of an element are approximately  $738 \text{ kJ/mol}$ ,  $1450 \text{ kJ/mol}$ ,  $7.7 \times 10^3 \text{ kJ/mol}$ , and  $1.1 \times 10^4 \text{ kJ/mol}$ . To which periodic group does this element belong? Why?

- 8.104** Match each of the elements on the right with its description on the left:

- |  |                           |
|--|---------------------------|
| (a) A greenish-yellow gas that reacts with water                   | Nitrogen ( $\text{N}_2$ ) |
| (b) A soft metal that reacts with water to produce hydrogen        | Boron (B)                 |
| (c) A metalloid that is hard and has a high melting point          | Aluminum (Al)             |
| (d) A colorless, odorless gas                                      | Fluorine ( $\text{F}_2$ ) |
| (e) A more reactive metal than iron, which does not corrode in air | Sodium (Na)               |

- 8.105 When magnesium metal is burned in air, it forms two products A and B. A reacts with water to form a basic solution. B reacts with water to form a similar solution as that of A plus a gas with a pungent odor. Identify A and B and write equations for the reactions.

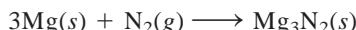
## SPECIAL PROBLEMS

- 8.106** In the late 1800s the British physicist Lord Rayleigh accurately determined the atomic masses of a number of elements, but he obtained a puzzling result with nitrogen. One of his methods of preparing nitrogen was by the thermal decomposition of ammonia:



Another method was to start with air and remove oxygen, carbon dioxide, and water vapor from it. Invariably, the nitrogen from air was a little denser (by about 0.5 percent) than the nitrogen from ammonia.

Later the English chemist Sir William Ramsay carried out an experiment in which he passed nitrogen, which he had obtained from air by Raleigh's procedure, over red-hot magnesium to convert it to magnesium nitride:



After all of the nitrogen had reacted with magnesium, Ramsay was left with an unknown gas that would not combine with anything. The atomic mass of this gas was determined to be 39.95 amu. Ramsay called the gas *argon*, which means "the lazy one" in Greek.

- (a) Later Rayleigh and Ramsay, with the help of Sir William Crookes, the inventor of the discharge tube, showed that argon was a new

element. Describe the type of experiment performed that led them to the conclusion.

- (b) Why did it take so long to discover argon?
- (c) Once argon had been discovered, why did it take relatively little time to discover the rest of the noble gases?
- (d) Why was helium the last noble gas to be discovered on Earth?
- (e) The only confirmed compound of radon is radon fluoride,  $\text{RnF}$ . Give two reasons why there are so few known radon compounds.
- 8.107 On the same graph, plot the effective nuclear charge (in parentheses) and atomic radius (see Figure 8.4) versus atomic number for the second-period elements: Li(1.30), Be(1.95), B(2.60), C(3.25), N(3.90), O(4.55), F(5.20), Ne(5.85). Comment on the trends.

- 8.108** The ionization energy of a certain element is  $412 \text{ kJ/mol}$ . When the atoms of this element are in the first excited state, however, the ionization energy is only  $126 \text{ kJ/mol}$ . Based on this information, calculate the wavelength of light emitted in a transition from the first excited state to the ground state.

- 8.109 Referring to Table 8.2, explain why the first ionization energy of helium is less than twice the

ionization energy of hydrogen, but the second ionization energy of helium is greater than twice the ionization energy of hydrogen. [Hint: According to Coulomb's law, the energy between two charges  $Q_1$  and  $Q_2$  separated by distance  $r$  is proportional to  $(Q_1 Q_2/r)$ .]

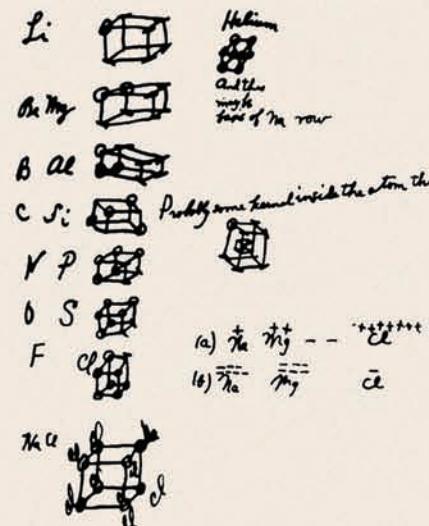
- 8.110** Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) is the most important nitrogen-containing fertilizer in the world. Describe how you would prepare this compound, given only air and water as the starting materials. You may have any device at your disposal for this task.

## ANSWERS TO PRACTICE EXERCISES

**8.1** (a)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ , (b) it is a representative element, (c) diamagnetic. **8.2** Li > Be > C. **8.3** (a)  $\text{Li}^+$ ,

(b)  $\text{Au}^{3+}$ , (c)  $\text{N}^{3-}$ . **8.4** (a) N, (b) Mg. **8.5** No. **8.6** (a) amphoteric, (b) acidic, (c) basic.

Lewis first sketched his idea about the octet rule on the back of an envelope.



## Chemical Bonding I: The Covalent Bond

### CHAPTER OUTLINE

- 9.1** Lewis Dot Symbols 280
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The Expanded Octet
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Use of Bond Enthalpies in Thermochemistry

### ESSENTIAL CONCEPTS

**The Ionic Bond** An ionic bond is the electrostatic force that holds the cations and anions in an ionic compound. The stability of ionic compounds is determined by their lattice energies.

**The Covalent Bond** Lewis postulated the formation of a covalent bond in which atoms share one or more pairs of electrons. The octet rule was formulated to predict the correctness of Lewis structures. This rule says that an atom other than hydrogen tends to form bonds until it is surrounded by eight valence electrons.

**Characteristics of Lewis Structures** In addition to covalent bonds, a Lewis structure also shows lone pairs, which are pairs of electrons not involved in bonding, on atoms and formal charges, which are the result of bookkeeping of electrons used in bonding. A resonance structure is one of two or more Lewis structures for a single molecule that cannot be described fully with only one Lewis structure.

**Exceptions to the Octet Rule** The octet rule applies mainly to the second-period elements. The three categories of exceptions to the octet rule are the incomplete octet, in which an atom in a molecule has fewer than eight valence electrons, the odd-electron molecules, which have an odd number of valence electrons, and the expanded octet, in which an atom has more than eight valence electrons. These exceptions can be explained by more refined theories of chemical bonding.

**Thermochemistry Based on Bond Enthalpy** From a knowledge of the strength of covalent bonds or bond enthalpies, it is possible to estimate the enthalpy change of a reaction.

### Interactive



### Activity Summary

- 1. Interactivity: Ionic Bonds (9.2)
- 2. Interactivity: Born-Haber Cycle for Lithium Fluoride (9.3)
- 3. Animation: Ionic versus Covalent Bonding (9.4)
- 4. Interactivity: Covalent Bonds (9.4)
- 5. Interactivity: Lewis Dot Structure (9.6)
- 6. Interactivity: Resonance (9.8)
- 7. Animation: Resonance (9.8)
- 8. Interactivity: Octet Rule Exception (9.9)

## 9.1 Lewis Dot Symbols

The development of the periodic table and concept of electron configuration gave chemists a rationale for molecule and compound formation. This explanation, formulated by the American chemist Gilbert Lewis, is that atoms combine to achieve a more stable electron configuration. Maximum stability results when an atom is isoelectronic with a noble gas.

When atoms interact to form a chemical bond, only their outer regions are in contact. For this reason, when we study chemical bonding, we are concerned primarily with the valence electrons of the atoms. To keep track of valence electrons in a chemical reaction, and to make sure that the total number of electrons does not change, chemists use a system of dots devised by Lewis and called Lewis dot symbols. A *Lewis dot symbol* consists of the symbol of an element and one dot for each valence electron in an atom of the element. Figure 9.1 shows the Lewis dot symbols for the representative elements and the noble gases. Note that, except for helium, the number of valence electrons each atom has is the same as the group number of the element. For example, Li is a Group 1A element and has one dot for one valence electron; Be, a Group 2A element, has two valence electrons (two dots); and so on. Elements in the same group have similar outer electron configurations and hence similar Lewis dot symbols. The transition metals, lanthanides, and actinides all have incompletely filled inner shells, and in general, we cannot write simple Lewis dot symbols for them.

In this chapter we will learn to use electron configurations and the periodic table to predict the type of bond atoms will form, as well as the number of bonds an atom of a particular element can form and the stability of the product.

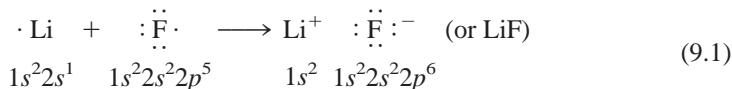
1 1A	•H	2 2A																		18 8A			
•Li	•Be•																						
•Na	•Mg•	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	He:	•B•	•C•	•N•	•O•	•F•	•Ne•
•K	•Ca•											•Al•	•Si•	•P•	•S•	•Cl•	•Ar•	•Ga•	•Ge•	•As•	•Se•	•Br•	•Kr•
•Rb	•Sr•											•In•	•Sn•	•Sb•	•Te•	•I•	•Xe•						
•Cs	•Ba•											•Tl•	•Pb•	•Bi•	•Po•	•At•	•Rn•						
•Fr	•Ra•																						

**Figure 9.1**

Lewis dot symbols for the representative elements and the noble gases. The number of unpaired dots corresponds to the number of bonds an atom of the element can form in a compound.

## 9.2 The Ionic Bond

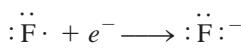
In Chapter 8 we saw that atoms of elements with low ionization energies tend to form cations, while those with high electron affinities tend to form anions. As a rule, the elements most likely to form cations in ionic compounds are the alkali metals and alkaline earth metals, and the elements most likely to form anions are the halogens and oxygen. Consequently, a wide variety of ionic compounds combine a Group 1A or Group 2A metal with a halogen or oxygen. An **ionic bond** is the electrostatic force that holds ions together in an ionic compound. Consider, for example, the reaction between lithium and fluorine to form lithium fluoride, a poisonous white powder used in lowering the melting point of solders and in manufacturing ceramics. The electron configuration of lithium is  $1s^22s^1$ , and that of fluorine is  $1s^22s^22p^5$ . When lithium and fluorine atoms come in contact with each other, the outer  $2s^1$  valence electron of lithium is transferred to the fluorine atom. Using Lewis dot symbols, we represent the reaction like this:



For convenience, imagine that this reaction occurs in separate steps—first the ionization of Li:



and then the acceptance of an electron by F:



Next, imagine the two separate ions joining to form a LiF unit:

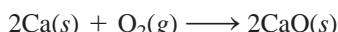


Note that the sum of these three equations is

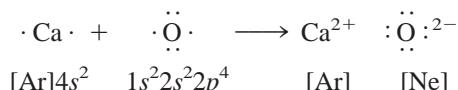


which is the same as Equation (9.1). The ionic bond in LiF is the electrostatic attraction between the positively charged lithium ion and the negatively charged fluoride ion. The compound itself is electrically neutral.

Many other common reactions lead to the formation of ionic bonds. For instance, calcium burns in oxygen to form calcium oxide:



Assuming that the diatomic O<sub>2</sub> molecule first splits into separate oxygen atoms (we will look at the energetics of this step later), we can represent the reaction with Lewis symbols:



There is a transfer of two electrons from the calcium atom to the oxygen atom. Note that the resulting calcium ion (Ca<sup>2+</sup>) has the argon electron configuration, the oxide ion (O<sup>2-</sup>) is isoelectronic with neon, and the compound (CaO) is electrically neutral.



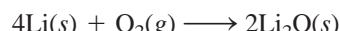
**Interactivity:**  
Ionic Bonds  
ARIS, Interactives



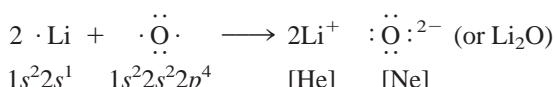
Lithium fluoride. Industrially, LiF (like most other ionic compounds) is obtained by purifying minerals containing the compound.

We normally write the empirical formulas of ionic compounds without showing the charges. The + and – are shown here to emphasize the transfer of electrons.

In many cases, the cation and the anion in a compound do not carry the same charges. For instance, when lithium burns in air to form lithium oxide ( $\text{Li}_2\text{O}$ ), the balanced equation is

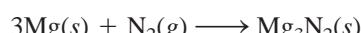


Using Lewis dot symbols, we write

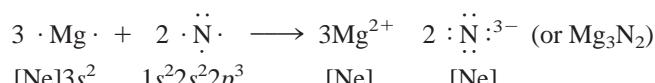


In this process, the oxygen atom receives two electrons (one from each of the two lithium atoms) to form the oxide ion. The  $\text{Li}^+$  ion is isoelectronic with helium.

When magnesium reacts with nitrogen at elevated temperatures, a white solid compound, magnesium nitride ( $Mg_3N_2$ ), forms:



or



The reaction involves the transfer of six electrons (two from each Mg atom) to two nitrogen atoms. The resulting magnesium ion ( $Mg^{2+}$ ) and the nitride ion ( $N^{3-}$ ) are both isoelectronic with neon. Because there are three +2 ions and two -3 ions, the charges balance and the compound is electrically neutral.

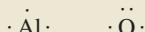


### Example 9.1

Use Lewis dot symbols to show the formation of aluminum oxide ( $\text{Al}_2\text{O}_3$ ).

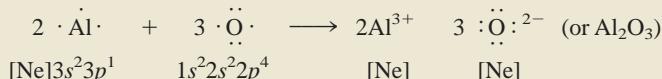
**Strategy** We use electroneutrality as our guide in writing formulas for ionic compounds, that is, the total positive charges on the cations must be equal to the total negative charges on the anions.

**Solution** According to Figure 9.1, the Lewis dot symbols of Al and O are



The mineral corundum ( $\text{Al}_2\text{O}_3$ ).

Because aluminum tends to form the cation ( $\text{Al}^{3+}$ ) and oxygen the anion ( $\text{O}^{2-}$ ) in ionic compounds, the transfer of electrons is from Al to O. There are three valence electrons in each Al atom; each O atom needs two electrons to form the  $\text{O}^{2-}$  ion, which is isoelectronic with neon. Thus, the simplest neutralizing ratio of  $\text{Al}^{3+}$  to  $\text{O}^{2-}$  is 2:3; two  $\text{Al}^{3+}$  ions have a total charge of +6, and three  $\text{O}^{2-}$  ions have a total charge of -6. So the empirical formula of aluminum oxide is  $\text{Al}_2\text{O}_3$ , and the reaction is



**Check** Make sure that the number of valence electrons (24) is the same on both sides of the equation. Are the subscripts in  $\text{Al}_2\text{O}_3$  reduced to the smallest possible whole numbers?

**Similar problems:** 9.17, 9.18.

**Practice Exercise** Use Lewis dot symbols to represent the formation of barium hydride.

## 9.3 Lattice Energy of Ionic Compounds

We can predict which elements are likely to form ionic compounds based on ionization energy and electron affinity, but how do we evaluate the stability of an ionic compound? Ionization energy and electron affinity are defined for processes occurring in the gas phase, but at 1 atm and 25°C all ionic compounds are solids. The solid state is a very different environment because each cation in a solid is surrounded by a specific number of anions, and vice versa. Thus, the overall stability of a solid ionic compound depends on the interactions of all these ions and not merely on the interaction of a single cation with a single anion. A quantitative measure of the stability of any ionic solid is its ***lattice energy***, defined as *the energy required to completely separate one mole of a solid ionic compound into gaseous ions.*

### The Born-Haber Cycle for Determining Lattice Energies

Lattice energy cannot be measured directly. However, if we know the structure and composition of an ionic compound, we can calculate the compound's lattice energy by using **Coulomb's law**, which states that *the potential energy ( $E$ ) between two ions is directly proportional to the product of their charges and inversely proportional to the distance of separation between them.* For a single  $\text{Li}^+$  ion and a single  $\text{F}^-$  ion separated by distance  $r$ , the potential energy of the system is given by

$$\begin{aligned} E &\propto \frac{Q_{\text{Li}^+} Q_{\text{F}^-}}{r} \\ &= k \frac{Q_{\text{Li}^+} Q_{\text{F}^-}}{r} \end{aligned} \quad (9.2)$$

Because energy = force × distance,  
Coulomb's law can also be stated as

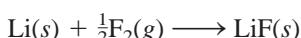
$$F = k \frac{Q_{\text{Li}^+} Q_{\text{F}^-}}{r^2}$$

where  $F$  is the force between the ions.

where  $Q_{\text{Li}^+}$  and  $Q_{\text{F}^-}$  are the charges on the  $\text{Li}^+$  and  $\text{F}^-$  ions and  $k$  is the proportionality constant. Because  $Q_{\text{Li}^+}$  is positive and  $Q_{\text{F}^-}$  is negative,  $E$  is a negative quantity, and the formation of an ionic bond from  $\text{Li}^+$  and  $\text{F}^-$  is an exothermic process. Consequently, energy must be supplied to reverse the process (in other words, the lattice energy of  $\text{LiF}$  is positive), and so a bonded pair of  $\text{Li}^+$  and  $\text{F}^-$  ions is more stable than separate  $\text{Li}^+$  and  $\text{F}^-$  ions.

We can also determine lattice energy indirectly, by assuming that the formation of an ionic compound takes place in a series of steps. This procedure, known as the **Born-Haber cycle**, relates lattice energies of ionic compounds to ionization energies, electron affinities, and other atomic and molecular properties. It is based on Hess's law (see Section 6.6). Developed by the German physicist Max Born and the German chemist Fritz Haber, the Born-Haber cycle defines the various steps that precede the formation of an ionic solid. We will illustrate its use to find the lattice energy of lithium fluoride.

Consider the reaction between lithium and fluorine:



The standard enthalpy change for this reaction is  $-594.1 \text{ kJ/mol}$ . (Because the reactants and product are in their standard states, that is, at 1 atm, the enthalpy change is also the standard enthalpy of formation for  $\text{LiF}$ .) Keeping in mind that the sum of enthalpy changes for the steps is equal to the enthalpy change for the overall reaction ( $-594.1 \text{ kJ/mol}$ ), we can trace the formation of  $\text{LiF}$  from its elements through five



**Interactivity:**  
Born-Haber Cycle for  
Lithium Fluoride  
ARIS, Interactives

separate steps. The process may not occur exactly this way, but this pathway enables us to analyze the energy changes of ionic compound formation, with the application of Hess's law.

- Convert solid lithium to lithium vapor (the direct conversion of a solid to a gas is called sublimation):



The energy of sublimation for lithium is 155.2 kJ/mol.

- Dissociate  $\frac{1}{2}$  mole of  $\text{F}_2$  gas into separate gaseous F atoms:



The energy needed to break the bonds in 1 mole of  $\text{F}_2$  molecules is 150.6 kJ. Here we are breaking the bonds in half a mole of  $\text{F}_2$ , so the enthalpy change is 150.6/2, or 75.3, kJ.

- Ionize 1 mole of gaseous Li atoms (see Table 8.3):

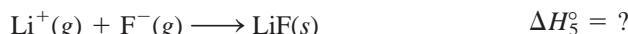


This process corresponds to the first ionization of lithium.

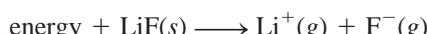
- Add 1 mole of electrons to 1 mole of gaseous F atoms. As discussed on page 259, the energy change for this process is just the opposite of electron affinity (see Table 8.3):



- Combine 1 mole of gaseous  $\text{Li}^+$  and 1 mole of  $\text{F}^-$  to form 1 mole of solid  $\text{LiF}$ :



The reverse of step 5,



defines the lattice energy of  $\text{LiF}$ . Thus, the lattice energy must have the same magnitude as  $\Delta H_5^\circ$  but an opposite sign. Although we cannot determine  $\Delta H_5^\circ$  directly, we can calculate its value by the following procedure:

1.	$\text{Li}(s) \longrightarrow \text{Li}(g)$	$\Delta H_1^\circ = 155.2 \text{ kJ/mol}$
2.	$\frac{1}{2}\text{F}_2(g) \longrightarrow \text{F}(g)$	$\Delta H_2^\circ = 75.3 \text{ kJ/mol}$
3.	$\text{Li}(g) \longrightarrow \text{Li}^+(g) + e^-$	$\Delta H_3^\circ = 520 \text{ kJ/mol}$
4.	$\text{F}(g) + e^- \longrightarrow \text{F}^-(g)$	$\Delta H_4^\circ = -328 \text{ kJ/mol}$
5.	$\text{Li}^+(g) + \text{F}^-(g) \longrightarrow \text{LiF}(s)$	$\Delta H_5^\circ = ?$

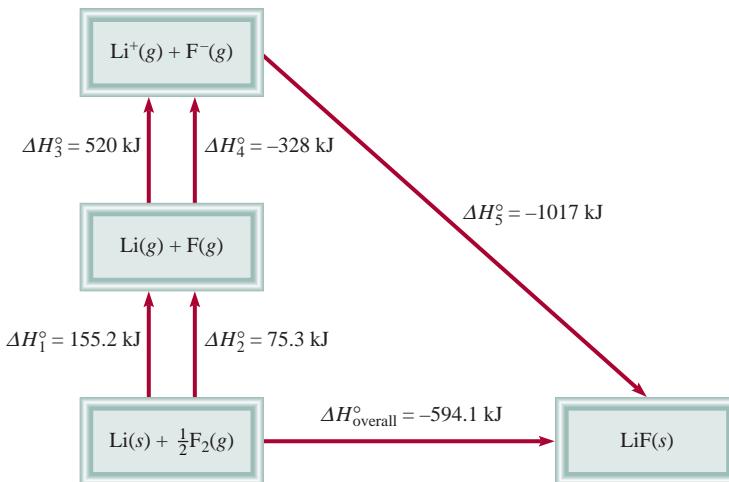


According to Hess's law, we can write

$$\Delta H_{\text{overall}}^\circ = \Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ + \Delta H_4^\circ + \Delta H_5^\circ$$

or

$$-594.1 \text{ kJ/mol} = 155.2 \text{ kJ/mol} + 75.3 \text{ kJ/mol} + 520 \text{ kJ/mol} - 328 \text{ kJ/mol} + \Delta H_5^\circ$$



**Figure 9.2**  
The Born-Haber cycle for the formation of 1 mole of solid LiF.

Hence,

$$\Delta H_5^\circ = -1017 \text{ kJ/mol}$$

and the lattice energy of LiF is +1017 kJ/mol.

Figure 9.2 summarizes the Born-Haber cycle for LiF. Steps 1, 2, and 3 all require the input of energy. On the other hand, steps 4 and 5 release energy. Because  $\Delta H_5^\circ$  is a large negative quantity, the lattice energy of LiF is a large positive quantity, which accounts for the stability of solid LiF. The greater the lattice energy, the more stable the ionic compound. Keep in mind that lattice energy is *always* a positive quantity because the separation of ions in a solid into ions in the gas phase is, by Coulomb's law, an endothermic process.

Table 9.1 lists the lattice energies and the melting points of several common ionic compounds. There is a rough correlation between lattice energy and melting point. The larger the lattice energy, the more stable the solid and the more tightly held the ions. It takes more energy to melt such a solid, and so the solid has a higher melting point than one with a smaller lattice energy. Note that MgCl<sub>2</sub>, MgO, and CaO have unusually high lattice energies. The first of these ionic compounds has a doubly charged cation (Mg<sup>2+</sup>) and in the second and third compounds there is an interaction between two doubly charged species (Mg<sup>2+</sup> or Ca<sup>2+</sup> and O<sup>2-</sup>). The coulombic attractions between two doubly charged species, or between a doubly charged ion and a singly charged ion, are much stronger than those between singly charged anions and cations.

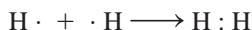
**TABLE 9.1**

Lattice Energies and Melting Points of Some Ionic Compounds

	Lattice Energy (kJ/mol)	Melting Point (°C)
LiF	1017	845
LiCl	828	610
NaCl	788	801
NaBr	736	750
MgCl <sub>2</sub>	2527	714
MgO	3890	2800
CaO	3414	2580

## 9.4 The Covalent Bond

Although the concept of molecules goes back to the seventeenth century, it was not until early in the twentieth century that chemists began to understand how and why molecules form. The first major breakthrough was Gilbert Lewis's suggestion that a chemical bond involves electron sharing by atoms. He depicted the formation of a chemical bond in H<sub>2</sub> as



This type of electron pairing is an example of a **covalent bond**, a bond in which two electrons are shared by two atoms. **Covalent compounds** are compounds that contain



**Animation:**  
Ionic versus Covalent Bonding  
ARIS, Animations

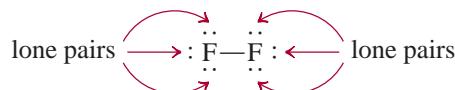
only covalent bonds. For the sake of simplicity, the shared pair of electrons is often represented by a single line. Thus, the covalent bond in the hydrogen molecule can be written as H—H. In a covalent bond, each electron in a shared pair is attracted to the nuclei of both atoms. This attraction holds the two atoms in H<sub>2</sub> together and is responsible for the formation of covalent bonds in other molecules.

This discussion applies only to representative elements. Remember that for these elements, the number of valence electrons is equal to the group number (Groups 1A–7A).

Covalent bonding between many-electron atoms involves only the valence electrons. Consider the fluorine molecule, F<sub>2</sub>. The electron configuration of F is 1s<sup>2</sup>2s<sup>2</sup>2p<sup>5</sup>. The 1s electrons are low in energy and stay near the nucleus most of the time. For this reason they do not participate in bond formation. Thus, each F atom has seven valence electrons (the 2s and 2p electrons). According to Figure 9.1, there is only one unpaired electron on F, so the formation of the F<sub>2</sub> molecule can be represented as follows:

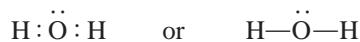


Note that only two valence electrons participate in the formation of F<sub>2</sub>. The other, non-bonding electrons, are called ***lone pairs***—pairs of valence electrons that are not involved in covalent bond formation. Thus, each F in F<sub>2</sub> has three lone pairs of electrons:



The structures we use to represent covalent compounds, such as H<sub>2</sub> and F<sub>2</sub>, are called Lewis structures. A ***Lewis structure*** is a representation of covalent bonding in which shared electron pairs are shown either as lines or as pairs of dots between two atoms, and lone pairs are shown as pairs of dots on individual atoms. Only valence electrons are shown in a Lewis structure.

Let us consider the Lewis structure of the water molecule. Figure 9.1 shows the Lewis dot symbol for oxygen with two unpaired dots or two unpaired electrons, as we expect that O might form two covalent bonds. Because hydrogen has only one electron, it can form only one covalent bond. Thus, the Lewis structure for water is



In this case, the O atom has two lone pairs. The hydrogen atom has no lone pairs because its only electron is used to form a covalent bond.

In the F<sub>2</sub> and H<sub>2</sub>O molecules, the F and O atoms achieve the stable noble gas configuration by sharing electrons:



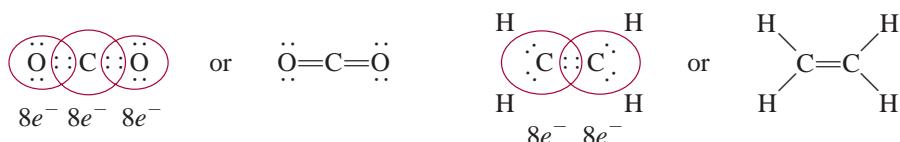
The formation of these molecules illustrates the ***octet rule***, formulated by Lewis: *An atom other than hydrogen tends to form bonds until it is surrounded by eight valence electrons.* In other words, a covalent bond forms when there are not enough electrons for each individual atom to have a complete octet. By sharing electrons in a covalent bond, the individual atoms can complete their octets. The requirement for hydrogen is that it attain the electron configuration of helium, or a total of two electrons.



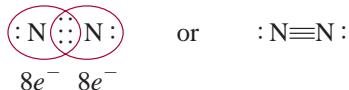
**Interactivity:**  
Covalent Bonds  
ARIS, Interactives

The octet rule works mainly for elements in the second period of the periodic table. These elements have only 2s and 2p subshells, which can hold a total of eight electrons. When an atom of one of these elements forms a covalent compound, it can attain the noble gas electron configuration [Ne] by sharing electrons with other atoms in the same compound. Later, we will discuss a number of important exceptions to the octet rule that give us further insight into the nature of chemical bonding.

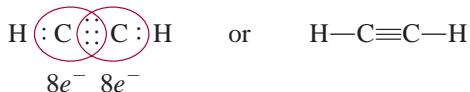
Atoms can form different types of covalent bonds. In a **single bond**, two atoms are held together by one electron pair. Many compounds are held together by **multiple bonds**, that is, bonds formed when two atoms share two or more pairs of electrons. If two atoms share two pairs of electrons, the covalent bond is called a **double bond**. Double bonds are found in molecules of carbon dioxide ( $\text{CO}_2$ ) and ethylene ( $\text{C}_2\text{H}_4$ ):



A **triple bond** arises when two atoms share three pairs of electrons, as in the nitrogen molecule ( $\text{N}_2$ ):

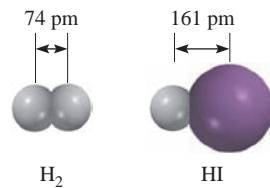


The acetylene molecule ( $\text{C}_2\text{H}_2$ ) also contains a triple bond, in this case between two carbon atoms:



Note that in ethylene and acetylene all the valence electrons are used in bonding; there are no lone pairs on the carbon atoms. In fact, with the exception of carbon monoxide, the vast majority of stable molecules containing carbon do not have lone pairs on the carbon atoms.

Multiple bonds are shorter than single covalent bonds. **Bond length** is defined as the distance between the nuclei of two covalently bonded atoms in a molecule (Figure 9.3). Table 9.2 shows some experimentally determined bond lengths. For a given pair of atoms, such as carbon and nitrogen, triple bonds are shorter than double bonds, which, in turn, are shorter than single bonds. The shorter multiple bonds are also more stable than single bonds, as we will see later.



**Figure 9.3**  
Bond length (in pm) in  $\text{H}_2$  and  $\text{HI}$ .

Shortly you will be introduced to the rules for writing proper Lewis structures. Here we simply want to become familiar with the language associated with them.

**TABLE 9.2**

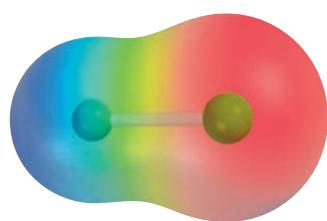
**Average Bond Lengths of Some Common Single, Double, and Triple Bonds**

Bond Type	Bond Length (pm)
C—H	107
C—O	143
C=O	121
C—C	154
C=C	133
C≡C	120
C—N	143
C=N	138
C≡N	116
N—O	136
N=O	122
O—H	96

## 9.5 Electronegativity

A covalent bond, as we have said, is the sharing of an electron pair by two atoms. In a molecule like  $\text{H}_2$ , in which the atoms are identical, we expect the electrons to be equally shared—that is, the electrons spend the same amount of time in the vicinity of each atom. However, in the covalently bonded HF molecule, the H and F atoms do not share the bonding electrons equally because H and F are different atoms:



**Figure 9.4**

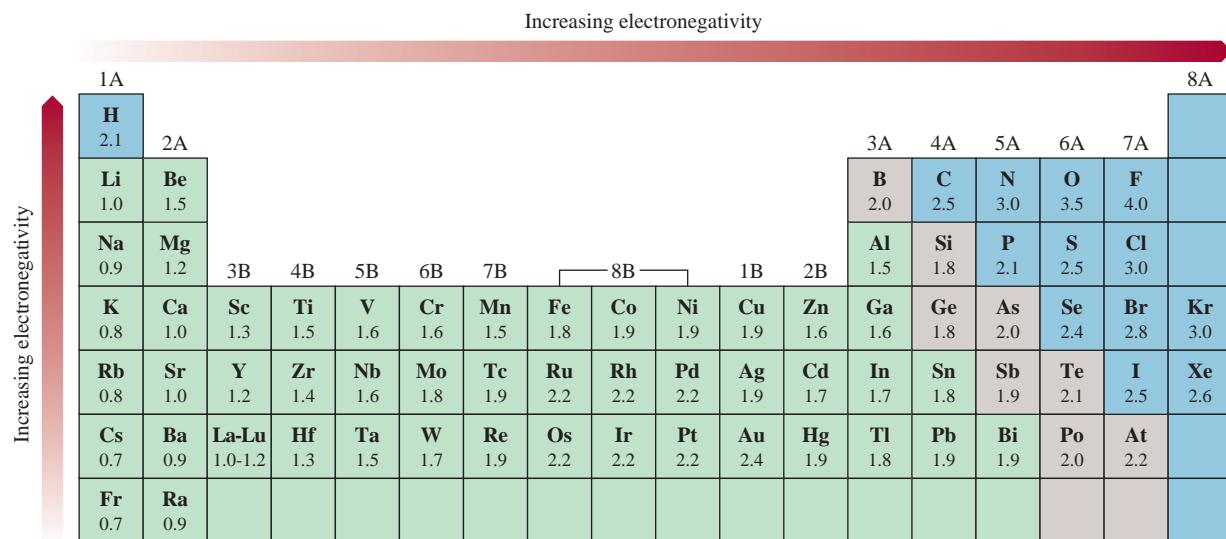
*Electrostatic potential map of the HF molecule. The distribution varies according to the colors of the rainbow. The most electron-rich region is red; the most electron-poor region is blue.*

**Electronegativity values have no units.**

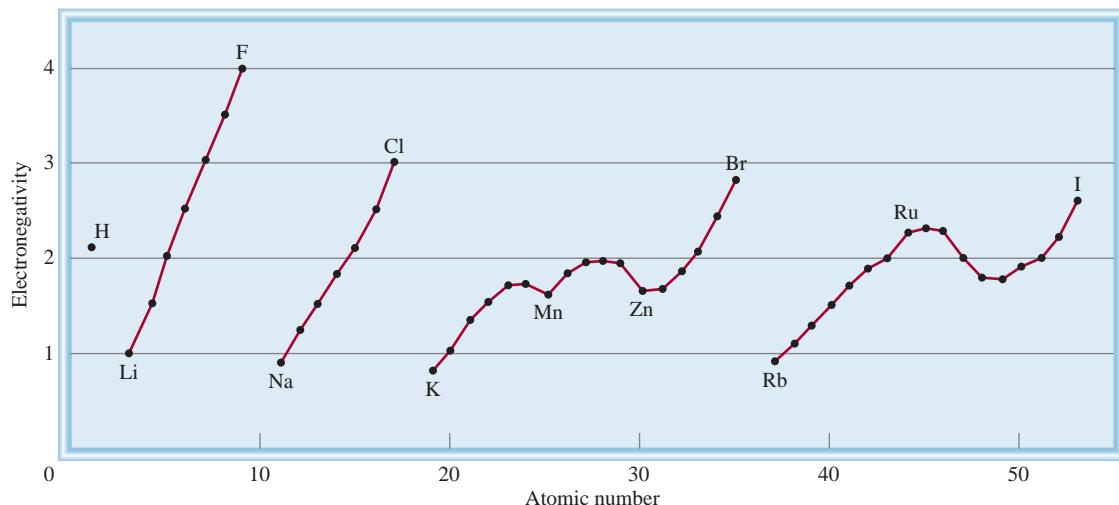
The bond in HF is called a **polar covalent bond**, or simply a **polar bond**, because *the electrons spend more time in the vicinity of one atom than the other*. Experimental evidence indicates that in the HF molecule the electrons spend more time near the F atom. We can think of this unequal sharing of electrons as a partial electron transfer or a shift in electron density, as it is more commonly described, from H to F (Figure 9.4). This “unequal sharing” of the bonding electron pair results in a relatively greater electron density near the fluorine atom and a correspondingly lower electron density near hydrogen. The HF bond and other polar bonds can be thought of as being intermediate between a (nonpolar) covalent bond, in which the sharing of electrons is exactly equal, and an ionic bond, in which the transfer of the electron(s) is nearly complete.

A property that helps us distinguish a nonpolar covalent bond from a polar covalent bond is **electronegativity**, *the ability of an atom to attract toward itself the electrons in a chemical bond*. Elements with high electronegativity have a greater tendency to attract electrons than do elements with low electronegativity. As we might expect, electronegativity is related to electron affinity and ionization energy. Thus, an atom such as fluorine, which has a high electron affinity (tends to pick up electrons easily) and a high ionization energy (does not lose electrons easily), has a high electronegativity. On the other hand, sodium has a low electron affinity, a low ionization energy, and a low electronegativity.

Electronegativity is a relative concept, meaning that an element’s electronegativity can be measured only in relation to the electronegativity of other elements. The American chemist Linus Pauling devised a method for calculating *relative* electronegativities of most elements. These values are shown in Figure 9.5. A careful examination of this chart reveals trends and relationships among electronegativity values of different elements. In general, electronegativity increases from left to right across a period in the periodic table, as the metallic character of the elements decreases. Within each group, electronegativity decreases with increasing atomic number, and increasing metallic character. Note that the transition metals do not follow

**Figure 9.5**

*The electronegativities of common elements.*

**Figure 9.6**

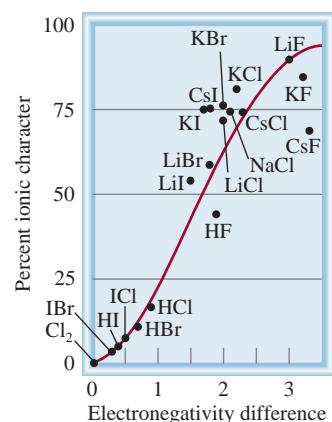
Variation of electronegativity with atomic number. The halogens have the highest electronegativities, and the alkali metals the lowest.

these trends. The most electronegative elements—the halogens, oxygen, nitrogen, and sulfur—are found in the upper right-hand corner of the periodic table, and the least electronegative elements (the alkali and alkaline earth metals) are clustered near the lower left-hand corner. These trends are readily apparent on a graph, as shown in Figure 9.6.

Atoms of elements with widely different electronegativities tend to form ionic bonds (such as those that exist in NaCl and CaO compounds) with each other because the atom of the less electronegative element gives up its electron(s) to the atom of the more electronegative element. An ionic bond generally joins an atom of a metallic element and an atom of a nonmetallic element. Atoms of elements with comparable electronegativities tend to form polar covalent bonds with each other because the shift in electron density is usually small. Most covalent bonds involve atoms of nonmetallic elements. Only atoms of the same element, which have the same electronegativity, can be joined by a pure covalent bond. These trends and characteristics are what we would expect, given our knowledge of ionization energies and electron affinities.

There is no sharp distinction between a polar covalent bond and an ionic bond, but the following rules are helpful as a rough guide. An ionic bond forms when the electronegativity difference between the two bonding atoms is 2.0 or more. This rule applies to most but not all ionic compounds. A polar covalent bond forms when the electronegativity difference between the atoms is in the range of 0.5–1.6. If the electronegativity difference is below 0.3, the bond is normally classified as a covalent bond, with little or no polarity. Sometimes chemists use the quantity *percent ionic character* to describe the nature of a bond. A purely ionic bond would have 100 percent ionic character, although no such bond is known, whereas a purely covalent bond (such as that in H<sub>2</sub>) has 0 percent ionic character. As Figure 9.7 shows, there is a correlation between the percent ionic character of a bond and the electronegativity difference between the bonding atoms.

Electronegativity and electron affinity are related but different concepts. Both indicate the tendency of an atom to attract electrons. However, electron affinity

**Figure 9.7**

Relation between percent ionic character and electronegativity difference.

refers to an isolated atom's attraction for an additional electron, whereas electronegativity signifies the ability of an atom in a chemical bond (with another atom) to attract the shared electrons. Furthermore, electron affinity is an experimentally measurable quantity, whereas electronegativity is an estimated number that cannot be measured.



The most electronegative elements are the nonmetals (Groups 5A–7A) and the least electronegative elements are the alkali and alkaline earth metals (Groups 1A–2A) and aluminum. Beryllium, the first member of Group 2A, forms mostly covalent compounds.

**Similar problems:** 9.37, 9.38.

### Example 9.2

Classify the following bonds as ionic, polar covalent, or covalent: (a) the bond in HCl, (b) the bond in KF, and (c) the CC bond in  $\text{H}_3\text{CCH}_3$ .

**Strategy** We follow the 2.0 rule of electronegativity difference and look up the values in Figure 9.5.

- Solution**
- The electronegativity difference between H and Cl is 0.9, which is appreciable but not large enough (by the 2.0 rule) to qualify HCl as an ionic compound. Therefore, the bond between H and Cl is polar covalent.
  - The electronegativity difference between K and F is 3.2, which is well above the 2.0 mark; therefore, the bond between K and F is ionic.
  - The two C atoms are identical in every respect—they are bonded to each other and each is bonded to three other H atoms. Therefore, the bond between them is purely covalent.

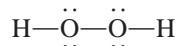
**Practice Exercise** Which of the following bonds is covalent, which is polar covalent, and which is ionic? (a) the bond in CsCl, (b) the bond in  $\text{H}_2\text{S}$ , (c) the NN bond in  $\text{H}_2\text{NNH}_2$ .

## Electronegativity and Oxidation Number

In Chapter 4 we introduced the rules for assigning oxidation numbers of elements in their compounds. The concept of electronegativity is the basis for these rules. In essence, oxidation number refers to the number of charges an atom would have if electrons were transferred completely to the more electronegative of the bonded atoms in a molecule.

Consider the  $\text{NH}_3$  molecule, in which the N atom forms three single bonds with the H atoms. Because N is more electronegative than H, electron density will be shifted from H to N. If the transfer were complete, each H would donate an electron to N, which would have a total charge of  $-3$  while each H would have a charge of  $+1$ . Thus, we assign an oxidation number of  $-3$  to N and an oxidation number of  $+1$  to H in  $\text{NH}_3$ .

Oxygen usually has an oxidation number of  $-2$  in its compounds, except in hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), whose Lewis structure is



A bond between identical atoms makes no contribution to the oxidation number of those atoms because the electron pair of that bond is *equally* shared. Because H has an oxidation number of  $+1$ , each O atom has an oxidation number of  $-1$ .

Can you see now why fluorine always has an oxidation number of  $-1$ ? It is the most electronegative element known, and it *usually* forms a single bond in its compounds. Therefore, it would bear a  $-1$  charge if electron transfer were complete.

## 9.6 Writing Lewis Structures

Although the octet rule and Lewis structures do not present a complete picture of covalent bonding, they do help to explain the bonding scheme in many compounds and account for the properties and reactions of molecules. For this reason, you should practice writing Lewis structures of compounds. The basic steps are as follows:



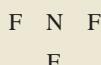
1. Write the skeletal structure of the compound, using chemical symbols and placing bonded atoms next to one another. For simple compounds, this task is fairly easy. For more complex compounds, we must either be given the information or make an intelligent guess about it. In general, the least electronegative atom occupies the central position. Hydrogen and fluorine usually occupy the terminal (end) positions in the Lewis structure.
2. Count the total number of valence electrons present, referring, if necessary, to Figure 9.1. For polyatomic anions, add the number of negative charges to that total. (For example, for the  $\text{CO}_3^{2-}$  ion we add two electrons because the  $2-$  charge indicates that there are two more electrons than are provided by the atoms.) For polyatomic cations, we subtract the number of positive charges from this total. (Thus, for  $\text{NH}_4^+$  we subtract one electron because the  $1+$  charge indicates a loss of one electron from the group of atoms.)
3. Draw a single covalent bond between the central atom and each of the surrounding atoms. Complete the octets of the atoms bonded to the central atom. (Remember that the valence shell of a hydrogen atom is complete with only two electrons.) Electrons belonging to the central or surrounding atoms must be shown as lone pairs if they are not involved in bonding. The total number of electrons to be used is that determined in step 2.
4. After completing steps 1–3, if the central atom has fewer than eight electrons, try adding double or triple bonds between the surrounding atoms and the central atom, using lone pairs from the surrounding atoms to complete the octet of the central atom.

### Example 9.3

Write the Lewis structure for nitrogen trifluoride ( $\text{NF}_3$ ) in which all three F atoms are bonded to the N atom.

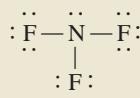
**Solution** We follow the preceding procedure for writing Lewis structure.

*Step 1:* The N atom is less electronegative than F, so the skeletal structure of  $\text{NF}_3$  is

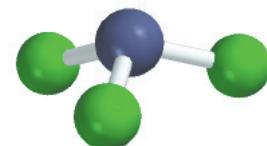


*Step 2:* The outer-shell electron configurations of N and F are  $2s^22p^3$  and  $2s^22p^5$ , respectively. Thus, there are  $5 + (3 \times 7)$ , or 26, valence electrons to account for in  $\text{NF}_3$ .

*Step 3:* We draw a single covalent bond between N and each F, and complete the octets for the F atoms. We place the remaining two electrons on N:



Because this structure satisfies the octet rule for all the atoms, step 4 is not required.



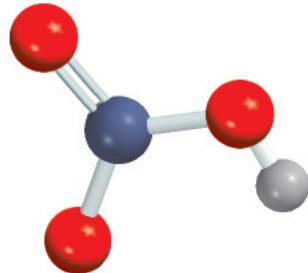
$\text{NF}_3$  is a colorless, odorless, unreactive gas.

(Continued)

**Similar problem:** 9.41.

**Check** Count the valence electrons in  $\text{NF}_3$  (in bonds and in lone pairs). The result is 26, the same as the total number of valence electrons on three F atoms ( $3 \times 7 = 21$ ) and one N atom (5).

**Practice Exercise** Write the Lewis structure for carbon disulfide ( $\text{CS}_2$ ).



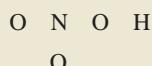
$\text{HNO}_3$  is a strong electrolyte.

### Example 9.4

Write the Lewis structure for nitric acid ( $\text{HNO}_3$ ) in which the three O atoms are bonded to the central N atom and the ionizable H atom is bonded to one of the O atoms.

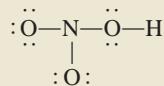
**Solution** We follow the procedure already outlined for writing Lewis structure.

*Step 1:* The skeletal structure of  $\text{HNO}_3$  is

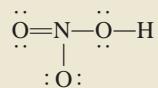


*Step 2:* The outer-shell electron configurations of N, O, and H are  $2s^22p^3$ ,  $2s^22p^4$ , and  $1s^1$ , respectively. Thus, there are  $5 + (3 \times 6) + 1$ , or 24, valence electrons to account for in  $\text{HNO}_3$ .

*Step 3:* We draw a single covalent bond between N and each of the three O atoms and between one O atom and the H atom. Then we fill in electrons to comply with the octet rule for the O atoms:



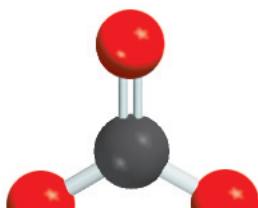
*Step 4:* We see that this structure satisfies the octet rule for all the O atoms but not for the N atom. The N atom has only six electrons. Therefore, we move a lone pair from one of the end O atoms to form another bond with N. Now the octet rule is also satisfied for the N atom:



**Similar problem:** 9.41.

**Check** Make sure that all the atoms (except H) satisfy the octet rule. Count the valence electrons in  $\text{HNO}_3$  (in bonds and in lone pairs). The result is 24, the same as the total number of valence electrons on three O atoms ( $3 \times 6 = 18$ ), one N atom (5), and one H atom (1).

**Practice Exercise** Write the Lewis structure for formic acid ( $\text{HCOOH}$ ).



### Example 9.5

Write the Lewis structure for the carbonate ion ( $\text{CO}_3^{2-}$ ).

**Solution** We follow the preceding procedure for writing Lewis structures and note that this is an anion with two negative charges.

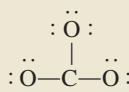
(Continued)

**Step 1:** We can deduce the skeletal structure of the carbonate ion by recognizing that C is less electronegative than O. Therefore, it is most likely to occupy a central position as follows:



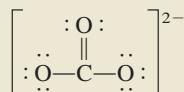
**Step 2:** The outer-shell electron configurations of C and O are  $2s^22p^2$  and  $2s^22p^4$ , respectively, and the ion itself has two negative charges. Thus, the total number of electrons is  $4 + (3 \times 6) + 2$ , or 24.

**Step 3:** We draw a single covalent bond between C and each O and comply with the octet rule for the O atoms:



This structure shows all 24 electrons.

**Step 4:** Although the octet rule is satisfied for the O atoms, it is not for the C atom. Therefore, we move a lone pair from one of the O atoms to form another bond with C. Now the octet rule is also satisfied for the C atom:



We use the brackets to indicate that the  $-2$  charge is on the whole molecule.

**Check** Make sure that all the atoms satisfy the octet rule. Count the valence electrons in  $\text{CO}_3^{2-}$  (in chemical bonds and in lone pairs). The result is 24, the same as the total number of valence electrons on three O atoms ( $3 \times 6 = 18$ ), one C atom (4), and two negative charges (2).

**Practice Exercise** Write the Lewis structure for the nitrite ion ( $\text{NO}_2^-$ ).

Similar problem: 9.42.

## 9.7 Formal Charge and Lewis Structure

By comparing the number of electrons in an isolated atom with the number of electrons that are associated with the same atom in a Lewis structure, we can determine the distribution of electrons in the molecule and draw the most plausible Lewis structure. The bookkeeping procedure is as follows: In an isolated atom, the number of electrons associated with the atom is simply the number of valence electrons. (As usual, we need not be concerned with the inner electrons.) In a molecule, electrons associated with the atom are the nonbonding electrons plus the electrons in the bonding pair(s) between the atom and other atom(s). However, because electrons are shared in a bond, we must divide the electrons in a bonding pair equally between the atoms forming the bond. An atom's **formal charge** is the electrical charge difference between the valence electrons in an isolated atom and the number of electrons assigned to that atom in a Lewis structure.

To assign the number of electrons on an atom in a Lewis structure, we proceed as follows:

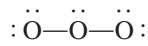
- All the atom's nonbonding electrons are assigned to the atom.
- We break the bond(s) between the atom and other atom(s) and assign half of the bonding electrons to the atom.



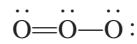
Liquid ozone below its boiling point ( $-111.3^{\circ}\text{C}$ ). Ozone is a toxic, light-blue gas with a pungent odor.

**By the same token, the breaking of a triple bond transfers three electrons to each of the bonding atoms.**

Let us illustrate the concept of formal charge using the ozone molecule ( $\text{O}_3$ ). Proceeding by steps, as we did in Examples 9.3 and 9.4, we draw the skeletal structure of  $\text{O}_3$  and then add bonds and electrons to satisfy the octet rule for the two end atoms:



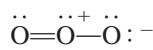
You can see that although all available electrons are used, the octet rule is not satisfied for the central atom. To remedy this, we convert a lone pair on one of the end atoms to a second bond between that end atom and the central atom, as follows:



The formal charge on each atom in  $\text{O}_3$  can now be calculated according to the following scheme:

$\begin{array}{c} \cdot\ddot{\text{O}}\cdots \\   \\ \cdot\ddot{\text{O}}=\text{O}-\ddot{\text{O}}\cdot \\   \\ \cdot\ddot{\text{O}}\cdots \end{array}$	$\begin{array}{c} \text{Valence } e^- \\ \hline e^- \text{ assigned to atom} \end{array}$	$\begin{array}{c} 6 & 6 & 6 \\ \hline 6 & 5 & 7 \end{array}$	$\begin{array}{c} \text{Difference} \\ (\text{formal charge}) \end{array}$	$\begin{array}{c} 0 & +1 & -1 \end{array}$
---	---	--	--	--

where the wavy red lines denote the breaking of the bonds. Note that the breaking of a single bond results in the transfer of an electron, the breaking of a double bond results in a transfer of two electrons to each of the bonding atoms, and so on. Thus, the formal charges of the atoms in  $\text{O}_3$  are



For single positive and negative charges, we normally omit the numeral 1.

When you write formal charges, these rules are helpful:

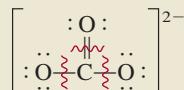
1. For molecules, the sum of the formal charges must add up to zero because molecules are electrically neutral species. (This rule applies, for example, to the  $\text{O}_3$  molecule.)
2. For cations, the sum of the formal charges must equal the positive charge.
3. For anions, the sum of the formal charges must equal the negative charge.

Keep in mind that formal charges do not represent actual charge separation within the molecule. In the  $\text{O}_3$  molecule, for example, there is no evidence that the central atom bears a net +1 charge or that one of the end atoms bears a -1 charge. Writing these charges on the atoms in the Lewis structure merely helps us keep track of the valence electrons in the molecule.

### Example 9.6

Write formal charges for the carbonate ion.

**Solution** The Lewis structure for the carbonate ion was developed in Example 9.5:



The formal charges on the atoms can be calculated using the given procedure.

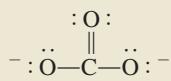
(Continued)

**The C atom:** The C atom has four valence electrons and there are no nonbonding electrons on the atom in the Lewis structure. The breaking of the double bond and two single bonds results in the transfer of four electrons to the C atom. Therefore, the formal charge is  $4 - 4 = 0$ .

**The O atom in  $\text{C}=\text{O}$ :** The O atom has six valence electrons and there are four nonbonding electrons on the atom. The breaking of the double bond results in the transfer of two electrons to the O atom. Here the formal charge is  $6 - 4 - 2 = 0$ .

**The O atom in  $\text{C}-\text{O}$ :** This atom has six nonbonding electrons and the breaking of the single bond transfers another electron to it. Therefore, the formal charge is  $6 - 6 - 1 = -1$ .

Thus, the Lewis structure for  $\text{CO}_3^{2-}$  with formal charges is



**Check** Note that the sum of the formal charges is  $-2$ , the same as the charge on the carbonate ion.

**Similar problem: 9.42.**

**Practice Exercise** Write formal charges for the nitrite ion ( $\text{NO}_2^-$ ).

Sometimes there is more than one acceptable Lewis structure for a given species. In such cases, we can often select the most plausible Lewis structure by using formal charges and the following guidelines:

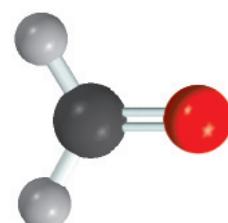
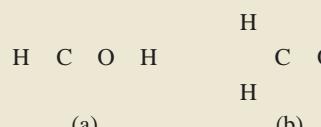
- For molecules, a Lewis structure in which there are no formal charges is preferable to one in which formal charges are present.
- Lewis structures with large formal charges (+2, +3, and/or  $-2$ ,  $-3$ , and so on) are less plausible than those with small formal charges.
- Among Lewis structures having similar distributions of formal charges, the most plausible structure is the one in which negative formal charges are placed on the more electronegative atoms.

### Example 9.7

Formaldehyde ( $\text{CH}_2\text{O}$ ), a liquid with a disagreeable odor, traditionally has been used to preserve laboratory specimens. Draw the most likely Lewis structure for the compound.

**Strategy** A plausible Lewis structure should satisfy the octet rule for all the elements, except H, and have the formal charges (if any) distributed according to electronegativity guidelines.

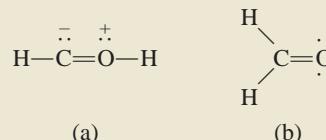
**Solution** The two possible skeletal structures are



$\text{CH}_2\text{O}$

*(Continued)*

First we draw the Lewis structures for each of these possibilities

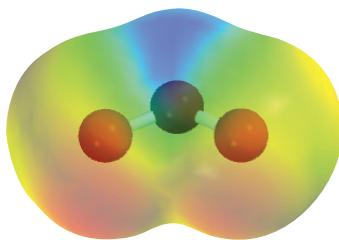


To show the formal charges, we follow the procedure given in Example 9.6. In (a), the C atom has a total of five electrons (one lone pair plus three electrons from the breaking of a single and a double bond). Because C has four valence electrons, the formal charge on the atom is  $4 - 5 = -1$ . The O atom has a total of five electrons (one lone pair and three electrons from the breaking of a single and a double bond). Because O has six valence electrons, the formal charge on the atom is  $6 - 5 = +1$ . In (b) the C atom has a total of four electrons from the breaking of two single bonds and a double bond, so its formal charge is  $4 - 4 = 0$ . The O atom has a total of six electrons (two lone pairs and two electrons from the breaking of the double bond). Therefore, the formal charge on the atom is  $6 - 6 = 0$ . Although both structures satisfy the octet rule, (b) is the more likely structure because it carries no formal charges.

**Check** In each case, make sure that the total number of valence electrons is 12. Can you suggest two other reasons why (a) is less plausible?

**Practice Exercise** Draw the most reasonable Lewis structure of a molecule that contains an N atom, a C atom, and an H atom.

**Similar problem:** 9.43.



Electrostatic potential map of O<sub>3</sub>. The electron density is evenly distributed between the two end O atoms.

## 9.8 The Concept of Resonance

Our drawing of the Lewis structure for ozone (O<sub>3</sub>) satisfied the octet rule for the central atom because we placed a double bond between it and one of the two end O atoms. In fact, we can put the double bond at either end of the molecule, as shown by these two equivalent Lewis structures:



However, neither one of these two Lewis structures accounts for the known bond lengths in O<sub>3</sub>.

We would expect the O—O bond in O<sub>3</sub> to be longer than the O=O bond because double bonds are known to be shorter than single bonds. Yet experimental evidence shows that both oxygen-to-oxygen bonds are equal in length (128 pm). We resolve this discrepancy by using *both* Lewis structures to represent the ozone molecule:

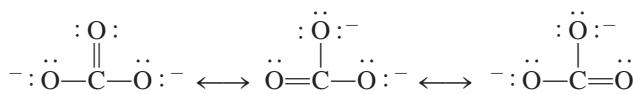


Each of these structures is called a resonance structure. A **resonance structure**, then, is *one of two or more Lewis structures for a single molecule that cannot be represented accurately by only one Lewis structure*. The double-headed arrow indicates that the structures shown are resonance structures.

The term **resonance** itself means *the use of two or more Lewis structures to represent a particular molecule*. Like the medieval European traveler to Africa who described a rhinoceros as a cross between a griffin and a unicorn, two familiar but imaginary animals, we describe ozone, a real molecule, in terms of two familiar but nonexistent structures.

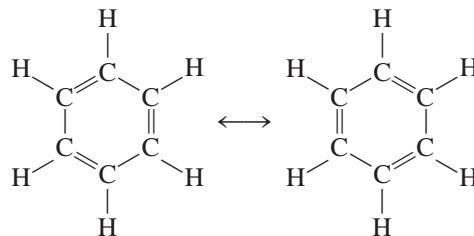
A common misconception about resonance is the notion that a molecule such as ozone somehow shifts quickly back and forth from one resonance structure to the other. Keep in mind that *neither* resonance structure adequately represents the actual molecule, which has its own unique, stable structure. “Resonance” is a human invention, designed to address the limitations in these simple bonding models. To extend the animal analogy, a rhinoceros is a distinct creature, not some oscillation between mythical griffin and unicorn!

The carbonate ion provides another example of resonance:



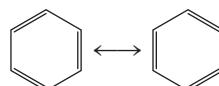
According to experimental evidence, all carbon-to-oxygen bonds in  $\text{CO}_3^{2-}$  are equivalent. Therefore, the properties of the carbonate ion are best explained by considering its resonance structures together.

The concept of resonance applies equally well to organic systems. A good example is the benzene molecule ( $\text{C}_6\text{H}_6$ ):



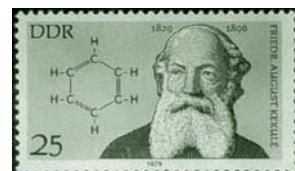
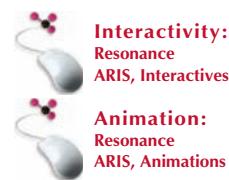
If one of these resonance structures corresponded to the actual structure of benzene, there would be two different bond lengths between adjacent C atoms, one characteristic of the single bond and the other of the double bond. In fact, the distance between all adjacent C atoms in benzene is 140 pm, which is shorter than a C—C bond (154 pm) and longer than a C=C bond (133 pm).

A simpler way of drawing the structure of the benzene molecule and other compounds containing the “benzene ring” is to show only the skeleton and not the carbon and hydrogen atoms. By this convention the resonance structures are represented by

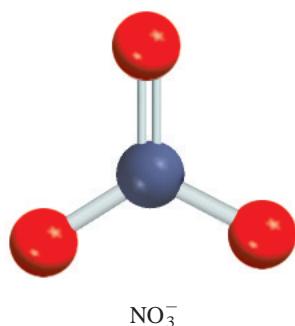


Note that the C atoms at the corners of the hexagon and the H atoms are all omitted, although they are understood to exist. Only the bonds between the C atoms are shown.

Remember this important rule for drawing resonance structures: The positions of electrons (that is, bonds), but not those of atoms, can be rearranged in different resonance structures. In other words, the same atoms must be bonded to one another in all the resonance structures for a given species.



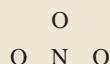
The hexagonal structure of benzene was first proposed by the German chemist August Kekulé (1829–1896).



Similar problems: 9.49, 9.54.

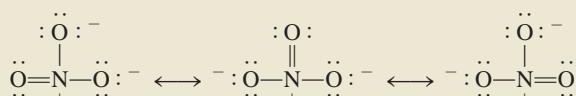
### Example 9.8

Draw resonance structures (including formal charges) for the nitrate ion,  $\text{NO}_3^-$ , which has the following skeletal arrangement:



**Strategy** We follow the procedure used for drawing Lewis structures and calculating formal charges in Examples 9.5 and 9.6.

**Solution** Just as in the case of the carbonate ion, we can draw three equivalent resonance structures for the nitrate ion:



**Check** Because N has five valence electrons and each O has six valence electrons and there is a net negative charge, the total number of valence electrons is  $5 + (3 \times 6) + 1 = 24$ , the same as the number of valence electrons in the  $\text{NO}_3^-$  ion.

**Practice Exercise** Draw resonance structures for the nitrite ion ( $\text{NO}_2^-$ ).



**Interactivity:**  
Octet Rule Exceptions  
ARIS, Interactives



Beryllium, unlike the other Group 2A elements, forms mostly covalent compounds of which  $\text{BeH}_2$  is an example.

## 9.9 Exceptions to the Octet Rule

As mentioned earlier, the octet rule applies mainly to the second-period elements. Exceptions to the octet rule fall into three categories characterized by an incomplete octet, an odd number of electrons, or more than eight valence electrons around the central atom.

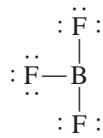
### The Incomplete Octet

In some compounds, the number of electrons surrounding the central atom in a stable molecule is fewer than eight. Consider, for example, beryllium, which is a Group 2A (and a second-period) element. The electron configuration of beryllium is  $1s^22s^2$ ; it has two valence electrons in the  $2s$  orbital. In the gas phase, beryllium hydride ( $\text{BeH}_2$ ) exists as discrete molecules. The Lewis structure of  $\text{BeH}_2$  is

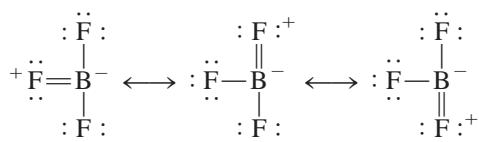


As you can see, only four electrons surround the Be atom, and there is no way to satisfy the octet rule for beryllium in this molecule.

Elements in Group 3A, particularly boron and aluminum, also tend to form compounds in which they are surrounded by fewer than eight electrons. Take boron as an example. Because its electron configuration is  $1s^22s^22p^1$ , it has a total of three valence electrons. Boron reacts with the halogens to form a class of compounds having the general formula  $\text{BX}_3$ , where X is a halogen atom. Thus, in boron trifluoride there are only six electrons around the boron atom:

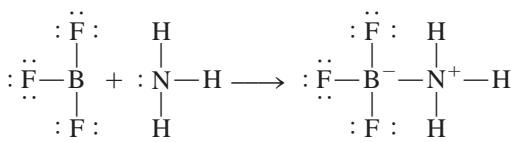


The following resonance structures all contain a double bond between B and F and satisfy the octet rule for boron:



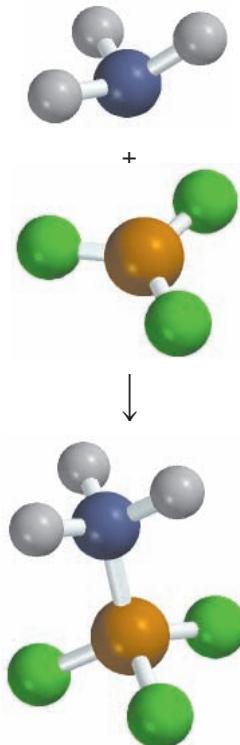
The fact that the B—F bond length in  $\text{BF}_3$  (130.9 pm) is shorter than a single bond (137.3 pm) lends support to the resonance structures even though in each case the negative formal charge is placed on the B atom and the positive formal charge on the F atom.

Although boron trifluoride is stable, it readily reacts with ammonia. This reaction is better represented by using the Lewis structure in which boron has only six valence electrons around it:



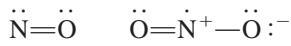
It seems that the properties of the  $\text{BF}_3$  molecule are best explained by all four resonance structures.

The B—N bond in the preceding compound is different from the covalent bonds discussed so far in the sense that both electrons are contributed by the N atom. This type of bond is called a *coordinate covalent bond* (also referred to as a *dative bond*), defined as a covalent bond in which one of the atoms donates both electrons. Although the properties of a coordinate covalent bond do not differ from those of a normal covalent bond (because all electrons are alike no matter what their source), the distinction is useful for keeping track of valence electrons and assigning formal charges.



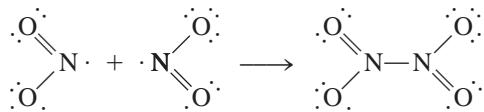
## Odd-Electron Molecules

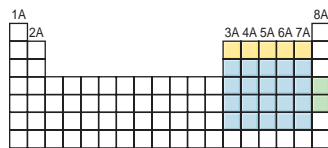
Some molecules contain an *odd* number of electrons. Among them are nitric oxide ( $\text{NO}$ ) and nitrogen dioxide ( $\text{NO}_2$ ):



Because we need an even number of electrons for complete pairing (to reach eight), the octet rule clearly cannot be satisfied for all the atoms in any of these molecules.

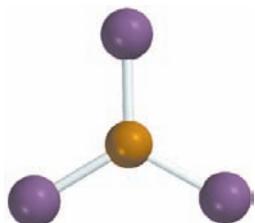
Odd-electron molecules are sometimes called *radicals*. Many radicals are highly reactive. The reason is that there is a tendency for the unpaired electron to form a covalent bond with an unpaired electron on another molecule. For example, when two nitrogen dioxide molecules collide, they form dinitrogen tetroxide in which the octet rule is satisfied for both the N and O atoms:





Yellow: second-period elements cannot have an expanded octet. Blue: third-period elements and beyond can have an expanded octet. Green: the noble gases usually only have an expanded octet.

**Sulfur dichloride** is a toxic, foul-smelling cherry-red liquid (boiling point: 59°C).

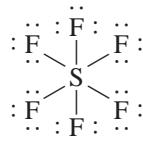


$\text{AlI}_3$  has a tendency to dimerize or form two units as  $\text{Al}_2\text{I}_6$ .

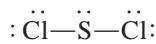
**Similar problem:** 9.60.

## The Expanded Octet

Atoms of the second-period elements cannot have more than eight valence electrons around the central atom, but atoms of elements in and beyond the third period of the periodic table form some compounds in which more than eight electrons surround the central atom. In addition to the 3s and 3p orbitals, elements in the third period also have 3d orbitals that can be used in bonding. These orbitals enable an atom to form an *expanded octet*. One compound in which there is an expanded octet is sulfur hexafluoride, a very stable compound. The electron configuration of sulfur is  $[\text{Ne}]3s^23p^4$ . In  $\text{SF}_6$ , each of sulfur's six valence electrons forms a covalent bond with a fluorine atom, so there are twelve electrons around the central sulfur atom:



In Chapter 10 we will see that these 12 electrons, or six bonding pairs, are accommodated in six orbitals that originate from the one 3s, the three 3p, and two of the five 3d orbitals. Sulfur also forms many compounds in which it obeys the octet rule. In sulfur dichloride, for instance, S is surrounded by only eight electrons:

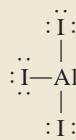


### Example 9.9

Draw the Lewis structure for aluminum triiodide ( $\text{AlI}_3$ ).

**Strategy** We follow the procedures used in Examples 9.5 and 9.6 to draw the Lewis structure and calculate formal charges.

**Solution** The outer-shell electron configurations of Al and I are  $3s^23p^1$  and  $5s^25p^5$ , respectively. The total number of valence electrons is  $3 + (3 \times 7)$  or 24. Because Al is less electronegative than I, it occupies a central position and forms three bonds with the I atoms:



Note that there are no formal charges on the Al and I atoms.

**Check** Although the octet rule is satisfied for the I atoms, there are only six valence electrons around the Al atom. Thus,  $\text{AlI}_3$  is an example of the incomplete octet.

**Practice Exercise** Draw the Lewis structure for  $\text{BeF}_2$ .

### Example 9.10

Draw the Lewis structure for phosphorus pentafluoride ( $\text{PF}_5$ ), in which all five F atoms are bonded to the central P atom.

(Continued)

**Strategy** Note that P is a third-period element. We follow the procedures given in Examples 9.5 and 9.6 to draw the Lewis structure and calculate formal charges.

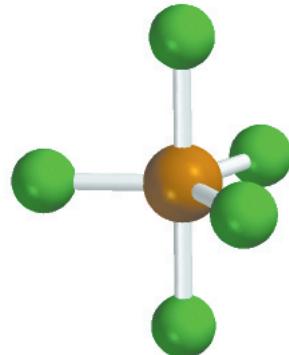
**Solution** The outer-shell electron configurations for P and F are  $3s^23p^3$  and  $2s^22p^5$ , respectively, and so the total number of valence electrons is  $5 + (5 \times 7)$ , or 40. Phosphorus, like sulfur, is a third-period element, and therefore it can have an expanded octet. The Lewis structure of  $\text{PF}_5$  is



Note that there are no formal charges on the P and F atoms.

**Check** Although the octet rule is satisfied for the F atoms, there are 10 valence electrons around the P atom, giving it an expanded octet.

**Practice Exercise** Draw the Lewis structure for arsenic pentafluoride ( $\text{AsF}_5$ ).



$\text{PF}_5$  is a reactive gaseous compound.

**Similar problem:** 9.62.

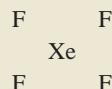
A final note about the expanded octet: In drawing Lewis structures of compounds containing a central atom from the third period and beyond, sometimes we find that the octet rule is satisfied for all the atoms but there are still valence electrons left to place. In such cases, the extra electrons should be placed as lone pairs on the central atom.

### Example 9.11

Draw a Lewis structure of the noble gas compound xenon tetrafluoride ( $\text{XeF}_4$ ) in which all F atoms are bonded to the central Xe atom.

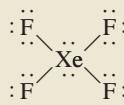
**Strategy** Note that Xe is a fifth-period element. We follow the procedures in Examples 9.5 and 9.6 for drawing the Lewis structure and calculating formal charges.

**Solution** *Step 1:* The skeletal structure of  $\text{XeF}_4$  is

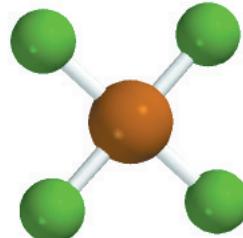


*Step 2:* The outer-shell electron configurations of Xe and F are  $5s^25p^6$  and  $2s^22p^5$ , respectively, and so the total number of valence electrons is  $8 + (4 \times 7)$  or 36.

*Step 3:* We draw a single covalent bond between all the bonding atoms. The octet rule is satisfied for the F atoms, each of which has three lone pairs. The sum of the lone pair electrons on the four F atoms ( $4 \times 6$ ) and the four bonding pairs ( $4 \times 2$ ) is 32. Therefore, the remaining four electrons are shown as two lone pairs on the Xe atom:



We see that the Xe atom has an expanded octet. There are no formal charges on the Xe and F atoms.



$\text{XeF}_4$

**Similar problem:** 9.41.

**Practice Exercise** Write the Lewis structure of sulfur tetrafluoride ( $\text{SF}_4$ ).

## 9.10 Bond Enthalpy

A measure of the stability of a molecule is its **bond enthalpy**, which is *the enthalpy change required to break a particular bond in 1 mole of gaseous molecules.* (Bond enthalpies in solids and liquids are affected by neighboring molecules.) The experimentally determined bond enthalpy of the diatomic hydrogen molecule, for example, is



This equation tells us that breaking the covalent bonds in 1 mole of gaseous  $\text{H}_2$  molecules requires 436.4 kJ of energy. For the less stable chlorine molecule,

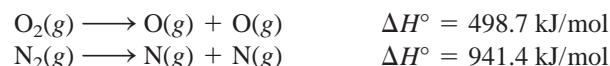


Bond enthalpies can also be directly measured for diatomic molecules containing unlike elements, such as  $\text{HCl}$ ,

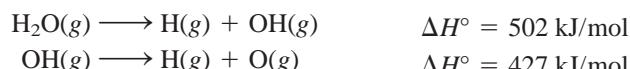


as well as for molecules containing double and triple bonds:

The Lewis structure of  $\text{O}_2$  is 



Measuring the strength of covalent bonds in polyatomic molecules is more complicated. For example, measurements show that the energy needed to break the first O—H bond in  $\text{H}_2\text{O}$  is different from that needed to break the second O—H bond:

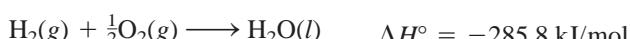


In each case, an O—H bond is broken, but the first step is more endothermic than the second. The difference between the two  $\Delta H^\circ$  values suggests that the second O—H bond itself has undergone change, because of the changes in the chemical environment.

Now we can understand why the bond enthalpy of the same O—H bond in two different molecules such as methanol ( $\text{CH}_3\text{OH}$ ) and water ( $\text{H}_2\text{O}$ ) will not be the same: their environments are different. Thus, for polyatomic molecules we speak of the *average* bond enthalpy of a particular bond. For example, we can measure the energy of the O—H bond in 10 different polyatomic molecules and obtain the average O—H bond enthalpy by dividing the sum of the bond enthalpies by 10. Table 9.3 lists the average bond enthalpies of a number of diatomic and polyatomic molecules. As stated earlier, triple bonds are stronger than double bonds, which, in turn, are stronger than single bonds.

### Use of Bond Enthalpies in Thermochemistry

A comparison of the thermochemical changes that take place during a number of reactions (Chapter 6) reveals a strikingly wide variation in the enthalpies of different reactions. For example, the combustion of hydrogen gas in oxygen gas is fairly exothermic:



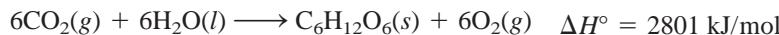
**TABLE 9.3** Some Bond Enthalpies of Diatomic Molecules\* and Average Bond Enthalpies for Bonds in Polyatomic Molecules

Bond	Bond Enthalpy (kJ/mol)	Bond	Bond Enthalpy (kJ/mol)
H—H	436.4	C—S	255
H—N	393	C=S	477
H—O	460	N—N	193
H—S	368	N=N	418
H—P	326	N≡N	941.4
H—F	568.2	N—O	176
H—Cl	431.9	N=O	607
H—Br	366.1	O—O	142
H—I	298.3	O=O	498.7
C—H	414	O—P	502
C—C	347	O=S	469
C=C	620	P—P	197
C≡C	812	P=P	489
C—N	276	S—S	268
C=N	615	S=S	352
C≡N	891	F—F	156.9
C—O	351	Cl—Cl	242.7
C=O <sup>†</sup>	745	Br—Br	192.5
C—P	263	I—I	151.0

\*Bond enthalpies for diatomic molecules (in color) have more significant figures than bond enthalpies for bonds in polyatomic molecules because the bond enthalpies of diatomic molecules are directly measurable quantities and not averaged over many compounds.

<sup>†</sup>The C=O bond enthalpy in CO<sub>2</sub> is 799 kJ/mol.

On the other hand, the formation of glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) from water and carbon dioxide, best achieved by photosynthesis, is highly endothermic:



We can account for such variations by looking at the stability of individual reactant and product molecules. After all, most chemical reactions involve the making and breaking of bonds. Therefore, knowing the bond enthalpies and hence the stability of molecules tells us something about the thermochemical nature of reactions that molecules undergo.

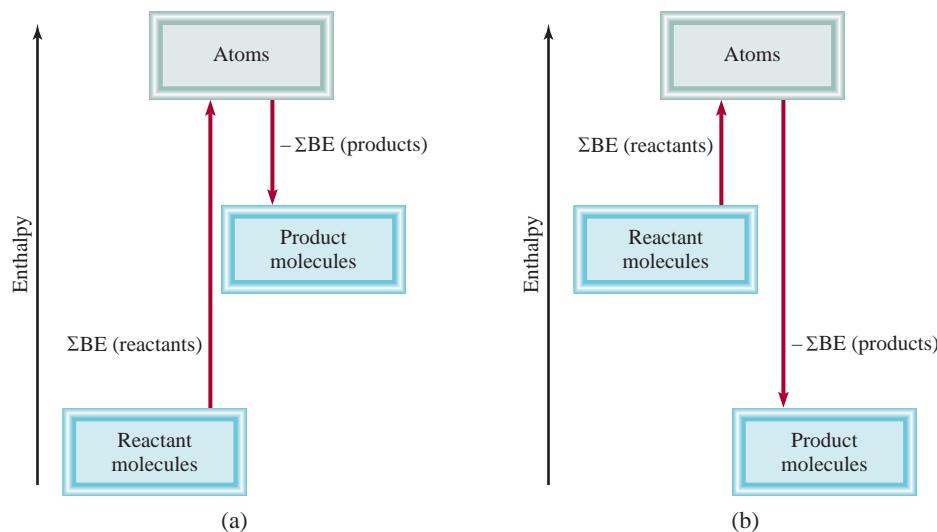
In many cases, it is possible to predict the approximate enthalpy of reaction by using the average bond enthalpies. Because energy is always required to break chemical bonds and chemical bond formation is always accompanied by a release of energy, we can estimate the enthalpy of a reaction by counting the total number of bonds broken and formed in the reaction and recording all the corresponding energy changes. The enthalpy of reaction in the *gas phase* is given by

$$\begin{aligned} \Delta H^\circ &= \Sigma \text{BE(reactants)} - \Sigma \text{BE(products)} \\ &= \text{total energy input} - \text{total energy released} \end{aligned} \quad (9.3)$$

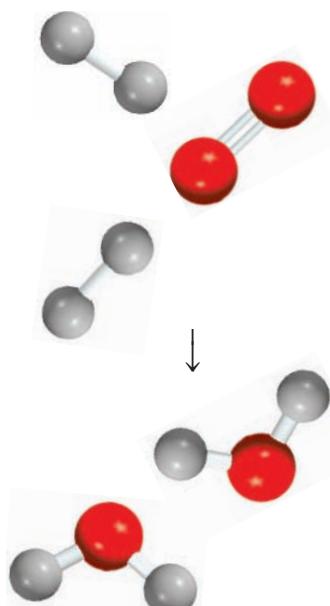
where BE stands for average bond enthalpy and  $\Sigma$  is the summation sign. As written, Equation (9.3) takes care of the sign convention for  $\Delta H^\circ$ . Thus, if the total energy

**Figure 9.8**

*Bond enthalpy changes in (a) an endothermic reaction and (b) an exothermic reaction.*

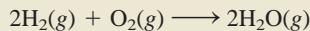


input is greater than the total energy released,  $\Delta H^\circ$  is positive and the reaction is endothermic. On the other hand, if more energy is released than absorbed,  $\Delta H^\circ$  is negative and the reaction is exothermic (Figure 9.8). If reactants and products are all diatomic molecules, then Equation (9.3) will yield accurate results because the bond enthalpies of diatomic molecules are accurately known. If some or all of the reactants and products are polyatomic molecules, Equation (9.3) will yield only approximate results because the bond enthalpies used will be averages.



### Example 9.12

Estimate the enthalpy change for the combustion of hydrogen gas:



**Strategy** Note that  $\text{H}_2\text{O}$  is a polyatomic molecule, and so we need to use the average bond enthalpy value for the O—H bond.

**Solution** We construct the following table:

Type of bonds broken	Number of bonds broken	Bond enthalpy (kJ/mol)	Energy change (kJ/mol)
H—H ( $\text{H}_2$ )	2	436.4	872.8
O=O ( $\text{O}_2$ )	2	498.7	498.7
Type of bonds formed	Number of bonds formed	Bond enthalpy (kJ/mol)	Energy change (kJ/mol)
O—H ( $\text{H}_2\text{O}$ )	4	460	1840

Next, we obtain the total energy input and total energy released:

$$\text{total energy input} = 872.8 \text{ kJ/mol} + 498.7 \text{ kJ/mol} = 1371.5 \text{ kJ/mol}$$

$$\text{total energy released} = 1840 \text{ kJ/mol}$$

(Continued)

Using Equation (9.3), we write

$$\Delta H^\circ = 1371.5 \text{ kJ/mol} - 1840 \text{ kJ/mol} = -469 \text{ kJ/mol}$$

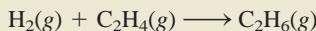
This result is only an estimate because the bond enthalpy of O—H is an average quantity. Alternatively, we can use Equation (6.18) and the data in Appendix 3 to calculate the enthalpy of reaction:

$$\begin{aligned}\Delta H^\circ &= 2\Delta H_f^\circ(\text{H}_2\text{O}) - [2\Delta H_f^\circ(\text{H}_2) + \Delta H_f^\circ(\text{O}_2)] \\ &= 2(-241.8 \text{ kJ/mol}) - 0 - 0 \\ &= -483.6 \text{ kJ/mol}\end{aligned}$$

**Check** Note that the estimated value based on average bond enthalpies is quite close to the value calculated using  $\Delta H_f^\circ$  data. In general, Equation (9.3) works best for reactions that are either quite endothermic or quite exothermic, that is, reactions for which  $\Delta H_{\text{rxn}}^\circ > 100 \text{ kJ/mol}$  or for which  $\Delta H_{\text{rxn}}^\circ < -100 \text{ kJ/mol}$ .

**Similar problem: 9.70.**

**Practice Exercise** For the reaction



- Estimate the enthalpy of reaction, using the bond enthalpy values in Table 9.3.
- Calculate the enthalpy of reaction, using standard enthalpies of formation. ( $\Delta H_f^\circ$  for  $\text{H}_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$  are 0, 52.3 kJ/mol, and  $-84.7 \text{ kJ/mol}$ , respectively.)

## KEY EQUATION

$$\Delta H^\circ = \Sigma \text{BE}(\text{reactants}) - \Sigma \text{BE}(\text{products}) \quad (9.3) \quad \text{Calculating enthalpy change of a reaction from bond enthalpies.}$$

## SUMMARY OF FACTS AND CONCEPTS

- A Lewis dot symbol shows the number of valence electrons possessed by an atom of a given element. Lewis dot symbols are useful mainly for the representative elements.
- In a covalent bond, two electrons (one pair) are shared by two atoms. In multiple covalent bonds, two or three electron pairs are shared by two atoms. Some bonded atoms possess lone pairs, that is, pairs of valence electrons not involved in bonding. The arrangement of bonding electrons and lone pairs around each atom in a molecule is represented by the Lewis structure.
- Electronegativity is a measure of the ability of an atom to attract electrons in a chemical bond.
- The octet rule predicts that atoms form enough covalent bonds to surround themselves with eight electrons each.

When one atom in a covalently bonded pair donates two electrons to the bond, the Lewis structure can include the formal charge on each atom as a means of keeping track of the valence electrons. There are exceptions to the octet rule, particularly for covalent beryllium compounds, elements in Group 3A, and elements in the third period and beyond in the periodic table.

- For some molecules or polyatomic ions, two or more Lewis structures based on the same skeletal structure satisfy the octet rule and appear chemically reasonable. Such resonance structures taken together represent the molecule or ion.
- The strength of a covalent bond is measured in terms of its bond enthalpy. Bond enthalpies can be used to estimate the enthalpy of reactions.

## KEY WORDS

Bond enthalpy, p. 302	Covalent bond, p. 285	Lattice energy, p. 283	Polar covalent bond, p. 288
Bond length, p. 287	Covalent compound, p. 285	Lewis dot symbol, p. 280	Resonance, p. 297
Born-Haber cycle, p. 283	Double bond, p. 287	Lewis structure, p. 286	Resonance structure, p. 296
Coordinate covalent bond, p. 299	Electronegativity, p. 288	Lone pair, p. 286	Single bond, p. 287
Coulomb's law, p. 283	Formal charge, p. 293	Multiple bond, p. 287	Triple bond, p. 287
	Ionic bond, p. 281	Octet rule, p. 286	

## QUESTIONS AND PROBLEMS

### Lewis Dot Symbols

#### Review Questions

- 9.1 What is a Lewis dot symbol? To what elements does the symbol mainly apply?
- 9.2 Use the second member of each group from Group 1A to Group 7A to show that the number of valence electrons on an atom of the element is the same as its group number.
- 9.3 Without referring to Figure 9.1, write Lewis dot symbols for atoms of the following elements: (a) Be, (b) K, (c) Ca, (d) Ga, (e) O, (f) Br, (g) N, (h) I, (i) As, (j) F.
- 9.4 Write Lewis dot symbols for the following ions: (a) Li<sup>+</sup>, (b) Cl<sup>-</sup>, (c) S<sup>2-</sup>, (d) Sr<sup>2+</sup>, (e) N<sup>3+</sup>.
- 9.5 Write Lewis dot symbols for the following atoms and ions: (a) I, (b) I<sup>-</sup>, (c) S, (d) S<sup>2-</sup>, (e) P, (f) P<sup>3-</sup>, (g) Na, (h) Na<sup>+</sup>, (i) Mg, (j) Mg<sup>2+</sup>, (k) Al, (l) Al<sup>3+</sup>, (m) Pb, (n) Pb<sup>2+</sup>.

### The Ionic Bond

#### Review Questions

- 9.6 Explain what an ionic bond is.
- 9.7 Explain how ionization energy and electron affinity determine whether atoms of elements will combine to form ionic compounds.
- 9.8 Name five metals and five nonmetals that are very likely to form ionic compounds. Write formulas for compounds that might result from the combination of these metals and nonmetals. Name these compounds.
- 9.9 Name one ionic compound that contains only nonmetallic elements.
- 9.10 Name one ionic compound that contains a polyatomic cation and a polyatomic anion (see Table 2.3).
- 9.11 Explain why ions with charges greater than 3 are seldom found in ionic compounds.

- 9.12 The term “molar mass” was introduced in Chapter 3. What is the advantage of using the term “molar mass” when we discuss ionic compounds?
- 9.13 In which of the following states would NaCl be electrically conducting? (a) solid, (b) molten (that is, melted), (c) dissolved in water. Explain your answers.
- 9.14 Beryllium forms a compound with chlorine that has the empirical formula BeCl<sub>2</sub>. How would you determine whether it is an ionic compound? (The compound is not soluble in water.)

#### Problems

- 9.15 An ionic bond is formed between a cation A<sup>+</sup> and an anion B<sup>-</sup>. How would the energy of the ionic bond [see Equation (9.2)] be affected by the following changes? (a) doubling the radius of A<sup>+</sup>, (b) tripling the charge on A<sup>+</sup>, (c) doubling the charges on A<sup>+</sup> and B<sup>-</sup>, (d) decreasing the radii of A<sup>+</sup> and B<sup>-</sup> to half their original values.
- 9.16 Give the empirical formulas and names of the compounds formed from the following pairs of ions: (a) Rb<sup>+</sup> and I<sup>-</sup>, (b) Cs<sup>+</sup> and SO<sub>4</sub><sup>2-</sup>, (c) Sr<sup>2+</sup> and N<sup>3-</sup>, (d) Al<sup>3+</sup> and S<sup>2-</sup>.
- 9.17 Use Lewis dot symbols to show the transfer of electrons between the following atoms to form cations and anions: (a) Na and F, (b) K and S, (c) Ba and O, (d) Al and N.
- 9.18 Write the Lewis dot symbols of the reactants and products in the following reactions. (First balance the equations.)
  - (a) Sr + Se → SrSe
  - (b) Ca + H<sub>2</sub> → CaH<sub>2</sub>
  - (c) Li + N<sub>2</sub> → Li<sub>3</sub>N
  - (d) Al + S → Al<sub>2</sub>S<sub>3</sub>
- 9.19 For each of the following pairs of elements, state whether the binary compound they form is likely to be ionic or covalent. Write the empirical formula and name of the compound: (a) I and Cl, (b) Mg and F.

- 9.20** For each of the following pairs of elements, state whether the binary compound they form is likely to be ionic or covalent. Write the empirical formula and name of the compound: (a) B and F, (b) K and Br.

## Lattice Energy of Ionic Compounds

### Review Questions

- 9.21 What is lattice energy and what role does it play in the stability of ionic compounds?
- 9.22 Explain how the lattice energy of an ionic compound such as KCl can be determined using the Born-Haber cycle. On what law is this procedure based?
- 9.23 Specify which compound in the following pairs of ionic compounds has the higher lattice energy: (a) KCl or MgO, (b) LiF or LiBr, (c) Mg<sub>3</sub>N<sub>2</sub> or NaCl. Explain your choice.
- 9.24 Compare the stability (in the solid state) of the following pairs of compounds: (a) LiF and LiF<sub>2</sub> (containing the Li<sup>2+</sup> ion), (b) Cs<sub>2</sub>O and CsO (containing the O<sup>-</sup> ion), (c) CaBr<sub>2</sub> and CaBr<sub>3</sub> (containing the Ca<sup>3+</sup> ion).

### Problems

- 9.25 Use the Born-Haber cycle outlined in Section 9.3 for LiF to calculate the lattice energy of NaCl. [The heat of sublimation of Na is 108 kJ/mol and  $\Delta H_f^\circ(\text{NaCl}) = -411 \text{ kJ/mol}$ . Energy needed to dissociate  $\frac{1}{2}$  mole of Cl<sub>2</sub> into Cl atoms = 121.4 kJ].
- 9.26** Calculate the lattice energy of calcium chloride given that the heat of sublimation of Ca is 121 kJ/mol and  $\Delta H_f^\circ(\text{CaCl}_2) = -795 \text{ kJ/mol}$ . (See Tables 8.2 and 8.3 for other data.)

## The Covalent Bond

### Review Questions

- 9.27 What is Lewis's contribution to our understanding of the covalent bond?
- 9.28 What is the difference between a Lewis dot symbol and a Lewis structure?
- 9.29 How many lone pairs are on the underlined atoms in these compounds? HBr, H<sub>2</sub>S, CH<sub>4</sub>.
- 9.30 Distinguish among single, double, and triple bonds in a molecule, and give an example of each.

## Electronegativity and Bond Type

### Review Questions

- 9.31 Define electronegativity, and explain the difference between electronegativity and electron affinity.

Describe in general how the electronegativities of the elements change according to position in the periodic table.

- 9.32** What is a polar covalent bond? Name two compounds that contain one or more polar covalent bonds.

### Problems

- 9.33** List these bonds in order of increasing ionic character: the lithium-to-fluorine bond in LiF, the potassium-to-oxygen bond in K<sub>2</sub>O, the nitrogen-to-nitrogen bond in N<sub>2</sub>, the sulfur-to-oxygen bond in SO<sub>2</sub>, the chlorine-to-fluorine bond in ClF<sub>3</sub>.
- 9.34** Arrange these bonds in order of increasing ionic character: carbon to hydrogen, fluorine to hydrogen, bromine to hydrogen, sodium to chlorine, potassium to fluorine, lithium to chlorine.
- 9.35 Four atoms are arbitrarily labeled D, E, F, and G. Their electronegativities are: D = 3.8, E = 3.3, F = 2.8, and G = 1.3. If the atoms of these elements form the molecules DE, DG, EG, and DF, how would you arrange these molecules in order of increasing covalent bond character?
- 9.36** List these bonds in order of increasing ionic character: cesium to fluorine, chlorine to chlorine, bromine to chlorine, silicon to carbon.
- 9.37 Classify these bonds as ionic, polar covalent, or covalent, and give your reasons: (a) the CC bond in H<sub>3</sub>CCH<sub>3</sub>, (b) the KI bond in KI, (c) the NB bond in H<sub>3</sub>NBCl<sub>3</sub>, (d) the ClO bond in ClO<sub>2</sub>.
- 9.38** Classify these bonds as ionic, polar covalent, or covalent, and give your reasons: (a) the SiSi bond in Cl<sub>3</sub>SiSiCl<sub>3</sub>, (b) the SiCl bond in Cl<sub>3</sub>SiSiCl<sub>3</sub>, (c) the CaF bond in CaF<sub>2</sub>, (d) the NH bond in NH<sub>3</sub>.

## Lewis Structure and the Octet Rule

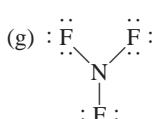
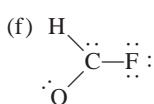
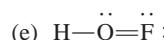
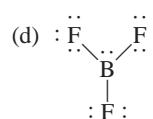
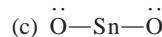
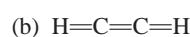
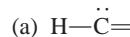
### Review Questions

- 9.39 Summarize the essential features of the Lewis octet rule. The octet rule applies mainly to the second-period elements. Explain.
- 9.40 Explain the concept of formal charge. Do formal charges on a molecule represent actual separation of charges?

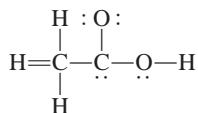
### Problems

- 9.41 Write Lewis structures for these molecules: (a) ICl, (b) PH<sub>3</sub>, (c) P<sub>4</sub> (each P is bonded to three other P atoms), (d) H<sub>2</sub>S, (e) N<sub>2</sub>H<sub>4</sub>, (f) HClO<sub>3</sub>, (g) COBr<sub>2</sub> (C is bonded to O and Br atoms).
- 9.42** Write Lewis structures for these ions: (a) O<sub>2</sub><sup>2-</sup>, (b) C<sub>2</sub><sup>2-</sup>, (c) NO<sup>+</sup>, (d) NH<sub>4</sub><sup>+</sup>. Show formal charges.
- 9.43 These Lewis structures are incorrect. Explain what is wrong with each one and give a correct Lewis

structure for the molecule. (Relative positions of atoms are shown correctly.)



- 9.44** The skeletal structure of acetic acid in this structure is correct, but some of the bonds are wrong. (a) Identify the incorrect bonds and explain what is wrong with them. (b) Write the correct Lewis structure for acetic acid.



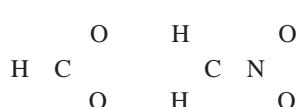
## Resonance

### Review Questions

- 9.45 Define bond length, resonance, and resonance structure.
- 9.46 Is it possible to “trap” a resonance structure of a compound for study? Explain.

### Problems

- 9.47 The resonance concept is sometimes described by analogy to a mule, which is a cross between a horse and a donkey. Compare this analogy with that used in this chapter, that is, the description of a rhinoceros as a cross between a griffin and a unicorn. Which description is more appropriate? Why?
- 9.48 What are the other two reasons for choosing (b) in Example 9.7?
- 9.49 Write Lewis structures for these species, including all resonance forms, and show formal charges: (a)  $\text{HCO}_2^-$ , (b)  $\text{CH}_2\text{NO}_2^-$ . Relative positions of the atoms are as follows:



- 9.50 Draw three resonance structures for the chlorate ion,  $\text{ClO}_3^-$ . Show formal charges.
- 9.51 Write three resonance structures for hydrazoic acid,  $\text{HN}_3$ . The atomic arrangement is HNNN. Show formal charges.

- 9.52** Draw two resonance structures for diazomethane,  $\text{CH}_2\text{N}_2$ . Show formal charges. The skeletal structure of the molecule is



- 9.53** Draw three reasonable resonance structures for the  $\text{OCN}^-$  ion. Show formal charges.

- 9.54** Draw three resonance structures for the molecule  $\text{N}_2\text{O}$  in which the atoms are arranged in the order NNO. Indicate formal charges.

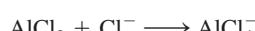
## Exceptions to the Octet Rule

### Review Questions

- 9.55 Why does the octet rule not hold for many compounds containing elements in the third period of the periodic table and beyond?
- 9.56 Give three examples of compounds that do not satisfy the octet rule. Write a Lewis structure for each.
- 9.57 Because fluorine has seven valence electrons ( $2s^22p^5$ ), seven covalent bonds in principle could form around the atom. Such a compound might be  $\text{FH}_7$  or  $\text{FCl}_7$ . These compounds have never been prepared. Why?
- 9.58 What is a coordinate covalent bond? Is it different from a normal covalent bond?

### Problems

- 9.59 The  $\text{BCl}_3$  molecule has an incomplete octet around B. Draw three resonance structures of the molecule in which the octet rule is satisfied for both the B and the Cl atoms. Show formal charges.
- 9.60** In the vapor phase, beryllium chloride consists of discrete molecular units  $\text{BeCl}_2$ . Is the octet rule satisfied for Be in this compound? If not, can you form an octet around Be by drawing another resonance structure? How plausible is this structure?
- 9.61 Of the noble gases, only Kr, Xe, and Rn are known to form a few compounds with O and/or F. Write Lewis structures for these molecules: (a)  $\text{XeF}_2$ , (b)  $\text{XeF}_4$ , (c)  $\text{XeF}_6$ , (d)  $\text{XeOF}_4$ , (e)  $\text{XeO}_2\text{F}_2$ . In each case Xe is the central atom.
- 9.62 Write a Lewis structure for  $\text{SbCl}_5$ . Is the octet rule obeyed in this molecule?
- 9.63 Write Lewis structures for  $\text{SeF}_4$  and  $\text{SeF}_6$ . Is the octet rule satisfied for Se?
- 9.64** Write Lewis structures for the reaction



What kind of bond is between Al and Cl in the product?

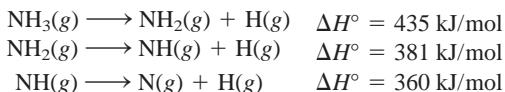
## Bond Enthalpies

### Review Questions

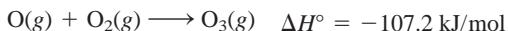
- 9.65 Define bond enthalpy. Bond enthalpies of polyatomic molecules are average values. Why?
- 9.66 Explain why the bond enthalpy of a molecule is usually defined in terms of a gas-phase reaction. Why are bond-breaking processes always endothermic and bond-forming processes always exothermic?

### Problems

- 9.67 From these data, calculate the average bond enthalpy for the N—H bond:



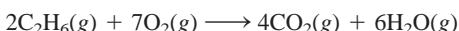
- 9.68 For the reaction



calculate the average bond enthalpy in O<sub>3</sub>.

- 9.69 The bond enthalpy of F<sub>2</sub>(g) is 156.9 kJ/mol. Calculate  $\Delta H_f^\circ$  for F(g).

- 9.70 (a) For the reaction



predict the enthalpy of reaction from the average bond enthalpies in Table 9.3. (b) Calculate the enthalpy of reaction from the standard enthalpies of formation (see Appendix 2) of the reactant and product molecules, and compare the result with your answer for part (a).

## Additional Problems

- 9.71 Match each of these energy changes with one of the processes given: ionization energy, electron affinity, bond enthalpy, standard enthalpy of formation.

- (a) F(g) + e<sup>-</sup> → F<sup>-</sup>(g)
- (b) F<sub>2</sub>(g) → 2F(g)
- (c) Na(g) → Na<sup>+</sup>(g) + e<sup>-</sup>
- (d) Na(s) +  $\frac{1}{2}\text{F}_2(g)$  → NaF(s)

- 9.72 The formulas for the fluorides of the third-period elements are NaF, MgF<sub>2</sub>, AlF<sub>3</sub>, SiF<sub>4</sub>, PF<sub>5</sub>, SF<sub>6</sub>, and ClF<sub>3</sub>. Classify these compounds as covalent or ionic.

- 9.73 Use the ionization energy (see Table 8.2) and electron affinity values (see Table 8.3) to calculate the energy change (in kilojoules) for these reactions:

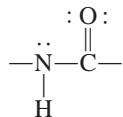
- (a) Li(g) + I(g) → Li<sup>+</sup>(g) + I<sup>-</sup>(g)
- (b) Na(g) + F(g) → Na<sup>+</sup>(g) + F<sup>-</sup>(g)
- (c) K(g) + Cl(g) → K<sup>+</sup>(g) + Cl<sup>-</sup>(g)

- 9.74 Describe some characteristics of an ionic compound such as KF that would distinguish it from a covalent compound such as CO<sub>2</sub>.

- 9.75 Write Lewis structures for BrF<sub>3</sub>, ClF<sub>5</sub>, and IF<sub>7</sub>. Identify those in which the octet rule is not obeyed.

- 9.76 Write three reasonable resonance structures of the azide ion N<sub>3</sub><sup>-</sup> in which the atoms are arranged as NNN. Show formal charges.

- 9.77 The amide group plays an important role in determining the structure of proteins:



Draw another resonance structure of this group. Show formal charges.

- 9.78 Give an example of an ion or molecule containing Al that (a) obeys the octet rule, (b) has an expanded octet, and (c) has an incomplete octet.

- 9.79 Draw four reasonable resonance structures for the PO<sub>3</sub>F<sup>2-</sup> ion. The central P atom is bonded to the three O atoms and to the F atom. Show formal charges.

- 9.80 Attempts to prepare these as stable species under atmospheric conditions have failed. Suggest reasons for the failure.

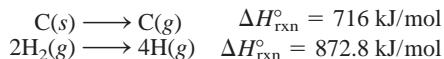


- 9.81 Draw reasonable resonance structures for these sulfur-containing ions: (a) HSO<sub>4</sub><sup>-</sup>, (b) SO<sub>4</sub><sup>2-</sup>, (c) HSO<sub>3</sub><sup>-</sup>, (d) SO<sub>3</sub><sup>2-</sup>.

- 9.82 True or false: (a) Formal charges represent actual separation of charges; (b)  $\Delta H_{\text{rxn}}^\circ$  can be estimated from bond enthalpies of reactants and products; (c) all second-period elements obey the octet rule in their compounds; (d) the resonance structures of a molecule can be separated from one another.

- 9.83 A rule for drawing plausible Lewis structures is that the central atom is invariably less electronegative than the surrounding atoms. Explain why this is so.

- 9.84 Using this information:



and the fact that the average C—H bond enthalpy is 414 kJ/mol, estimate the standard enthalpy of formation of methane (CH<sub>4</sub>).

- 9.85 Based on energy considerations, which of these two reactions will occur more readily?

- (a) Cl(g) + CH<sub>4</sub>(g) → CH<sub>3</sub>Cl(g) + H(g)
- (b) Cl(g) + CH<sub>4</sub>(g) → CH<sub>3</sub>(g) + HCl(g)

(Hint: Refer to Table 9.3, and assume that the average bond enthalpy of the C—Cl bond is 338 kJ/mol.)

- 9.86 Which of these molecules has the shortest nitrogen-to-nitrogen bond? Explain.



9.87 Most organic acids can be represented as RCOOH, in which COOH is the carboxyl group and R is the rest of the molecule. (For example, R is CH<sub>3</sub> in acetic acid, CH<sub>3</sub>COOH.) (a) Draw a Lewis structure of the carboxyl group. (b) Upon ionization, the carboxyl group is converted to the carboxylate group, COO<sup>-</sup>. Draw resonance structures of the carboxylate group.

**9.88** Which of these molecules or ions are isoelectronic: NH<sub>4</sub><sup>+</sup>, C<sub>6</sub>H<sub>6</sub>, CO, CH<sub>4</sub>, N<sub>2</sub>, B<sub>3</sub>N<sub>3</sub>H<sub>6</sub>?

9.89 These species have been detected in interstellar space: (a) CH, (b) OH, (c) C<sub>2</sub>, (d) HNC, (e) HCO. Draw Lewis structures of these species and indicate whether they are diamagnetic or paramagnetic.

**9.90** The amide ion, NH<sub>2</sub><sup>-</sup>, is a Brønsted base. Represent the reaction between the amide ion and water in terms of Lewis structures.

9.91 Draw Lewis structures of these organic molecules: (a) tetrafluoroethylene (C<sub>2</sub>F<sub>4</sub>), (b) propane (C<sub>3</sub>H<sub>8</sub>), (c) butadiene (CH<sub>2</sub>CHCHCH<sub>2</sub>), (d) propyne (CH<sub>3</sub>CCH), (e) benzoic acid (C<sub>6</sub>H<sub>5</sub>COOH). (*Hint:* To draw C<sub>6</sub>H<sub>5</sub>COOH, replace an H atom in benzene with a COOH group.)

**9.92** The triiodide ion (I<sub>3</sub><sup>-</sup>) in which the I atoms are arranged as III is stable, but the corresponding F<sub>3</sub><sup>-</sup> ion does not exist. Explain.

9.93 Compare the bond enthalpy of F<sub>2</sub> with the energy change for this process:

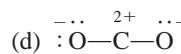
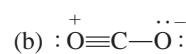
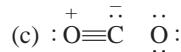
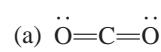


Which is the preferred dissociation for F<sub>2</sub>, energetically speaking?

**9.94** Methyl isocyanate, CH<sub>3</sub>NCO, is used to make certain pesticides. In December 1984, water leaked into a tank containing this substance at a chemical plant to produce a toxic cloud that killed thousands of people in Bhopal, India. Draw Lewis structures for this compound, showing formal charges.

9.95 The chlorine nitrate molecule (ClONO<sub>2</sub>) is believed to be involved in the destruction of ozone in the Antarctic stratosphere. Draw a plausible Lewis structure for the molecule.

**9.96** Several resonance structures of the molecule CO<sub>2</sub> are given here. Explain why some of them are likely to be of little importance in describing the bonding in this molecule.

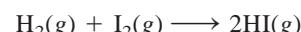


9.97 Draw a Lewis structure for each of these organic molecules in which the carbon atoms are bonded to each other by single bonds: C<sub>2</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>10</sub>, C<sub>5</sub>H<sub>12</sub>.

**9.98** Draw Lewis structures for these chlorofluorocarbons (CFCs), which are partly responsible for the depletion of ozone in the stratosphere: CFCl<sub>3</sub>, CF<sub>2</sub>Cl<sub>2</sub>, CHF<sub>2</sub>Cl, CF<sub>3</sub>CHF<sub>2</sub>.

9.99 Draw Lewis structures for these organic molecules, in each of which there is one C=C bond and the rest of the carbon atoms are joined by C—C bonds: C<sub>2</sub>H<sub>3</sub>F, C<sub>3</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>8</sub>.

**9.100** Calculate ΔH° for the reaction



using (a) Equation (9.3) and (b) Equation (6.18), given that ΔH<sub>f</sub><sup>°</sup> for I<sub>2</sub>(g) is 61.0 kJ/mol.

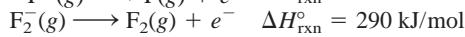
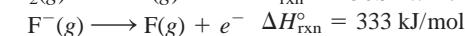
9.101 Draw Lewis structures of these organic molecules: (a) methanol (CH<sub>3</sub>OH); (b) ethanol (CH<sub>3</sub>CH<sub>2</sub>OH); (c) tetraethyllead [Pb(CH<sub>3</sub>CH<sub>3</sub>)<sub>4</sub>], which was used in “leaded” gasoline; (d) methylamine (CH<sub>3</sub>NH<sub>2</sub>); (e) mustard gas (ClCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>Cl), a poisonous gas used in World War I; (f) urea [(NH<sub>2</sub>)<sub>2</sub>CO], a fertilizer; (g) glycine (NH<sub>2</sub>CH<sub>2</sub>COOH), an amino acid.

**9.102** Write Lewis structures for these four isoelectronic species: (a) CO, (b) NO<sup>+</sup>, (c) CN<sup>-</sup>, (d) N<sub>2</sub>. Show formal charges.

9.103 Oxygen forms three types of ionic compounds in which the anions are oxide (O<sup>2-</sup>), peroxide (O<sub>2</sub><sup>2-</sup>), and superoxide (O<sub>2</sub><sup>-</sup>). Draw Lewis structures of these ions.

**9.104** Comment on the correctness of this statement: All compounds containing a noble gas atom violate the octet rule.

9.105 (a) From these data:



calculate the bond enthalpy of the F<sub>2</sub><sup>-</sup> ion. (b) Explain the difference between the bond enthalpies of F<sub>2</sub> and F<sub>2</sub><sup>-</sup>.

**9.106** Write three resonance structures for the isocyanate ion (CNO<sup>-</sup>). Rank them in importance.

9.107 The only known argon-containing compound is HArF, which was prepared in 2000. Draw a Lewis structure of the compound.

**9.108** Experiments show that it takes 1656 kJ/mol to break all the bonds in methane (CH<sub>4</sub>) and 4006 kJ/mol to break all the bonds in propane (C<sub>3</sub>H<sub>8</sub>). Based on these data, calculate the average bond enthalpy of the C—C bond.

9.109 Among the common inhaled anesthetics are halothane: CF<sub>3</sub>CHClBr

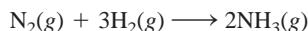
enflurane: CHFCICF<sub>2</sub>OCHF<sub>2</sub>

isoflurane: CF<sub>3</sub>CHClOCHF<sub>2</sub>

methoxyflurane: CHCl<sub>2</sub>CF<sub>2</sub>OCH<sub>3</sub>

Draw Lewis structures of these molecules.

- 9.110** Industrially, ammonia is synthesized by the Haber process at high pressures and temperatures:



Calculate the enthalpy change for the reaction using (a) bond enthalpies and Equation (9.3) and (b) the  $\Delta H_f^\circ$  values in Appendix 2.

## SPECIAL PROBLEMS

- 9.111** The neutral hydroxyl radical ( $\text{OH}$ ) plays an important role in atmospheric chemistry. It is highly reactive and has a tendency to combine with an  $\text{H}$  atom from other compounds, causing them to break up. Thus, it is sometimes called a “detergent” radical because it helps to clean up the atmosphere.

- (a) Write the Lewis structure for the radical.
- (b) Refer to Table 9.3 and explain why the radical has a high affinity for  $\text{H}$  atoms.
- (c) Estimate the enthalpy change for the following reaction:



- (d) The radical is generated when sunlight hits water vapor. Calculate the maximum wavelength (in nanometers) required to break up an  $\text{O}-\text{H}$  bond in  $\text{H}_2\text{O}$ .

- 9.112** Ethylene dichloride ( $\text{C}_2\text{H}_4\text{Cl}_2$ ) is used to make vinyl chloride ( $\text{C}_2\text{H}_3\text{Cl}$ ), which, in turn, is used to manufacture the plastic poly(vinyl chloride) (PVC), found in piping, siding, floor tiles, and toys.

- (a) Write the Lewis structures of ethylene dichloride and vinyl chloride. Classify the bonds as covalent or polar.
- (b) Poly(vinyl chloride) is a polymer; that is, it is a molecule with very high molar mass (on the order of thousands to millions of grams). It is formed by joining many vinyl chloride molecules together. The repeating unit in poly(vinyl chloride) is  $-\text{CH}_2-\text{CHCl}-$ . Draw a portion of the molecule showing three such repeating units.

(c) Calculate the enthalpy change when  $1.0 \times 10^3$  kg of vinyl chloride react to form poly(vinyl chloride). Comment on your answer in relation to industrial design for such a process.

- 9.113** Sulfuric acid ( $\text{H}_2\text{SO}_4$ ), the most important industrial chemical in the world, is prepared by oxidizing sulfur to sulfur dioxide and then to sulfur trioxide. Although sulfur trioxide reacts with water to form sulfuric acid, it forms a mist of fine droplets of  $\text{H}_2\text{SO}_4$  with water vapor that is hard to condense. Instead, sulfur trioxide is first dissolved in 98 percent sulfuric acid to form oleum ( $\text{H}_2\text{S}_2\text{O}_7$ ). On treatment with water, concentrated sulfuric acid can be generated. Write equations for all the steps and draw Lewis structures of oleum.

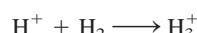
- 9.114** The species  $\text{H}_3^+$  is the simplest polyatomic ion. The geometry of the ion is that of an equilateral triangle.

- (a) Draw three resonance structures to represent the ion.
- (b) Given the following information



and  $\text{H}_2 \longrightarrow 2\text{H} \quad \Delta H^\circ = 436.4 \text{ kJ/mol}$

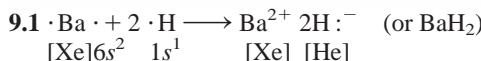
calculate  $\Delta H^\circ$  for the reaction



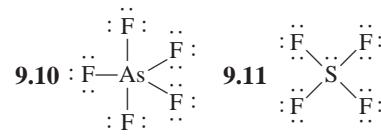
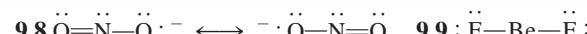
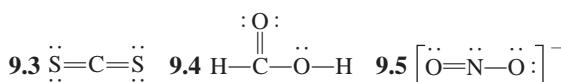
- 9.115** The bond enthalpy of the  $\text{C}-\text{N}$  bond in the amide group of proteins (see Problem 9.77) can be treated as an average of  $\text{C}-\text{N}$  and  $\text{C}=\text{N}$  bonds. Calculate the maximum wavelength of light needed to break the bond.

- 9.116** In 1999 an unusual cation containing only nitrogen ( $\text{N}_5^+$ ) was prepared. Draw three resonance structures of the ion, showing formal charges. (Hint: The N atoms are joined in a linear fashion.)

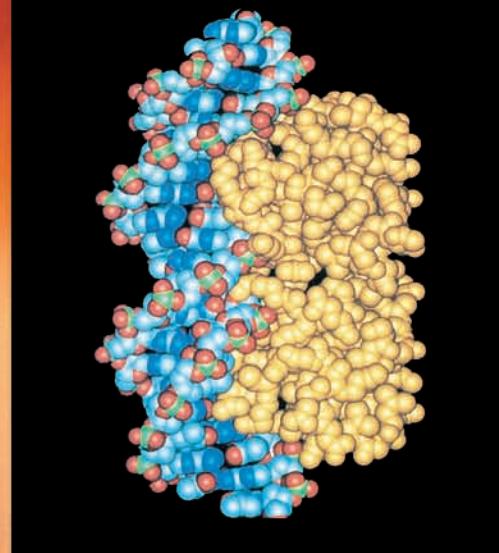
## ANSWERS TO PRACTICE EXERCISES



- 9.2** (a) Ionic, (b) polar covalent, (c) covalent.



- 9.12** (a)  $-119 \text{ kJ/mol}$ , (b)  $-137.0 \text{ kJ/mol}$ .



Molecular models are used to study complex biochemical reactions such as those between protein and DNA molecules.

## Chemical Bonding II: Molecular Geometry and Hybridization of Atomic Orbitals

### CHAPTER OUTLINE

#### 10.1 Molecular Geometry 313

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#### 10.2 Dipole Moments 322

#### 10.3 Valence Bond Theory 325

#### 10.4 Hybridization of Atomic Orbitals 328

$sp^3$  Hybridization •  $sp$  Hybridization •  $sp^2$  Hybridization • Procedure for Hybridizing Atomic Orbitals • Hybridization of  $s$ ,  $p$ , and  $d$  Orbitals

#### 10.5 Hybridization in Molecules Containing Double and Triple Bonds 337

#### 10.6 Molecular Orbital Theory 340

Bonding and Antibonding Molecular Orbitals • Molecular Orbital Configurations

### Interactive Activity Summary

1. Animation: VSEPR (10.1)
2. Interactivity: Determining Molecular Shape (10.1)
3. Animation: Polarity of Molecules (10.2)
4. Interactivity: Molecular Polarity (10.2)
5. Animation: Hybridization (10.4)
6. Interactivity: Determining Orbital Hybridization (10.4)
7. Animation: Sigma and Pi Bonds (10.5)
8. Interactivity: Energy Levels of Bonding—Homonuclear Diatomic Molecules (10.6)

### ESSENTIAL CONCEPTS

**Molecular Geometry** Molecular geometry refers to the three-dimensional arrangement of atoms in a molecule. For relatively small molecules, in which the central atom contains two to six bonds, geometries can be reliably predicted by the valence-shell electron-pair repulsion (VSEPR) model. This model is based on the assumption that chemical bonds and lone pairs tend to remain as far apart as possible to minimize repulsion.

**Dipole Moments** In a diatomic molecule the difference in the electronegativities of bonding atoms results in a polar bond and a dipole moment. The dipole moment of a molecule made up of three or more atoms depends on both the polarity of the bonds and molecular geometry. Dipole moment measurements can help us distinguish between different possible geometries of a molecule.

**Hybridization of Atomic Orbitals** Hybridization is the quantum mechanical description of chemical bonding. Atomic orbitals are hybridized, or mixed, to form hybrid orbitals. These orbitals then interact with other atomic orbitals to form chemical bonds. Various molecular geometries can be generated by different hybridizations. The hybridization concept accounts for the exception to the octet rule and also explains the formation of double and triple bonds.

**Molecular Orbital Theory** Molecular orbital theory describes bonding in terms of the combination of atomic orbitals to form orbitals that are associated with the molecule as a whole. Molecules are stable if the number of electrons in bonding molecular orbitals is greater than that in antibonding molecular orbitals. We write electron configurations for molecular orbitals as we do for atomic orbitals, using the Pauli exclusion principle and Hund's rule.

## 10.1 Molecular Geometry

Molecular geometry is the three-dimensional arrangement of atoms in a molecule. A molecule's geometry affects its physical and chemical properties, such as melting point, boiling point, density, and the types of reactions it undergoes. In general, bond lengths and bond angles must be determined by experiment. However, there is a simple procedure that enables us to predict with considerable success the overall geometry of a molecule or ion if we know the number of electrons surrounding a central atom in its Lewis structure. The basis of this approach is the assumption that electron pairs in the valence shell of an atom repel one another. The **valence shell** is *the outermost electron-occupied shell of an atom; it holds the electrons that are usually involved in bonding*. In a covalent bond, a pair of electrons, often called the **bonding pair**, is responsible for holding two atoms together. However, in a polyatomic molecule, where there are two or more bonds between the central atom and the surrounding atoms, the repulsion between electrons in different bonding pairs causes them to remain as far apart as possible. The geometry that the molecule ultimately assumes (as defined by the positions of all the atoms) minimizes the repulsion. This approach to the study of molecular geometry is called the **valence-shell electron-pair repulsion (VSEPR) model**, because *it accounts for the geometric arrangements of electron pairs around a central atom in terms of the electrostatic repulsion between electron pairs*.

The term “central atom” means an atom that is not a terminal atom in a polyatomic molecule.

Two general rules govern the use of the VSEPR model:

- As far as electron-pair repulsion is concerned, double bonds and triple bonds can be treated like single bonds. This approximation is good for qualitative purposes. However, you should realize that in reality multiple bonds are “larger” than single bonds; that is, because there are two or three bonds between two atoms, the electron density occupies more space.
- If a molecule has two or more resonance structures, we can apply the VSEPR model to any one of them. Formal charges are usually not shown.

VSEPR is pronounced “vesper.”



**Animation:**  
VSEPR  
ARIS, Animations

With this model in mind, we can predict the geometry of molecules (and ions) in a systematic way. For this purpose, it is convenient to divide molecules into two categories, according to whether or not the central atom has lone pairs.

### Molecules in Which the Central Atom Has No Lone Pairs

For simplicity we will consider molecules that contain atoms of only two elements, A and B, of which A is the central atom. These molecules have the general formula  $AB_x$ , where  $x$  is an integer 2, 3, . . . . (If  $x = 1$ , we have the diatomic molecule AB, which is linear by definition.) In the vast majority of cases,  $x$  is between 2 and 6.

Table 10.1 shows five possible arrangements of electron pairs around the central atom A. As a result of mutual repulsion, the electron pairs stay as far from one another as possible. Note that the table shows arrangements of the electron pairs but not the positions of the atoms that surround the central atom. Molecules in which the central atom has no lone pairs have one of these five arrangements of bonding pairs. Using Table 10.1 as a reference, let us take a close look at the geometry of molecules with the formulas  $AB_2$ ,  $AB_3$ ,  $AB_4$ ,  $AB_5$ , and  $AB_6$ .

#### $AB_2$ : Beryllium Chloride ( $BeCl_2$ )

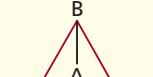
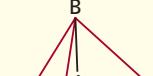
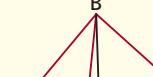
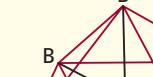
The Lewis structure of beryllium chloride in the gaseous state is



**Interactivity:**  
Determining Molecular Shape  
ARIS, Interactives

TABLE 10.1

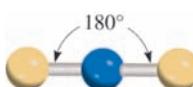
**Arrangement of Electron Pairs About a Central Atom (A) in a Molecule and Geometry of Some Simple Molecules and Ions in Which the Central Atom Has No Lone Pairs**

Number of Electron Pairs	Arrangement of Electron Pairs*	Molecular Geometry*	Examples
2	 Linear	B—A—B Linear	BeCl <sub>2</sub> , HgCl <sub>2</sub>
3	 Trigonal planar	 Trigonal planar	BF <sub>3</sub>
4	 Tetrahedral	 Tetrahedral	CH <sub>4</sub> , NH <sub>4</sub> <sup>+</sup>
5	 Trigonal bipyramidal	 Trigonal bipyramidal	PCl <sub>5</sub>
6	 Octahedral	 Octahedral	SF <sub>6</sub>

\*The colored lines are used only to show the overall shapes; they do not represent bonds.

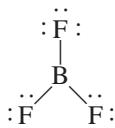
Because the bonding pairs repel each other, they must be at opposite ends of a straight line in order for them to be as far apart as possible. Thus, the ClBeCl angle is predicted to be 180°, and the molecule is linear (see Table 10.1). The “ball-and-stick” model of BeCl<sub>2</sub> is

The blue and yellow spheres are for atoms in general.

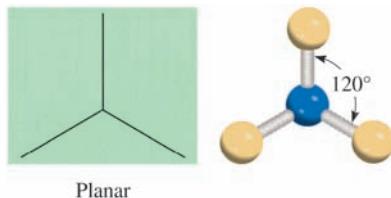


***AB<sub>3</sub>: Boron Trifluoride (BF<sub>3</sub>)***

Boron trifluoride contains three covalent bonds, or bonding pairs. In the most stable arrangement, the three BF bonds point to the corners of an equilateral triangle with B in the center of the triangle:



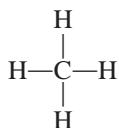
According to Table 10.1, the geometry of  $\text{BF}_3$  is *trigonal planar* because the three end atoms are at the corners of an equilateral triangle that is planar:



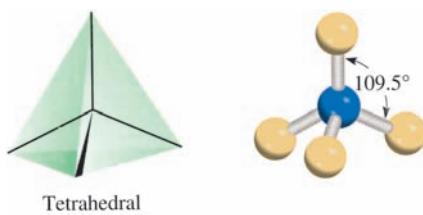
Thus, each of the three FBF angles is  $120^\circ$ , and all four atoms lie in the same plane.

***AB<sub>4</sub>: Methane (CH<sub>4</sub>)***

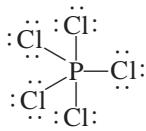
The Lewis structure of methane is



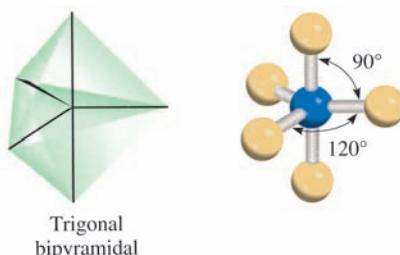
Because there are four bonding pairs, the geometry of  $\text{CH}_4$  is tetrahedral (see Table 10.1). A *tetrahedron* has four sides (the prefix *tetra* means “four”), or faces, all of which are equilateral triangles. In a tetrahedral molecule, the central atom (C in this case) is located at the center of the tetrahedron and the other four atoms are at the corners. The bond angles are all  $109.5^\circ$ .

***AB<sub>5</sub>: Phosphorus Pentachloride (PCl<sub>5</sub>)***

The Lewis structure of phosphorus pentachloride (in the gas phase) is



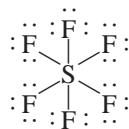
The only way to minimize the repulsive forces among the five bonding pairs is to arrange the PCl bonds in the form of a trigonal bipyramidal (see Table 10.1). A trigonal bipyramidal can be generated by joining two tetrahedrons along a common triangular base:



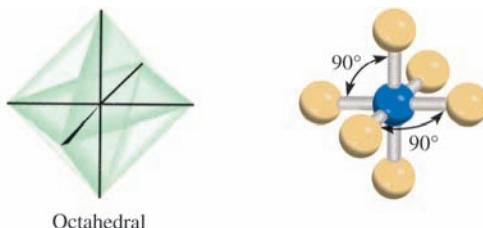
The central atom (P in this case) is at the center of the common triangle with the surrounding atoms positioned at the five corners of the trigonal bipyramidal. The atoms that are above and below the triangular plane are said to occupy *axial* positions, and those that are in the triangular plane are said to occupy *equatorial* positions. The angle between any two equatorial bonds is 120°; that between an axial bond and an equatorial bond is 90°, and that between the two axial bonds is 180°.

### *AB<sub>6</sub>: Sulfur Hexafluoride (SF<sub>6</sub>)*

The Lewis structure of sulfur hexafluoride is



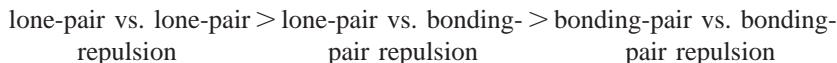
The most stable arrangement of the six SF bonding pairs is in the shape of an octahedron, shown in Table 10.1. An octahedron has eight sides (the prefix *octa* means “eight”). It can be generated by joining two square pyramids on a common base. The central atom (S in this case) is at the center of the square base and the surrounding atoms are at the six corners. All bond angles are 90° except the one made by the bonds between the central atom and the pairs of atoms that are diametrically opposite each other. That angle is 180°. Because the six bonds are equivalent in an octahedral molecule, we cannot use the terms “axial” and “equatorial” as in a trigonal bipyramidal molecule.



## Molecules in Which the Central Atom Has One or More Lone Pairs

Determining the geometry of a molecule is more complicated if the central atom has both lone pairs and bonding pairs. In such molecules there are three types of repulsive forces—those between bonding pairs, those between lone pairs, and those

between a bonding pair and a lone pair. In general, according to the VSEPR model, the repulsive forces decrease in the following order:

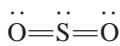


Electrons in a bond are held by the attractive forces exerted by the nuclei of the two bonded atoms. These electrons have less “spatial distribution” than lone pairs; that is, they take up less space than lone-pair electrons, which are associated with only one particular atom. Because lone-pair electrons in a molecule occupy more space, they experience greater repulsion from neighboring lone pairs and bonding pairs. To keep track of the total number of bonding pairs and lone pairs, we designate molecules with lone pairs as  $\text{AB}_x\text{E}_y$ , where A is the central atom, B is a surrounding atom, and E is a lone pair on A. Both x and y are integers;  $x = 2, 3, \dots$ , and  $y = 1, 2, \dots$ . Thus, the values of x and y indicate the number of surrounding atoms and number of lone pairs on the central atom, respectively. The simplest such molecule would be a triatomic molecule with one lone pair on the central atom and the formula is  $\text{AB}_2\text{E}$ .

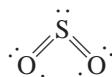
As the following examples show, in most cases the presence of lone pairs on the central atom makes it difficult to predict the bond angles accurately.

### ***AB<sub>2</sub>E: Sulfur Dioxide (SO<sub>2</sub>)***

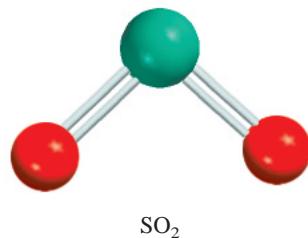
The Lewis structure of sulfur dioxide is



Because VSEPR treats double bonds as though they were single, the  $\text{SO}_2$  molecule can be viewed as consisting of three electron pairs on the central S atom. Of these, two are bonding pairs and one is a lone pair. In Table 10.1 we see that the overall arrangement of three electron pairs is trigonal planar. But because one of the electron pairs is a lone pair, the  $\text{SO}_2$  molecule has a “bent” shape.

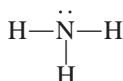


Because the lone-pair versus bonding-pair repulsion is greater than the bonding-pair versus bonding-pair repulsion, the two sulfur-to-oxygen bonds are pushed together slightly and the OSO angle is less than  $120^\circ$ .



### ***AB<sub>3</sub>E: Ammonia (NH<sub>3</sub>)***

The ammonia molecule contains three bonding pairs and one lone pair:

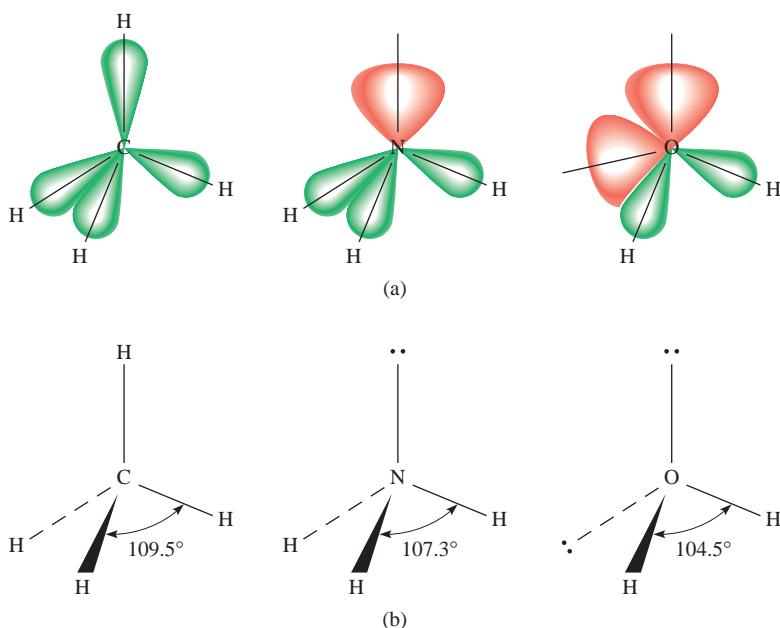


As Table 10.1 shows, the overall arrangement of four electron pairs is tetrahedral. But in  $\text{NH}_3$  one of the electron pairs is a lone pair, so the geometry of  $\text{NH}_3$  is trigonal pyramidal (so called because it looks like a pyramid, with the N atom at the apex). Because the lone pair repels the bonding pairs more strongly, the three NH bonding pairs are pushed closer together:



**Figure 10.1**

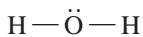
(a) The relative sizes of bonding pairs and lone pairs in  $\text{CH}_4$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$ . (b) The bond angles in  $\text{CH}_4$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$ . Note that the dashed lines represent a bond axes behind the plane of the paper, the wedged lines represent a bond axes in front of the plane of the paper, and the thin solid lines represent bonds in the plane of the paper.



Thus, the HNH angle in ammonia is smaller than the ideal tetrahedral angle of  $109.5^\circ$  (Figure 10.1).

### $\text{AB}_2\text{E}_2$ : Water ( $\text{H}_2\text{O}$ )

A water molecule contains two bonding pairs and two lone pairs:

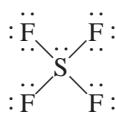


The overall arrangement of the four electron pairs in water is tetrahedral, the same as in ammonia. However, unlike ammonia, water has two lone pairs on the central O atom. These lone pairs tend to be as far from each other as possible. Consequently, the two OH bonding pairs are pushed toward each other, and we predict an even greater deviation from the tetrahedral angle than in  $\text{NH}_3$ . As Figure 10.1 shows, the HOH angle is  $104.5^\circ$ . The geometry of  $\text{H}_2\text{O}$  is bent:

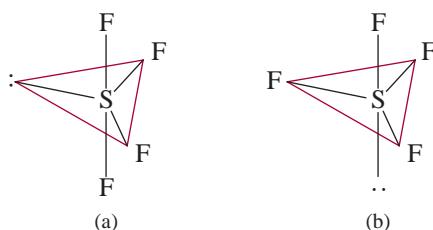


### $\text{AB}_4\text{E}$ : Sulfur Tetrafluoride ( $\text{SF}_4$ )

The Lewis structure of  $\text{SF}_4$  is



The central sulfur atom has five electron pairs whose arrangement, according to Table 10.1, is trigonal bipyramidal. In the  $\text{SF}_4$  molecule, however, one of the electron pairs is a lone pair, so the molecule must have one of the following geometries:



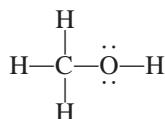
In (a) the lone pair occupies an equatorial position, and in (b) it occupies an axial position. The axial position has three neighboring pairs at  $90^\circ$  and one at  $180^\circ$ , while the equatorial position has two neighboring pairs at  $90^\circ$  and two more at  $120^\circ$ . The repulsion is smaller for (a), and indeed (a) is the structure observed experimentally. This shape is sometimes described as a seesaw (if you turn the structure  $90^\circ$  clockwise to view it). The angle between the axial F atoms and S is  $173^\circ$ , and that between the equatorial F atoms and S is  $102^\circ$ .

Table 10.2 shows the geometries of simple molecules in which the central atom has one or more lone pairs, including some that we have not discussed.



# Geometry of Molecules with More Than One Central Atom

So far we have discussed the geometry of molecules having only one central atom. The overall geometry of molecules with more than one central atom is difficult to define in most cases. Often we can describe only the shape around each of the central atoms. For example, consider methanol,  $\text{CH}_3\text{OH}$ , whose Lewis structure is shown next:

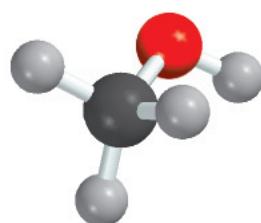


The two central (nonterminal) atoms in methanol are C and O. We can say that the three CH and the CO bonding pairs are tetrahedrally arranged about the C atom. The HCH and OCH bond angles are approximately  $109^\circ$ . The O atom here is like the one in water in that it has two lone pairs and two bonding pairs. Therefore, the HOC portion of the molecule is bent, and the angle HOC is approximately equal to  $105^\circ$  (Figure 10.2).

# Guidelines for Applying the VSEPR Model

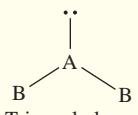
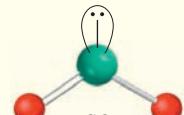
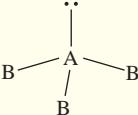
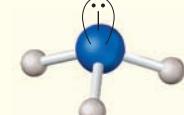
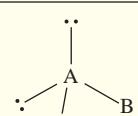
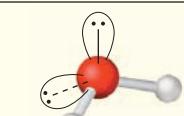
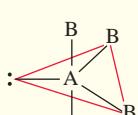
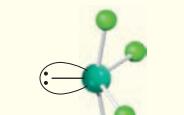
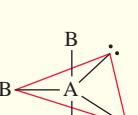
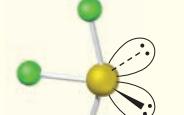
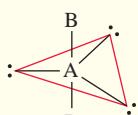
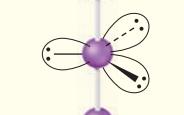
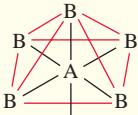
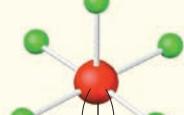
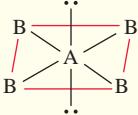
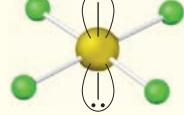
Having studied the geometries of molecules in two categories (central atoms with and without lone pairs), let us consider some rules for applying the VSEPR model to all types of molecules:

1. Write the Lewis structure of the molecule, considering only the electron pairs around the central atom (that is, the atom that is bonded to more than one other atom).
  2. Count the number of electron pairs around the central atom (bonding pairs and lone pairs). Treat double and triple bonds as though they were single bonds. Refer to Table 10.1 to predict the overall arrangement of the electron pairs.
  3. Use Tables 10.1 and 10.2 to predict the geometry of the molecule.



**Figure 10.2**  
*The geometry of CH<sub>3</sub>OH.*

**TABLE 10.2****Geometry of Simple Molecules and Ions in Which the Central Atom Has One or More Lone Pairs**

Class of molecule	Total number of electron pairs	Number of bonding pairs	Number of lone pairs	Arrangement of electron pairs*	Geometry	Examples
AB <sub>2</sub> E	3	2	1	 Trigonal planar	Bent	 SO <sub>2</sub>
AB <sub>3</sub> E	4	3	1	 Tetrahedral	Trigonal pyramidal	 NH <sub>3</sub>
AB <sub>2</sub> E <sub>2</sub>	4	2	2	 Tetrahedral	Bent	 H <sub>2</sub> O
AB <sub>4</sub> E	5	4	1	 Trigonal bipyramidal	Distorted tetrahedron (or seesaw)	 SF <sub>4</sub>
AB <sub>3</sub> E <sub>2</sub>	5	3	2	 Trigonal bipyramidal	T-shaped	 ClF <sub>3</sub>
AB <sub>2</sub> E <sub>3</sub>	5	2	3	 Trigonal bipyramidal	Linear	 I <sub>3</sub> <sup>-</sup>
AB <sub>5</sub> E	6	5	1	 Octahedral	Square pyramidal	 BrF <sub>5</sub>
AB <sub>4</sub> E <sub>2</sub>	6	4	2	 Octahedral	Square planar	 XeF <sub>4</sub>

\*The colored lines are used to show the overall shapes, not bonds.

4. In predicting bond angles, note that a lone pair repels another lone pair or a bonding pair more strongly than a bonding pair repels another bonding pair. Remember that in general there is no easy way to predict bond angles accurately when the central atom possesses one or more lone pairs.

The VSEPR model generates reliable predictions of the geometries of a variety of molecular structures. Chemists use the VSEPR approach because of its simplicity. Although there are some theoretical concerns about whether “electron-pair repulsion” actually determines molecular shapes, the assumption that it does leads to useful (and generally reliable) predictions. We need not ask more of any model at this stage in the study of chemistry. Example 10.1 illustrates the application of VSEPR.

### Example 10.1

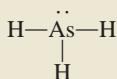
Use the VSEPR model to predict the geometry of the following molecules and ions:

(a)  $\text{AsH}_3$ , (b)  $\text{OF}_2$ , (c)  $\text{AlCl}_4^-$ , (d)  $\text{I}_3^-$ , (e)  $\text{C}_2\text{H}_4$ .

**Strategy** The sequence of steps in determining molecular geometry is as follows:

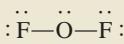
draw Lewis  $\longrightarrow$  find arrangement  $\longrightarrow$  find arrangement  $\longrightarrow$  determine geometry  
structure of electron pairs of bonding pairs based on bonding pairs

**Solution** (a) The Lewis structure of  $\text{AsH}_3$  is



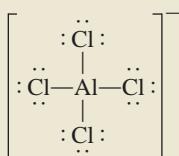
There are four electron pairs around the central atom; therefore, the electron pair arrangement is tetrahedral (see Table 10.1). Recall that the geometry of a molecule is determined only by the arrangement of atoms (in this case the As and H atoms). Thus, removing the lone pair leaves us with three bonding pairs and a trigonal pyramidal geometry, like  $\text{NH}_3$ . We cannot predict the  $\text{HAsH}$  angle accurately, but we know that it is less than  $109.5^\circ$  because the repulsion of the bonding electron pairs in the As—H bonds by the lone pair on As is greater than the repulsion between the bonding pairs.

(b) The Lewis structure of  $\text{OF}_2$  is



There are four electron pairs around the central atom; therefore, the electron pair arrangement is tetrahedral (see Table 10.1). Recall that the geometry of a molecule is determined only by the arrangement of atoms (in this case the O and F atoms). Thus, removing the two lone pairs leaves us with two bonding pairs and a bent geometry, like  $\text{H}_2\text{O}$ . We cannot predict the  $\text{FOF}$  angle accurately, but we know that it must be less than  $109.5^\circ$  because the repulsion of the bonding electron pairs in the O—F bonds by the lone pairs on O is greater than the repulsion between the bonding pairs.

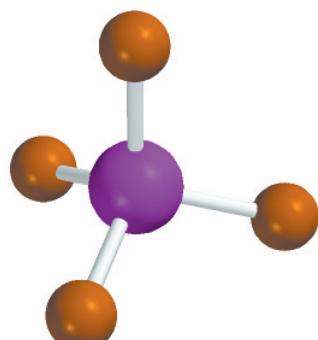
(c) The Lewis structure of  $\text{AlCl}_4^-$  is



$\text{AsH}_3$

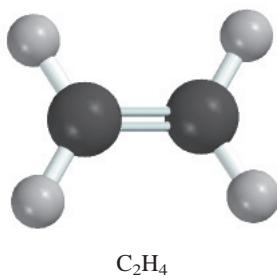
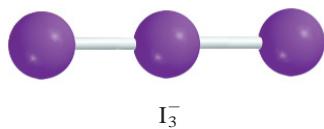


$\text{OF}_2$



$\text{AlCl}_4^-$

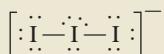
(Continued)



Similar problems: 10.7, 10.8, 10.9.

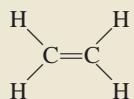
There are four electron pairs around the central atom; therefore, the electron pair arrangement is tetrahedral. Because there are no lone pairs present, the arrangement of the bonding pairs is the same as the electron pair arrangement. Therefore,  $\text{AlCl}_4^-$  has a tetrahedral geometry and the Cl-Al-Cl angles are all  $109.5^\circ$ .

(d) The Lewis structure of  $\text{I}_3^-$  is

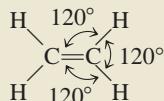


There are five electron pairs around the central I atom; therefore, the electron pair arrangement is trigonal bipyramidal. Of the five electron pairs, three are lone pairs and two are bonding pairs. Recall that the lone pairs preferentially occupy the equatorial positions in a trigonal bipyramidal (see Table 10.2). Thus, removing the lone pairs leaves us with a linear geometry for  $\text{I}_3^-$ , that is, all three I atoms lie in a straight line.

(e) The Lewis structure of  $\text{C}_2\text{H}_4$  is



The C=C bond is treated as though it were a single bond in the VSEPR model. Because there are three electron pairs around each C atom and there are no lone pairs present, the arrangement around each C atom has a trigonal planar shape like  $\text{BF}_3$ , discussed earlier. Thus, the predicted bond angles in  $\text{C}_2\text{H}_4$  are all  $120^\circ$ .



**Comment** (1) The  $\text{I}_3^-$  ion is one of the few structures for which the bond angle ( $180^\circ$ ) can be predicted accurately even though the central atom contains lone pairs. (2) In  $\text{C}_2\text{H}_4$ , all six atoms lie in the same plane. The overall planar geometry is not predicted by the VSEPR model, but we will see why the molecule prefers to be planar later. In reality, the angles are close, but not equal, to  $120^\circ$  because the bonds are not all equivalent.

**Practice Exercise** Use the VSEPR model to predict the geometry of (a)  $\text{SiBr}_4$ , (b)  $\text{CS}_2$ , and (c)  $\text{NO}_3^-$ .

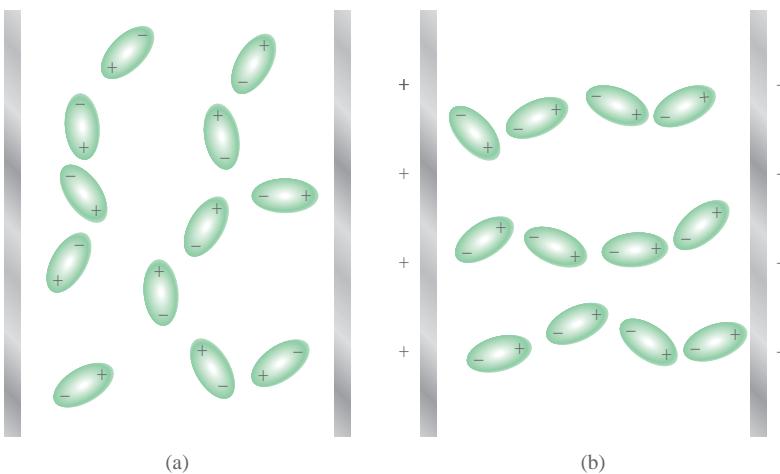
## 10.2 Dipole Moments

In Section 9.2, we learned that hydrogen fluoride is a covalent compound with a polar bond. There is a shift of electron density from H to F because the F atom is more electronegative than the H atom (see Figure 9.3). The shift of electron density is symbolized by placing a crossed arrow ( $\overrightarrow{\longleftrightarrow}$ ) above the Lewis structure to indicate the direction of the shift. For example,



The consequent charge separation can be represented as





**Figure 10.3**  
*Behavior of polar molecules (a) in the absence of an external electric field and (b) when the electric field is turned on. Non-polar molecules are not affected by an electric field.*

where  $\delta$  (delta) denotes a partial charge. This separation of charges can be confirmed in an electric field (Figure 10.3). When the field is turned on, HF molecules orient their negative ends toward the positive plate and their positive ends toward the negative plate. This alignment of molecules can be detected experimentally.

A quantitative measure of the polarity of a bond is its **dipole moment** ( $\mu$ ), which is the product of the charge  $Q$  and the distance  $r$  between the charges:

$$\mu = Q \times r \quad (10.1)$$

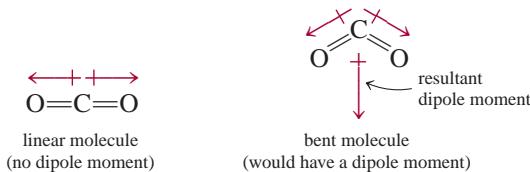
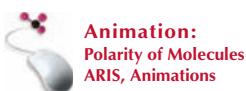
To maintain electrical neutrality, the charges on both ends of an electrically neutral diatomic molecule must be equal in magnitude and opposite in sign. However, in Equation (10.1),  $Q$  refers only to the magnitude of the charge and not to its sign, so  $\mu$  is always positive. Dipole moments are usually expressed in debye units (D), named for the Dutch-American chemist and physicist Peter Debye. The conversion factor is

In a diatomic molecule like HF, the charge  $Q$  is equal to  $\delta+$  and  $\delta-$ .

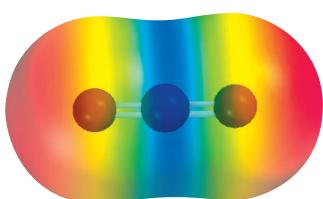
$$1 \text{ D} = 3.336 \times 10^{-30} \text{ C m}$$

where C is coulomb and m is meter.

Diatom molecules containing atoms of *different* elements (for example, HCl, CO, and NO) *have dipole moments* and are called **polar molecules**. Diatomic molecules containing atoms of the *same* element (for example, H<sub>2</sub>, O<sub>2</sub>, and F<sub>2</sub>) are examples of **nonpolar molecules** because they *do not have dipole moments*. For a molecule made up of three or more atoms, both the polarity of the bonds and the molecular geometry determine whether there is a dipole moment. Even if polar bonds are present, the molecule will not necessarily have a dipole moment. Carbon dioxide (CO<sub>2</sub>), for example, is a triatomic molecule, so its geometry is either linear or bent:



The arrows show the shift of electron density from the less electronegative carbon atom to the more electronegative oxygen atom. In each case, the dipole moment of the entire molecule is made up of two *bond moments*, that is, individual dipole



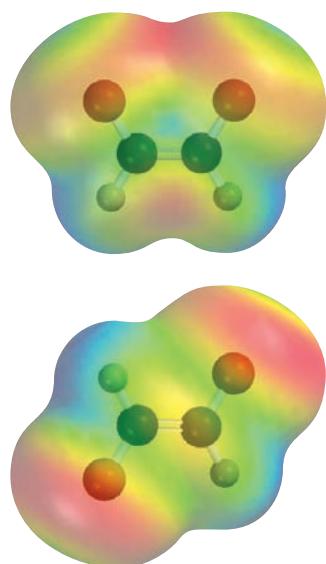
Each carbon-to-oxygen bond is polar, with the electron density shifted toward the more electronegative oxygen atom. However, the linear geometry of the molecule results in the cancellation of the two bond moments.

**TABLE 10.3 Dipole Moments of Some Polar Molecules**

Molecule	Geometry	Dipole Moment (D)
HF	Linear	1.92
HCl	Linear	1.08
HBr	Linear	0.78
HI	Linear	0.38
H <sub>2</sub> O	Bent	1.87
H <sub>2</sub> S	Bent	1.10
NH <sub>3</sub>	Trigonal pyramidal	1.46
SO <sub>2</sub>	Bent	1.60



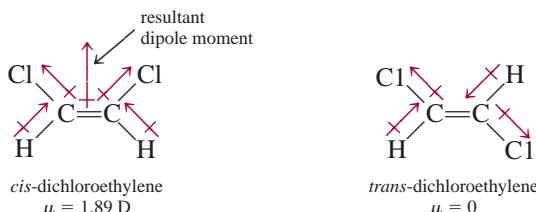
The VSEPR model predicts that CO<sub>2</sub> is a linear molecule.



In *cis*-dichloroethylene (top), the bond moments reinforce one another and the molecule is polar. The opposite holds for *trans*-dichloroethylene (bottom) and the molecule is nonpolar.

moments in the polar C=O bonds. The bond moment is a *vector quantity*, which means that it has both magnitude and direction. The measured dipole moment is equal to the vector sum of the bond moments. The two bond moments in CO<sub>2</sub> are equal in magnitude. Because they point in opposite directions in a linear CO<sub>2</sub> molecule, the sum or resultant dipole moment would be zero. On the other hand, if the CO<sub>2</sub> molecule were bent, the two bond moments would partially reinforce each other, so that the molecule would have a dipole moment. Experimentally it is found that carbon dioxide has no dipole moment. Therefore, we conclude that the carbon dioxide molecule is linear. The linear nature of carbon dioxide has been confirmed through other experimental measurements.

Dipole moments can be used to distinguish between molecules that have the same formula but different structures. For example, the following molecules both exist; they have the same molecular formula (C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>), the same number and type of bonds, but different molecular structures:



Because *cis*-dichloroethylene is a polar molecule but *trans*-dichloroethylene is not, they can readily be distinguished by a dipole moment measurement. Additionally, as we will see in Chapter 11, the strength of intermolecular forces is partially determined by whether molecules possess a dipole moment. Table 10.3 lists the dipole moments of several polar molecules.

Example 10.2 shows how we can predict whether a molecule possesses a dipole moment if we know its molecular geometry.

### Example 10.2

Predict whether each of the following molecules has a dipole moment: (a) IBr, (b) BF<sub>3</sub> (trigonal planar), (c) CH<sub>2</sub>Cl<sub>2</sub> (tetrahedral).

(Continued)

**Strategy** Keep in mind that the dipole moment of a molecule depends on both the difference in electronegativities of the elements present and its geometry. A molecule can have polar bonds (if the bonded atoms have different electronegativities), but it may not possess a dipole moment if it has a highly symmetrical geometry.

**Solution** (a) Because IBr (iodine bromide) is diatomic, it has a linear geometry. Bromine is more electronegative than iodine (see Figure 9.4), so IBr is polar with bromine at the negative end.



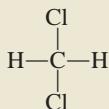
Thus, the molecule does have a dipole moment.

(b) Because fluorine is more electronegative than boron, each B—F bond in  $\text{BF}_3$  (boron trifluoride) is polar and the three bond moments are equal. However, the symmetry of a trigonal planar shape means that the three bond moments exactly cancel one another:

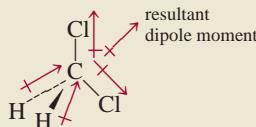


An analogy is an object that is pulled in the directions shown by the three bond moments. If the forces are equal, the object will not move. Consequently,  $\text{BF}_3$  has no dipole moment; it is a nonpolar molecule.

(c) The Lewis structure of  $\text{CH}_2\text{Cl}_2$  (methylene chloride) is

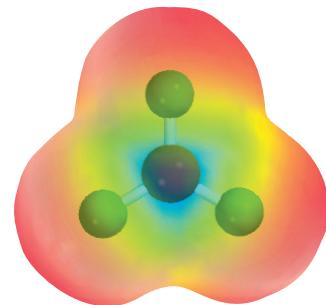


This molecule is similar to  $\text{CH}_4$  in that it has an overall tetrahedral shape. However, because not all the bonds are identical, there are three different bond angles: HCH, HCCl, and ClCCl. These bond angles are close to, but not equal to,  $109.5^\circ$ . Because chlorine is more electronegative than carbon, which is more electronegative than hydrogen, the bond moments do not cancel and the molecule possesses a dipole moment:

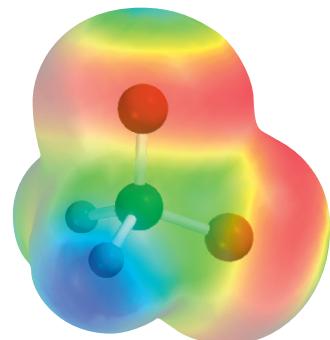


Thus,  $\text{CH}_2\text{Cl}_2$  is a polar molecule.

**Practice Exercise** Does the  $\text{AlCl}_3$  molecule have a dipole moment?



Electrostatic potential map shows that the electron density is symmetrically distributed in the  $\text{BF}_3$  molecule.



Electrostatic potential map of  $\text{CH}_2\text{Cl}_2$ . The electron density is shifted toward the electronegative Cl atoms.

**Similar problems:** 10.19, 10.21, 10.22.

## 10.3 Valence Bond Theory

The VSEPR model, based largely on Lewis structures, provides a relatively simple and straightforward method for predicting the geometry of molecules. But as we noted earlier, the Lewis theory of chemical bonding does not clearly explain why chemical bonds exist. Relating the formation of a covalent bond to the pairing of electrons was a step in the right direction, but it did not go far enough. For example, the Lewis

theory describes the single bond between the H atoms in  $\text{H}_2$  and that between the F atoms in  $\text{F}_2$  in essentially the same way—as the pairing of two electrons. Yet these two molecules have quite different bond enthalpies and bond lengths (436.4 kJ/mol and 74 pm for  $\text{H}_2$  and 150.6 kJ/mol and 142 pm for  $\text{F}_2$ ). These and many other facts cannot be explained by the Lewis theory. For a more complete explanation of chemical bond formation we look to quantum mechanics. In fact, the quantum mechanical study of chemical bonding also provides a means for understanding molecular geometry.

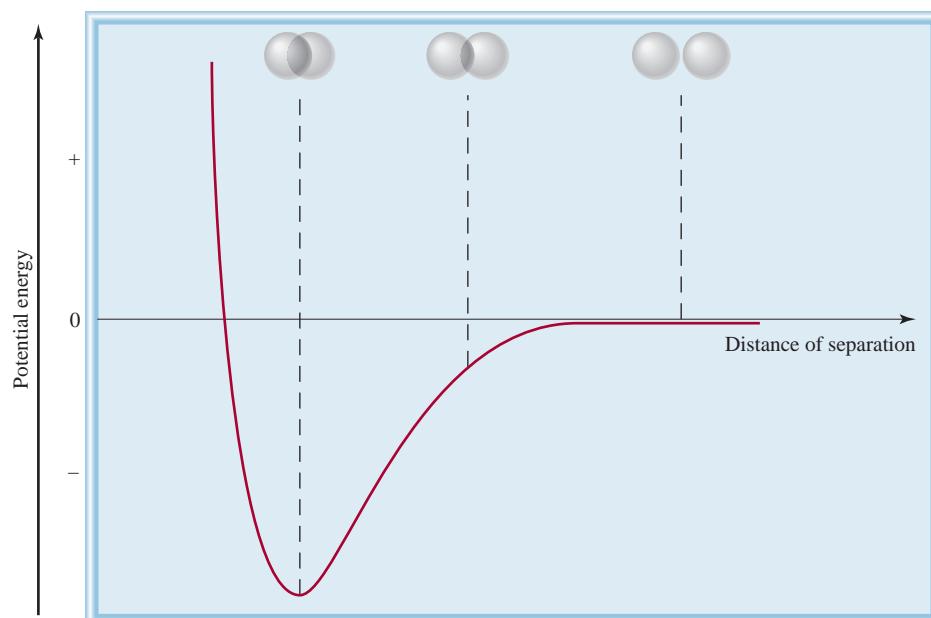
At present, two quantum mechanical theories are used to describe covalent bond formation and the electronic structure of molecules. *Valence bond (VB) theory* assumes that the electrons in a molecule occupy atomic orbitals of the individual atoms. It enables us to retain a picture of individual atoms taking part in the bond formation. The second theory, called *molecular orbital (MO) theory*, assumes the formation of molecular orbitals from the atomic orbitals. Neither theory perfectly explains all aspects of bonding, but each has contributed something to our understanding of many observed molecular properties.

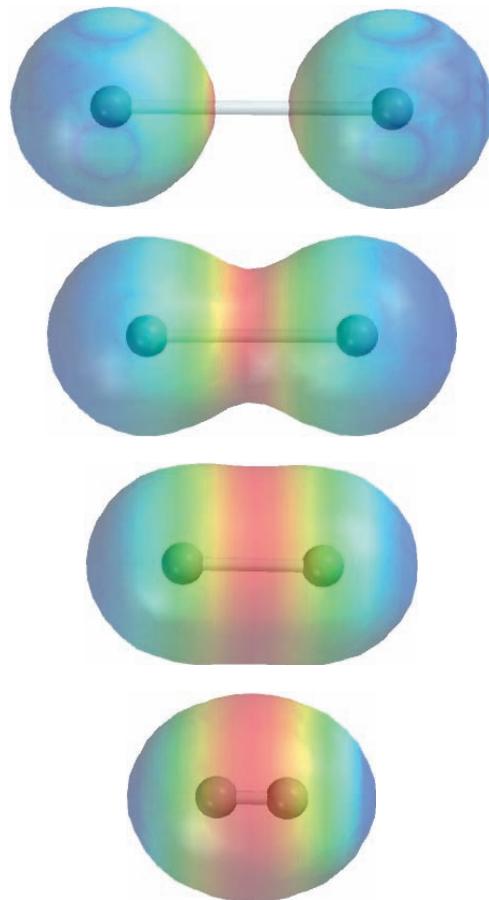
Let us start our discussion of valence bond theory by considering the formation of a  $\text{H}_2$  molecule from two H atoms. The Lewis theory describes the H—H bond in terms of the pairing of the two electrons on the H atoms. In the framework of valence bond theory, the covalent H—H bond is formed by the *overlap* of the two 1s orbitals in the H atoms. By overlap, we mean that the two orbitals share a common region in space.

What happens to two H atoms as they move toward each other and form a bond? Initially, when the two atoms are far apart, there is no interaction. We say that the potential energy of this system (that is, the two H atoms) is zero. As the atoms approach each other, each electron is attracted by the nucleus of the other atom; at the same time, the electrons repel each other, as do the nuclei. While the atoms are still separated, attraction is stronger than repulsion, so that the potential energy of the system *decreases* (that is, it becomes negative) as the atoms approach each other (Figure 10.4). This trend continues until the potential energy reaches a minimum value. At this point, when the system has the lowest potential energy, it is most stable. This condition corresponds to substantial overlap of the 1s orbitals and the formation of a

**Recall that an object has potential energy by virtue of its position.**

**Figure 10.4**  
Change in potential energy of two H atoms with their distance of separation. At the point of minimum potential energy, the  $\text{H}_2$  molecule is in its most stable state and the bond length is 74 pm. The spheres represent the 1s orbitals.



**Figure 10.5**

*Top to bottom:* As two H atoms approach each other, their 1s orbitals begin to interact and each electron begins to feel the attraction of the other proton. Gradually, the electron density builds up in the region between the two nuclei (red color). Eventually, a stable H<sub>2</sub> molecule is formed when the internuclear distance is 74 pm.

stable H<sub>2</sub> molecule. If the distance between nuclei were to decrease further, the potential energy would rise steeply and finally become positive as a result of the increased electron-electron and nuclear-nuclear repulsions. In accord with the law of conservation of energy, the decrease in potential energy as a result of H<sub>2</sub> formation must be accompanied by a release of energy. Experiments show that as a H<sub>2</sub> molecule is formed from two H atoms, heat is given off. The converse is also true. To break a H—H bond, energy must be supplied to the molecule. Figure 10.5 is another way of viewing the formation of an H<sub>2</sub> molecule.

Thus, valence bond theory gives a clearer picture of chemical bond formation than the Lewis theory does. Valence bond theory states that a stable molecule forms from reacting atoms when the potential energy of the system has decreased to a minimum; the Lewis theory ignores energy changes in chemical bond formation.

The concept of overlapping atomic orbitals applies equally well to diatomic molecules other than H<sub>2</sub>. Thus, a stable F<sub>2</sub> molecule forms when the 2p orbitals (containing the unpaired electrons) in the two F atoms overlap to form a covalent bond. Similarly, the formation of the HF molecule can be explained by the overlap of the 1s orbital in H with the 2p orbital in F. In each case, VB theory accounts for the changes in potential energy as the distance between the reacting atoms changes. Because the orbitals involved are not the same kind in all cases, we can see why the bond enthalpies and bond lengths in H<sub>2</sub>, F<sub>2</sub>, and HF might be different. As we stated earlier, Lewis theory treats *all* covalent bonds the same way and offers no explanation for the differences among covalent bonds.

The orbital diagram of the F atom is shown on p. 231.

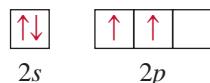
## 10.4 Hybridization of Atomic Orbitals

The concept of atomic orbital overlap should apply also to polyatomic molecules. However, a satisfactory bonding scheme must account for molecular geometry. We will discuss three examples of VB treatment of bonding in polyatomic molecules.

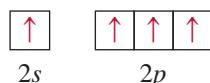


### $sp^3$ Hybridization

Consider the  $\text{CH}_4$  molecule. Focusing only on the valence electrons, we can represent the orbital diagram of C as

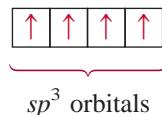


Because the carbon atom has two unpaired electrons (one in each of the two  $2p$  orbitals), it can form only two bonds with hydrogen in its ground state. Although the species  $\text{CH}_2$  is known, it is very unstable. To account for the four C—H bonds in methane, we can try to promote (that is, energetically excite) an electron from the  $2s$  orbital to the  $2p$  orbital:



Now there are four unpaired electrons on C that could form four C—H bonds. However, the geometry is wrong, because three of the HCH bond angles would have to be  $90^\circ$  (remember that the three  $2p$  orbitals on carbon are mutually perpendicular), and yet all HCH angles are  $109.5^\circ$ .

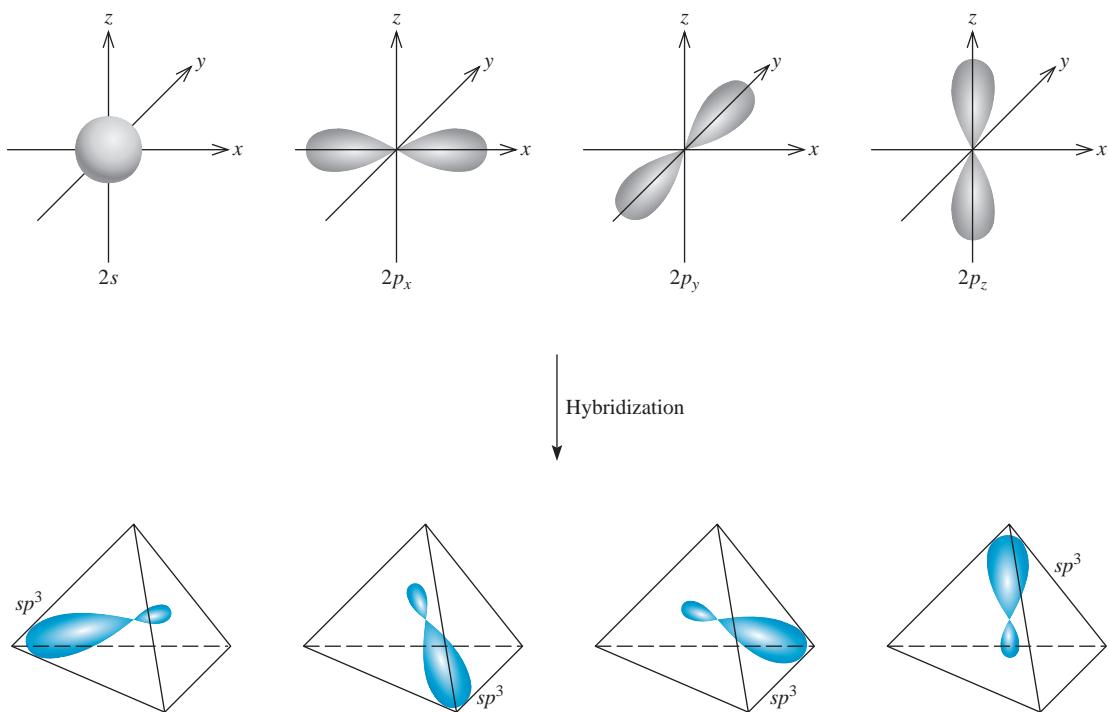
To explain the bonding in methane, VB theory uses hypothetical **hybrid orbitals**, which are *atomic orbitals obtained when two or more nonequivalent orbitals of the same atom combine in preparation for covalent bond formation*. **Hybridization** is the term applied to *the mixing of atomic orbitals in an atom (usually a central atom) to generate a set of hybrid orbitals*. We can generate four equivalent hybrid orbitals for carbon by mixing the  $2s$  orbital and the three  $2p$  orbitals:



$sp^3$  is pronounced “s-p three.”

Because the new orbitals are formed from one  $s$  and three  $p$  orbitals, they are called  $sp^3$  hybrid orbitals. Figure 10.6 shows the shape and orientations of the  $sp^3$  orbitals. These four hybrid orbitals are directed toward the four corners of a regular tetrahedron. Figure 10.7 shows the formation of four covalent bonds between the carbon  $sp^3$  hybrid orbitals and the hydrogen  $1s$  orbitals in  $\text{CH}_4$ . Thus,  $\text{CH}_4$  has a tetrahedral shape, and all the HCH angles are  $109.5^\circ$ . Note that although energy is required to bring about hybridization, this input is more than compensated for by the energy released upon the formation of C—H bonds. (Recall that bond formation is an exothermic process.)

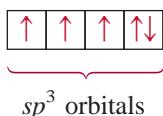
The following analogy is useful for understanding hybridization. Suppose that we have a beaker of a red solution and three beakers of blue solutions and that the volume of each is 50 mL. The red solution corresponds to one  $2s$  orbital, the blue solutions represent three  $2p$  orbitals, and the four equal volumes symbolize four separate orbitals. By mixing the solutions we obtain 200 mL of a purple solution, which

**Figure 10.6**

Formation of  $sp^3$  hybrid orbitals from one 2s and three 2p orbitals. The  $sp^3$  orbitals point to the corners of a tetrahedron.

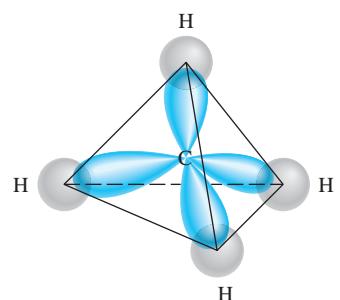
can be divided into four 50-mL portions (that is, the hybridization process generates four  $sp^3$  orbitals). Just as the purple color is made up of the red and blue components of the original solutions, the  $sp^3$  hybrid orbitals possess both s and p orbital characteristics.

Another example of  $sp^3$  hybridization is ammonia ( $NH_3$ ). Table 10.1 shows that the arrangement of four electron pairs is tetrahedral, so that the bonding in  $NH_3$  can be explained by assuming that N, like C in  $CH_4$ , is  $sp^3$ -hybridized. The ground-state electron configuration of N is  $1s^2 2s^2 2p^3$ , so that the orbital diagram for the  $sp^3$  hybridized N atom is

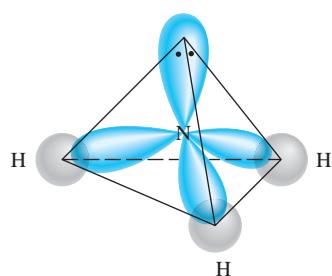


Three of the four hybrid orbitals form covalent N—H bonds, and the fourth hybrid orbital accommodates the lone pair on nitrogen (Figure 10.8). Repulsion between the lone-pair electrons and electrons in the bonding orbitals decreases the HNH bond angles from  $109.5^\circ$  to  $107.3^\circ$ .

It is important to understand the relationship between hybridization and the VSEPR model. We use hybridization to describe the bonding scheme only when the arrangement of electron pairs has been predicted using VSEPR. If the VSEPR model predicts a tetrahedral arrangement of electron pairs, then we assume that one s and three p orbitals are hybridized to form four  $sp^3$  hybrid orbitals. The following are examples of other types of hybridization.

**Figure 10.7**

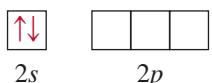
Formation of four bonds between the carbon  $sp^3$  hybrid orbitals and the hydrogen 1s orbitals in  $CH_4$ .

**Figure 10.8**

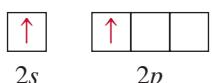
The  $sp^3$ -hybridized N atom in  $\text{NH}_3$ . Three  $sp^3$  hybrid orbitals form bonds with the H atoms. The fourth is occupied by nitrogen's lone pair.

### $sp$ Hybridization

The beryllium chloride ( $\text{BeCl}_2$ ) molecule is predicted to be linear by VSEPR. The orbital diagram for the valence electrons in Be is



We know that in its ground state Be does not form covalent bonds with Cl because its electrons are paired in the  $2s$  orbital. So we turn to hybridization for an explanation of Be's bonding behavior. First, we promote a  $2s$  electron to a  $2p$  orbital, resulting in



Now there are two Be orbitals available for bonding, the  $2s$  and  $2p$ . However, if two Cl atoms were to combine with Be in this excited state, one Cl atom would share a  $2s$  electron and the other Cl would share a  $2p$  electron, making two nonequivalent  $\text{BeCl}$  bonds. This scheme contradicts experimental evidence. In the actual  $\text{BeCl}_2$  molecule, the two  $\text{BeCl}$  bonds are identical in every respect. Thus, the  $2s$  and  $2p$  orbitals must be mixed, or hybridized, to form two equivalent  $sp$  hybrid orbitals:

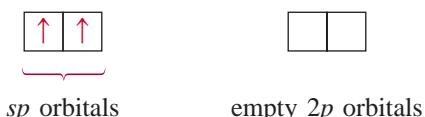
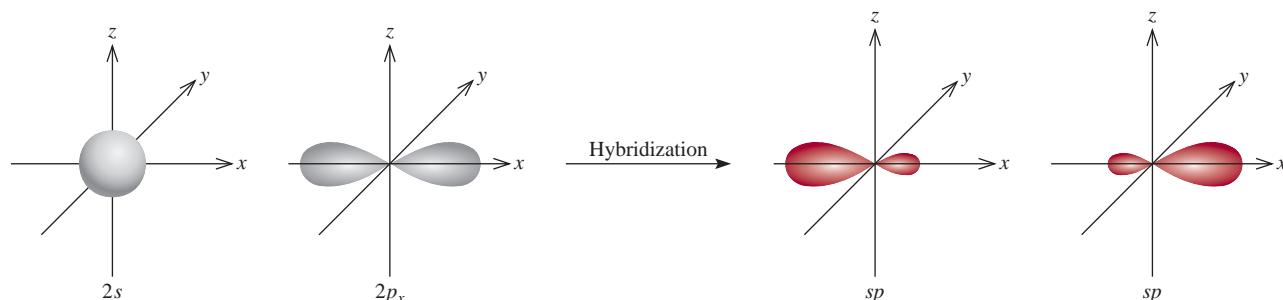
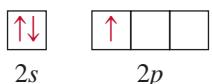


Figure 10.9 shows the shape and orientation of the  $sp$  orbitals. These two hybrid orbitals lie on the same line, the  $x$ -axis, so that the angle between them is  $180^\circ$ . Each of the  $\text{BeCl}$  bonds is then formed by the overlap of a Be  $sp$  hybrid orbital and a Cl  $3p$  orbital, and the resulting  $\text{BeCl}_2$  molecule has a linear geometry (Figure 10.10).

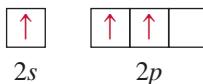
### $sp^2$ Hybridization

Next we will look at the  $\text{BF}_3$  (boron trifluoride) molecule, known to have planar geometry based on VSEPR. Considering only the valence electrons, the orbital diagram of B is

**Figure 10.9**

Formation of  $sp$  hybrid orbitals from one  $2s$  and one  $2p$  orbital.

First, we promote a  $2s$  electron to an empty  $2p$  orbital:



Mixing the  $2s$  orbital with the two  $2p$  orbitals generates three  $sp^2$  hybrid orbitals:

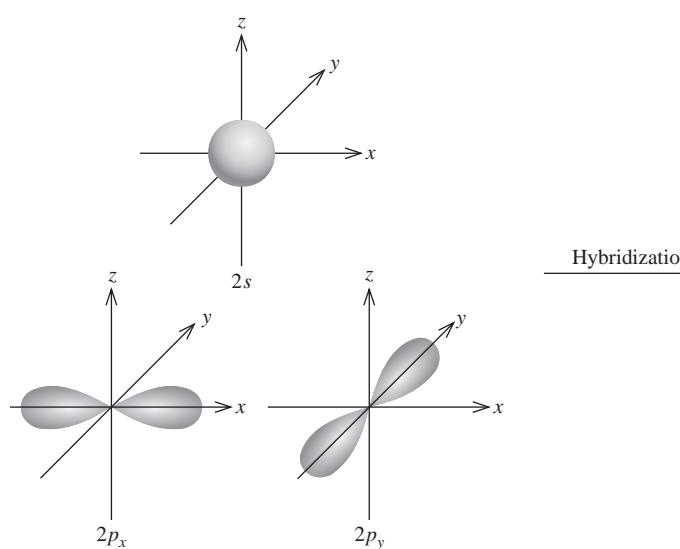


$sp^2$  is pronounced “*s-p two.*”

These three  $sp^2$  orbitals lie in the same plane, and the angle between any two of them is  $120^\circ$  (Figure 10.11). Each of the  $BF$  bonds is formed by the overlap of a boron  $sp^2$  hybrid orbital and a fluorine  $2p$  orbital (Figure 10.12). The  $BF_3$  molecule is planar with all the  $FBF$  angles equal to  $120^\circ$ . This result conforms to experimental findings and also to VSEPR predictions.

You may have noticed an interesting connection between hybridization and the octet rule. Regardless of the type of hybridization, an atom starting with one  $s$  and three  $p$  orbitals would still possess four orbitals, enough to accommodate a total of eight electrons in a compound. For elements in the second period of the periodic table, eight is the maximum number of electrons that an atom of any of these elements can accommodate in the valence shell. This is the reason that the octet rule is usually obeyed by the second-period elements.

The situation is different for an atom of a third-period element. If we use only the  $3s$  and  $3p$  orbitals of the atom to form hybrid orbitals in a molecule, then the octet rule applies. However, in some molecules the same atom may use one or more  $3d$  orbitals, in addition to the  $3s$  and  $3p$  orbitals, to form hybrid orbitals. In these cases, the octet rule does not hold. We will see specific examples of the participation of the  $3d$  orbital in hybridization shortly.



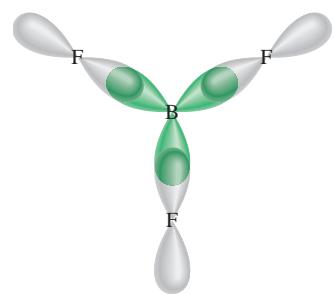
**Figure 10.11**

Formation of  $sp^2$  hybrid orbitals from one  $2s$  and two  $2p$  orbitals. The  $sp^2$  orbitals point to the corners of an equilateral triangle.



**Figure 10.10**

The linear geometry of  $BeCl_2$  can be explained by assuming that  $Be$  is  $sp$ -hybridized. The two  $sp$  hybrid orbitals overlap with the two chlorine  $3p$  orbitals to form two covalent bonds.



**Figure 10.12**

The  $sp^2$  hybrid orbitals of boron overlap with the  $2p$  orbitals of fluorine. The  $BF_3$  molecule is planar, and all the  $FBF$  angles are  $120^\circ$ .

To summarize our discussion of hybridization, we note that

1. The concept of hybridization is not applied to isolated atoms. It is a theoretical model used only to explain covalent bonding.
2. Hybridization is the mixing of at least two nonequivalent atomic orbitals, for example,  $s$  and  $p$  orbitals. Therefore, a hybrid orbital is not a pure atomic orbital. Hybrid orbitals and pure atomic orbitals have very different shapes.
3. The number of hybrid orbitals generated is equal to the number of pure atomic orbitals that participate in the hybridization process.
4. Hybridization requires an input of energy; however, the system more than recovers this energy during bond formation.
5. Covalent bonds in polyatomic molecules and ions are formed by the overlap of hybrid orbitals, or of hybrid orbitals with unhybridized ones. Therefore, the hybridization bonding scheme is still within the framework of valence bond theory; electrons in a molecule are assumed to occupy hybrid orbitals of the individual atoms.

Table 10.4 summarizes  $sp$ ,  $sp^2$ , and  $sp^3$  hybridization (as well as other types that we will discuss shortly).

### Procedure for Hybridizing Atomic Orbitals

Before going on to discuss the hybridization of  $d$  orbitals, let us specify what we need to know to apply hybridization to bonding in polyatomic molecules in general. In essence, hybridization simply extends Lewis theory and the VSEPR model. To assign a suitable state of hybridization to the central atom in a molecule, we must have some idea about the geometry of the molecule. The steps are as follows:

1. Draw the Lewis structure of the molecule.
2. Predict the overall arrangement of the electron pairs (both bonding pairs and lone pairs) using the VSEPR model (see Table 10.1).
3. Deduce the hybridization of the central atom by matching the arrangement of the electron pairs with those of the hybrid orbitals shown in Table 10.4.

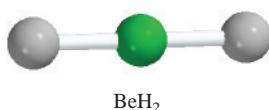
### Example 10.3

Determine the hybridization state of the central (underlined) atom in each of the following molecules: (a)  $\underline{\text{BeH}}_2$ , (b)  $\underline{\text{AlI}}_3$ , and (c)  $\underline{\text{PF}}_3$ . Describe the hybridization process and determine the molecular geometry in each case.

**Strategy** The steps for determining the hybridization of the central atom in a molecule are:

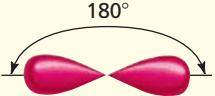
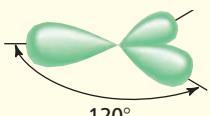
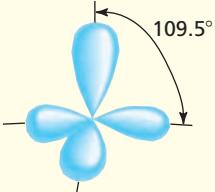
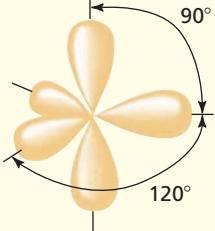
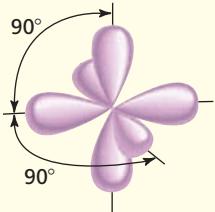
draw Lewis structure of the molecule	use VSEPR to determine the electron pair arrangement surrounding the central atom (Table 10.1)	use Table 10.4 to determine the hybridization state of the central atom
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**Solution** (a) The ground-state electron configuration of Be is  $1s^22s^2$  and the Be atom has two valence electrons. The Lewis structure of  $\text{BeH}_2$  is



(Continued)

**TABLE 10.4** Important Hybrid Orbitals and Their Shapes

Pure Atomic Orbitals of the Central Atom	Hybridization of the Central Atom	Number of Hybrid Orbitals	Shape of Hybrid Orbitals	Examples
<i>s, p</i>	<i>sp</i>	2		BeCl <sub>2</sub>
<i>s, p, p</i>	<i>sp</i> <sup>2</sup>	3		BF <sub>3</sub>
<i>s, p, p, p</i>	<i>sp</i> <sup>3</sup>	4		CH <sub>4</sub> , NH <sub>4</sub> <sup>+</sup>
<i>s, p, p, p, d</i>	<i>sp</i> <sup>3</sup> <i>d</i>	5		PCl <sub>5</sub>
<i>s, p, p, p, d, d</i>	<i>sp</i> <sup>3</sup> <i>d</i> <sup>2</sup>	6		SF <sub>6</sub>

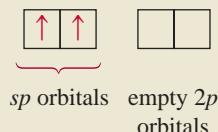
There are two bonding pairs around Be; therefore, the electron pair arrangement is linear. We conclude that Be uses  $sp$  hybrid orbitals in bonding with H, because  $sp$  orbitals have a linear arrangement (see Table 10.4). The hybridization process can be imagined as follows. First we draw the orbital diagram for the ground state of Be:



By promoting a  $2s$  electron to the  $2p$  orbital, we get the excited state:

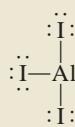


The  $2s$  and  $2p$  orbitals then mix to form two hybrid orbitals:



The two Be—H bonds are formed by the overlap of the Be  $sp$  orbitals with the  $1s$  orbitals of the H atoms. Thus,  $\text{BeH}_2$  is a linear molecule.

- (b) The ground-state electron configuration of Al is  $[\text{Ne}]3s^23p^1$ . Therefore, the Al atom has three valence electrons. The Lewis structure of  $\text{AlI}_3$  is



$\text{AlI}_3$

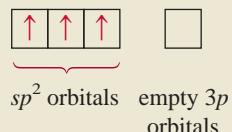
There are three pairs of electrons around Al; therefore, the electron pair arrangement is trigonal planar. We conclude that Al uses  $sp^2$  hybrid orbitals in bonding with I because  $sp^2$  orbitals have a trigonal planar arrangement (see Table 10.4). The orbital diagram of the ground-state Al atom is



By promoting a  $3s$  electron into the  $3p$  orbital we obtain the following excited state:



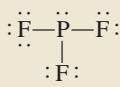
The  $3s$  and two  $3p$  orbitals then mix to form three  $sp^2$  hybrid orbitals:



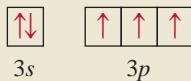
The  $sp^2$  hybrid orbitals overlap with the  $5p$  orbitals of I to form three covalent Al—I bonds. We predict that the  $\text{AlI}_3$  molecule is trigonal planar and all the  $\text{AlII}$  angles are  $120^\circ$ .

(Continued)

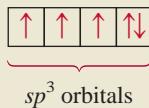
- (c) The ground-state electron configuration of P is  $[\text{Ne}]3s^23p^3$ . Therefore, the P atom has five valence electrons. The Lewis structure of  $\text{PF}_3$  is



There are four pairs of electrons around P; therefore, the electron pair arrangement is tetrahedral. We conclude that P uses  $sp^3$  hybrid orbitals in bonding to F, because  $sp^3$  orbitals have a tetrahedral arrangement (see Table 10.4). The hybridization process can be imagined to take place as follows. The orbital diagram of the ground-state P atom is



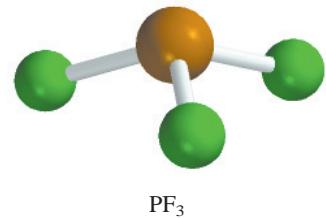
By mixing the  $3s$  and  $3p$  orbitals, we obtain four  $sp^3$  hybrid orbitals.



As in the case of  $\text{NH}_3$ , one of the  $sp^3$  hybrid orbitals is used to accommodate the lone pair on P. The other three  $sp^3$  hybrid orbitals form covalent P—F bonds with the  $2p$  orbitals of F. We predict the geometry of the molecule to be trigonal pyramidal; the PFP angle should be somewhat less than  $109.5^\circ$ .

**Similar problems:** 10.31, 10.32.

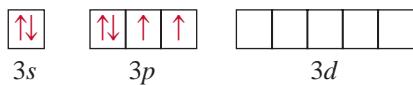
**Practice Exercise** Determine the hybridization state of the underlined atoms in the following compounds: (a) SiBr<sub>4</sub> and (b) BCl<sub>3</sub>.



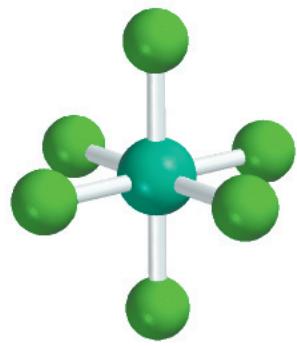
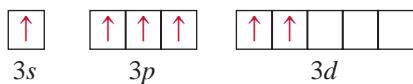
## Hybridization of *s*, *p*, and *d* Orbitals

We have seen that hybridization neatly explains bonding that involves *s* and *p* orbitals. For elements in the third period and beyond, however, we cannot always account for molecular geometry by assuming that only *s* and *p* orbitals hybridize. To understand the formation of molecules with trigonal bipyramidal and octahedral geometries, for instance, we must include *d* orbitals in the hybridization concept.

Consider the  $\text{SF}_6$  molecule as an example. In Section 10.1 we saw that this molecule has octahedral geometry, which is also the arrangement of the six electron pairs. Table 10.4 shows that the S atom is  $sp^3d^2$ -hybridized in  $\text{SF}_6$ . The ground-state electron configuration of S is  $[\text{Ne}]3s^23p^4$ :

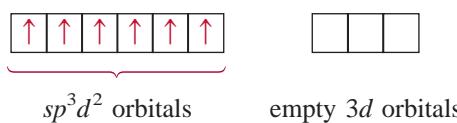


Because the  $3d$  level is quite close in energy to the  $3s$  and  $3p$  levels, we can promote  $3s$  and  $3p$  electrons to two of the  $3d$  orbitals:

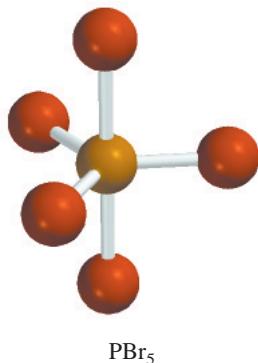


$sp^3d^2$  is pronounced “*s-p three d two.*”

Mixing the 3s, three 3p, and two 3d orbitals generates six  $sp^3d^2$  hybrid orbitals:



The six S—F bonds are formed by the overlap of the hybrid orbitals of the S atom with the 2p orbitals of the F atoms. Because there are 12 electrons around the S atom, the octet rule is violated. The use of *d* orbitals in addition to *s* and *p* orbitals to form an expanded octet (see Section 9.9) is an example of *valence-shell expansion*. Second-period elements, unlike third-period elements, do not have 2*d* energy levels, so they can never expand their valence shells. (Recall that when  $n = 2$ ,  $l = 0$  and 1. Thus, we can only have 2s and 2p orbitals.) Hence, atoms of second-period elements can never be surrounded by more than eight electrons in any of their compounds.

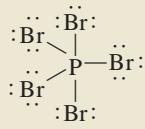


### Example 10.4

Describe the hybridization state of phosphorus in phosphorus pentabromide ( $\text{PBr}_5$ ).

**Strategy** Follow the same procedure shown in Example 10.3.

**Solution** The ground-state electron configuration of P is  $[\text{Ne}]3s^23p^3$ . Therefore, the P atom has five valence electrons. The Lewis structure of  $\text{PBr}_5$  is



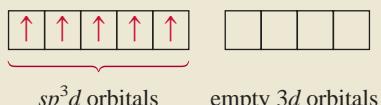
There are five pairs of electrons around P; therefore, the electron pair arrangement is trigonal bipyramidal. We conclude that P uses  $sp^3d$  hybrid orbitals in bonding to Br, because  $sp^3d$  hybrid orbitals have a trigonal bipyramidal arrangement (see Table 10.4). The hybridization process can be imagined as follows. The orbital diagram of the ground-state P atom is



Promoting a 3s electron into a 3d orbital results in the following excited state:



Mixing the one 3s, three 3p, and one 3d orbitals generates five  $sp^3d$  hybrid orbitals:



These hybrid orbitals overlap the 4p orbitals of Br to form five covalent P—Br bonds. Because there are no lone pairs on the P atom, the geometry of  $\text{PBr}_5$  is trigonal bipyramidal.

**Similar problem:** 10.40.

**Practice Exercise** Describe the hybridization state of Se in  $\text{SeF}_6$ .

## 10.5 Hybridization in Molecules Containing Double and Triple Bonds

The concept of hybridization is useful also for molecules with double and triple bonds. Consider the ethylene molecule,  $C_2H_4$ , as an example. In Example 10.1 we saw that  $C_2H_4$  contains a carbon-carbon double bond and has planar geometry. Both the geometry and the bonding can be understood if we assume that each carbon atom is  $sp^2$ -hybridized. Figure 10.13 shows orbital diagrams of this hybridization process. We assume that only the  $2p_x$  and  $2p_y$  orbitals combine with the  $2s$  orbital, and that the  $2p_z$  orbital remains unchanged. Figure 10.14 shows that the  $2p_z$  orbital is perpendicular to the plane of the hybrid orbitals. Now, how do we account for the bonding of the C atoms? As Figure 10.15(a) shows, each carbon atom uses the three  $sp^2$  hybrid orbitals to form two bonds with the two hydrogen 1s orbitals and one bond with the  $sp^2$  hybrid orbital of the adjacent C atom. In addition, the two unhybridized  $2p_z$  orbitals of the C atoms form another bond by overlapping sideways [Figure 10.15(b)].

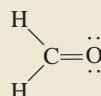
A distinction is made between the two types of covalent bonds in  $C_2H_4$ . The three bonds formed by each C atom in Figure 10.15(a) are all ***sigma bonds ( $\sigma$  bonds)***, *covalent bonds formed by orbitals overlapping end-to-end, with the electron density concentrated between the nuclei of the bonding atoms*. The second type is called a ***pi bond ( $\pi$  bond)***, which is defined as *a covalent bond formed by sideways overlapping orbitals with electron density concentrated above and below the plane of the nuclei of the bonding atoms*. The two C atoms form a pi bond, as shown in Figure 10.15(b). This pi bond formation gives ethylene its planar geometry. Figure 10.15(c) shows the orientation of the sigma and pi bonds. Figure 10.16 is yet another way of looking at the planar  $C_2H_4$  molecule and the formation of the pi bond. Although we normally represent the carbon-carbon double bond as  $C=C$  (as in a Lewis structure), it is important to keep in mind that the two bonds are different types: One is a sigma bond and the other is a pi bond. In fact, the bond enthalpies of the carbon-carbon pi and sigma bonds are about 270 kJ/mol and 350 kJ/mol, respectively.

The acetylene molecule ( $C_2H_2$ ) contains a carbon-carbon triple bond. Because the molecule is linear, we can explain its geometry and bonding by assuming that each C atom is  $sp$ -hybridized by mixing the  $2s$  with the  $2p_x$  orbital (Figure 10.17). As Figure 10.18 shows, the two  $sp$  hybrid orbitals of each C atom form one sigma bond with a hydrogen 1s orbital and another sigma bond with the other C atom. In addition, two pi bonds are formed by the sideways overlap of the unhybridized  $2p_y$  and  $2p_z$  orbitals. Thus, the  $C\equiv C$  bond is made up of one sigma bond and two pi bonds.

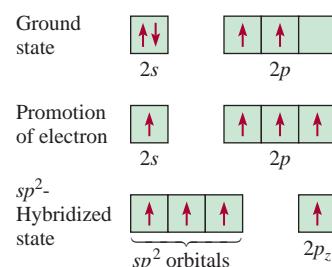
The following rule helps us predict hybridization in molecules containing multiple bonds: If the central atom forms a double bond, it is  $sp^2$ -hybridized; if it forms two double bonds or a triple bond, it is  $sp$ -hybridized. Note that this rule applies only to atoms of the second-period elements. Atoms of third-period elements and beyond that form multiple bonds present a more complicated picture and will not be dealt with here.

### Example 10.5

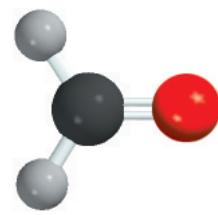
Describe the bonding in the formaldehyde molecule whose Lewis structure is



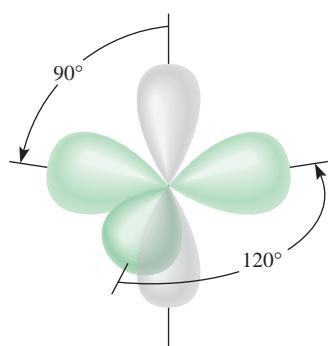
Assume that the O atom is  $sp^2$ -hybridized.



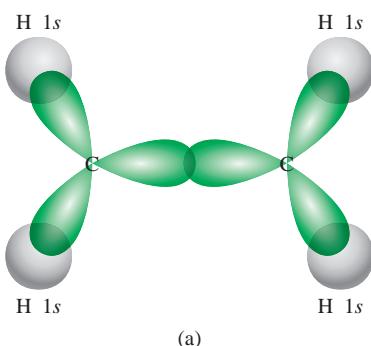
**Figure 10.13**  
*The  $sp^2$  hybridization of a carbon atom. The  $2s$  orbital is mixed with only two  $2p$  orbitals to form three equivalent  $sp^2$  hybrid orbitals. This process leaves an electron in the unhybridized orbital, the  $2p_z$  orbital.*



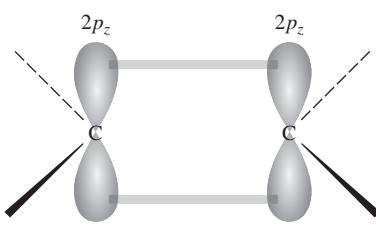
(Continued)

**Figure 10.14**

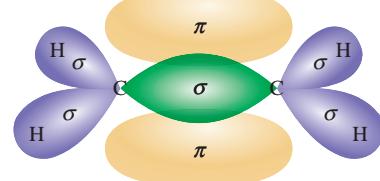
Each carbon atom in the  $C_2H_4$  molecule has three  $sp^2$  hybrid orbitals (green) and one unhybridized  $2p_z$  orbital (gray), which is perpendicular to the plane of the hybrid orbitals.



(a)



(b)



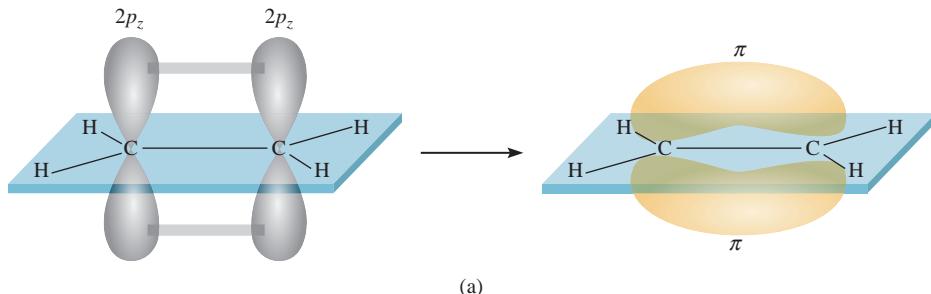
(c)

**Figure 10.15**

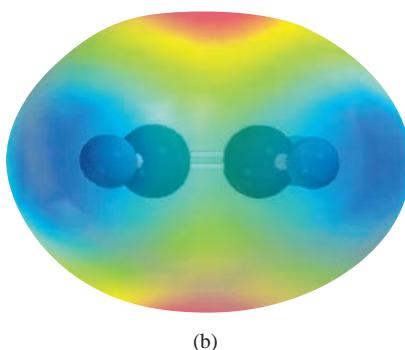
Bonding in ethylene,  $C_2H_4$ . (a) Top view of the sigma bonds between carbon atoms and between carbon and hydrogen atoms. All the atoms lie in the same plane, making  $C_2H_4$  a planar molecule. (b) Side view showing how the two  $2p_z$  orbitals on the two carbon atoms overlap, leading to the formation of a pi bond. (c) The interactions in (a) and (b) lead to the formation of the sigma bonds and the pi bond in ethylene. Note that the pi bond lies above and below the plane of the molecule.

**Figure 10.16**

(a) Another view of pi bond formation in the  $C_2H_4$  molecule. Note that all six atoms are in the same plane. It is the overlap of the  $2p_z$  orbitals that causes the molecule to assume a planar structure. (b) Electrostatic potential map of  $C_2H_4$ .



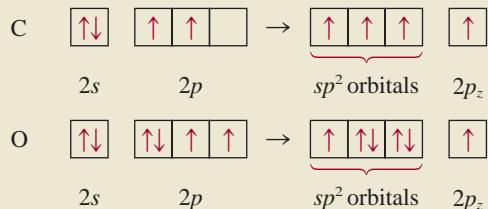
(a)



(b)

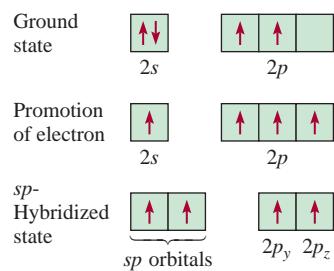
**Strategy** Follow the procedure shown in Example 10.3.

**Solution** There are three pairs of electrons around the C atom; therefore, the electron pair arrangement is trigonal planar. (Recall that a double bond is treated as a single bond in the VSEPR model.) We conclude that C uses  $sp^2$  hybrid orbitals in bonding, because  $sp^2$  hybrid orbitals have a trigonal planar arrangement (see Table 10.4). We can imagine the hybridization processes for C and O as follows:



Carbon has one electron in each of the three  $sp^2$  orbitals, which are used to form sigma bonds with the H atoms and the O atom. There is also an electron in the  $2p_z$  orbital, which forms a pi bond with oxygen. Oxygen has two electrons in two of its  $sp^2$  hybrid orbitals. These are the lone pairs on oxygen. Its third  $sp^2$  hybrid orbital with one electron is used to form a sigma bond with carbon. The  $2p_z$  orbital (with one electron) overlaps with the  $2p_z$  orbital of C to form a pi bond (Figure 10.19).

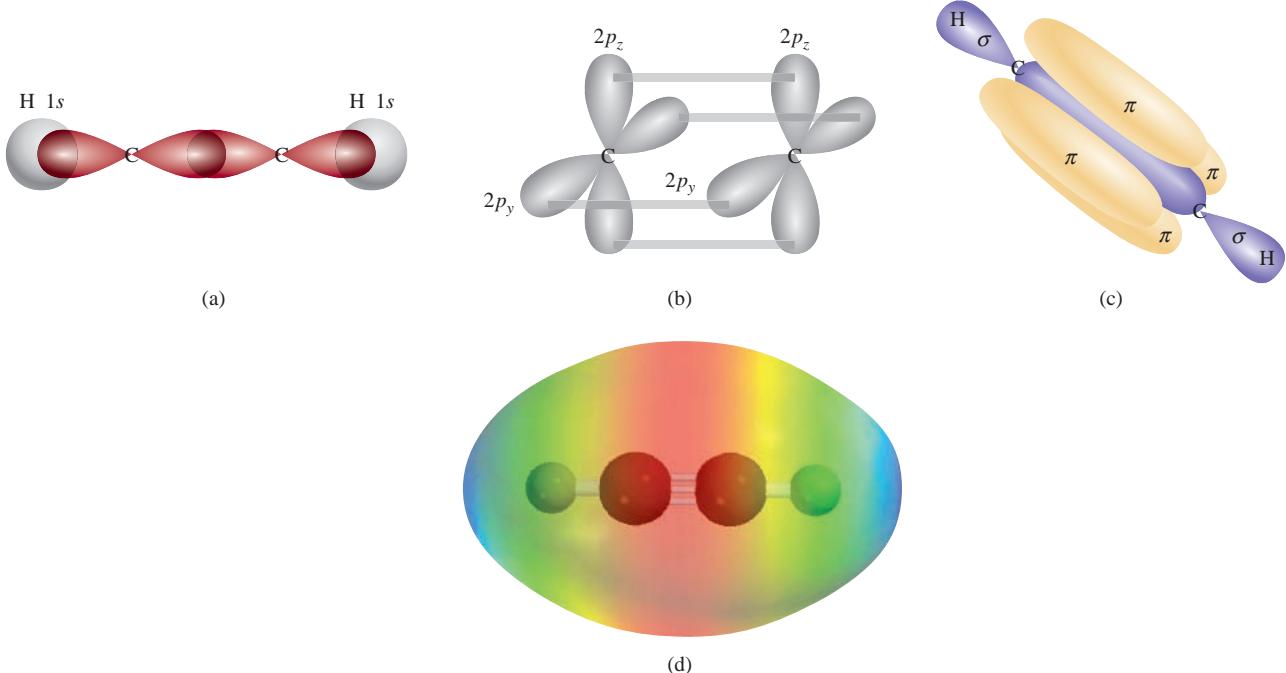
**Practice Exercise** Describe the bonding in the hydrogen cyanide molecule, HCN. Assume that N is  $sp$ -hybridized.



**Figure 10.17**

The  $sp$  hybridization of a carbon atom. The  $2s$  orbital is mixed with only one  $2p$  orbital to form two  $sp$  hybrid orbitals. This process leaves an electron in each of the two unhybridized  $2p$  orbitals, namely, the  $2p_y$  and  $2p_z$  orbitals.

Similar problems: 10.36, 10.39.

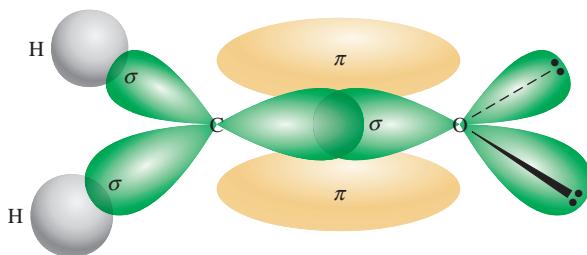


**Figure 10.18**

Bonding in acetylene,  $C_2H_2$ . (a) Top view showing the overlap of the  $sp$  orbitals between the C atoms and the overlap of the  $sp$  orbital with the  $1s$  orbital between the C and H atoms. All the atoms lie along a straight line; therefore acetylene is a linear molecule. (b) Side view showing the overlap of the two  $2p_y$  orbitals and of the two  $2p_z$  orbitals of the two carbon atoms, which leads to the formation of two pi bonds. (c) Formation of the sigma and pi bonds as a result of the interactions in (a) and (b). (d) Electrostatic potential map of  $C_2H_2$ .

**Figure 10.19**

Bonding in the formaldehyde molecule. A sigma bond is formed by the overlap of the  $sp^2$  hybrid orbital of carbon and the  $sp^2$  hybrid orbital of oxygen; a pi bond is formed by the overlap of the  $2p_z$  orbitals of the carbon and oxygen atoms. The two lone pairs on oxygen are placed in the other two  $sp^2$  orbitals of oxygen.



## 10.6 Molecular Orbital Theory

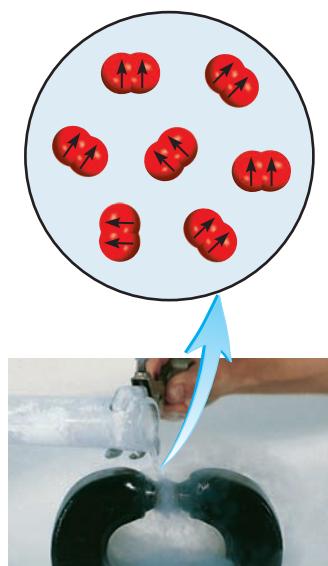
Valence bond theory is one of the two quantum mechanical approaches that explain bonding in molecules. It accounts, at least qualitatively, for the stability of the covalent bond in terms of overlapping atomic orbitals. Using the concept of hybridization, valence bond theory can explain molecular geometries predicted by the VSEPR model. However, the assumption that electrons in a molecule occupy atomic orbitals of the individual atoms can be only an approximation, because each bonding electron in a molecule must be in an orbital that is characteristic of the molecule as a whole.

In some cases, valence bond theory cannot satisfactorily account for observed properties of molecules. Consider the oxygen molecule, whose Lewis structure is



According to this description, all the electrons in  $\text{O}_2$  are paired and oxygen should therefore be diamagnetic. But experiments have shown that the oxygen molecule has two unpaired electrons (Figure 10.20). This finding suggests a fundamental deficiency in valence bond theory, one that justifies searching for an alternative bonding approach that accounts for the properties of  $\text{O}_2$  and other molecules that do not match the predictions of valence bond theory.

Magnetic and other properties of molecules are sometimes better explained by another quantum mechanical approach called *molecular orbital (MO) theory*. Molecular orbital theory describes covalent bonds in terms of **molecular orbitals**, which result from interaction of the atomic orbitals of the bonding atoms and are associated with the entire molecule. The difference between a molecular orbital and an atomic orbital is that an atomic orbital is associated with only one atom.

**Figure 10.20**

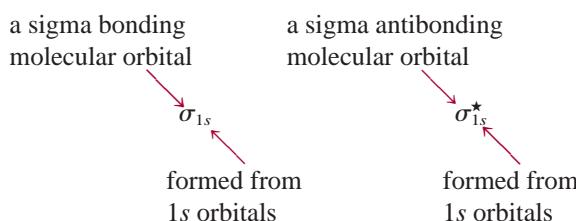
Liquid oxygen caught between the poles of a magnet, because the  $\text{O}_2$  molecules are paramagnetic, having two parallel spins.

### Bonding and Antibonding Molecular Orbitals

According to MO theory, the overlap of the 1s orbitals of two hydrogen atoms leads to the formation of two molecular orbitals: one bonding molecular orbital and one antibonding molecular orbital. A **bonding molecular orbital** has lower energy and greater stability than the atomic orbitals from which it was formed. An **antibonding molecular orbital** has higher energy and lower stability than the atomic orbitals from which it was formed. As the names “bonding” and “antibonding” suggest, placing electrons in a bonding molecular orbital yields a stable covalent bond, whereas placing electrons in an antibonding molecular orbital results in an unstable bond.

In the bonding molecular orbital, the electron density is greatest between the nuclei of the bonding atoms. In the antibonding molecular orbital, on the other hand, the electron density decreases to zero between the nuclei. We can understand this distinction if we recall that electrons in orbitals have wave characteristics. A property unique to waves enables waves of the same type to interact in such a way that the resultant wave has either an enhanced amplitude or a diminished amplitude. In the former case, we call the interaction *constructive interference*; in the latter case, it is *destructive interference* (Figure 10.21).

The formation of bonding molecular orbitals corresponds to constructive interference (the increase in amplitude is analogous to the buildup of electron density between the two nuclei). The formation of antibonding molecular orbitals corresponds to destructive interference (the decrease in amplitude is analogous to the decrease in electron density between the two nuclei). The constructive and destructive interactions between the two 1s orbitals in the H<sub>2</sub> molecule, then, lead to the formation of a sigma bonding molecular orbital ( $\sigma_{1s}$ ) and a sigma antibonding molecular orbital  $\sigma_{1s}^*$ :



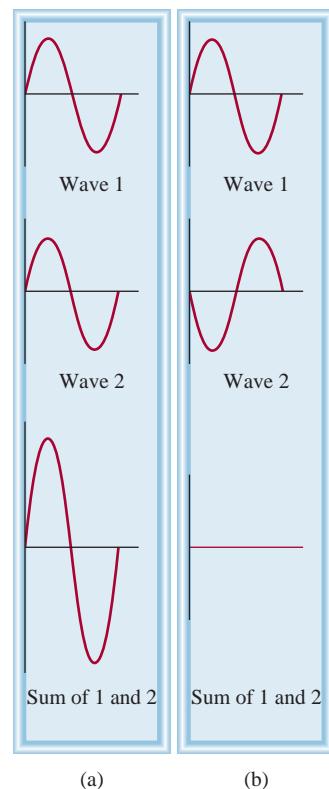
where the star denotes an antibonding molecular orbital.

In a **sigma molecular orbital** (bonding or antibonding) the electron density is concentrated symmetrically around a line between the two nuclei of the bonding atoms. Two electrons in a sigma molecular orbital form a sigma bond (see Section 10.5). Remember that a single covalent bond (such as H—H or F—F) is almost always a sigma bond.

Figure 10.22 shows the *molecular orbital energy level diagram*—that is, the relative energy levels of the orbitals produced in the formation of the H<sub>2</sub> molecule—and the constructive and destructive interactions between the two 1s orbitals. Notice that in the antibonding molecular orbital there is a *node* between the nuclei that signifies zero electron density. The nuclei are repelled by each other's positive charges, rather than held together. Electrons in the antibonding molecular orbital have higher energy (and less stability) than they would have in the isolated atoms. On the other hand, electrons in the bonding molecular orbital have less energy (and hence greater stability) than they would have in the isolated atoms.

Although we have used the hydrogen molecule to illustrate molecular orbital formation, the concept is equally applicable to other molecules. In the H<sub>2</sub> molecule, we consider only the interaction between 1s orbitals; with more complex molecules, we need to consider additional atomic orbitals as well. Nevertheless, for all s orbitals, the process is the same as for 1s orbitals. Thus, the interaction between two 2s or 3s orbitals can be understood in terms of the molecular orbital energy level diagram and the formation of bonding and antibonding molecular orbitals shown in Figure 10.22.

For p orbitals, the process is more complex because they can interact with each other in two different ways. For example, two 2p orbitals can approach each other end-to-end to produce a sigma bonding and a sigma antibonding molecular orbital, as shown in Figure 10.23(a). Alternatively, the two p orbitals can overlap

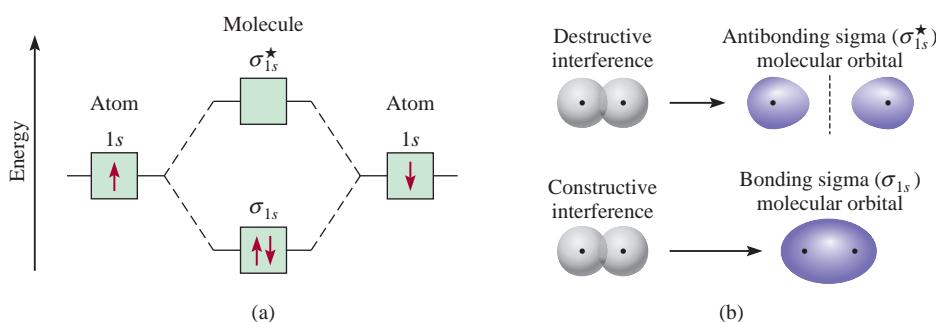


**Figure 10.21**  
*Constructive interference (a) and destructive interference (b) of two waves of the same wavelength and amplitude.*

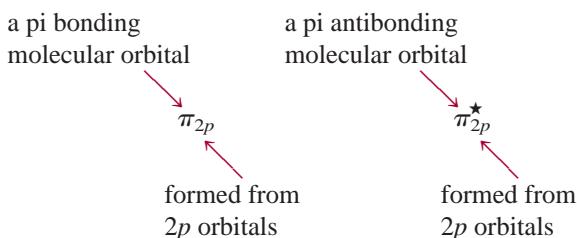
**The two electrons in the sigma molecular orbital are paired. The Pauli exclusion principle applies to molecules as well as to atoms.**

**Figure 10.22**

(a) Energy levels of bonding and antibonding molecular orbitals in the  $H_2$  molecule. Note that the two electrons in the  $\sigma_{1s}$  orbital must have opposite spins in accord with the Pauli exclusion principle. Keep in mind that the higher the energy of the molecular orbital, the less stable the electrons in that molecular orbital. (b) Constructive and destructive interactions between the two hydrogen 1s orbitals lead to the formation of a bonding and an antibonding molecular orbital. In the bonding molecular orbital, there is a buildup between the nuclei of electron density, which acts as a negatively charged “glue” to hold the positively charged nuclei together.



sideways to generate a bonding and an antibonding pi molecular orbital [Figure 10.23(b)].



In a ***pi molecular orbital*** (bonding or antibonding), the electron density is concentrated above and below a line joining the two nuclei of the bonding atoms. Two electrons in a pi molecular orbital form a pi bond (see Section 10.5). A double bond is almost always composed of a sigma bond and a pi bond; a triple bond is always a sigma bond plus two pi bonds.

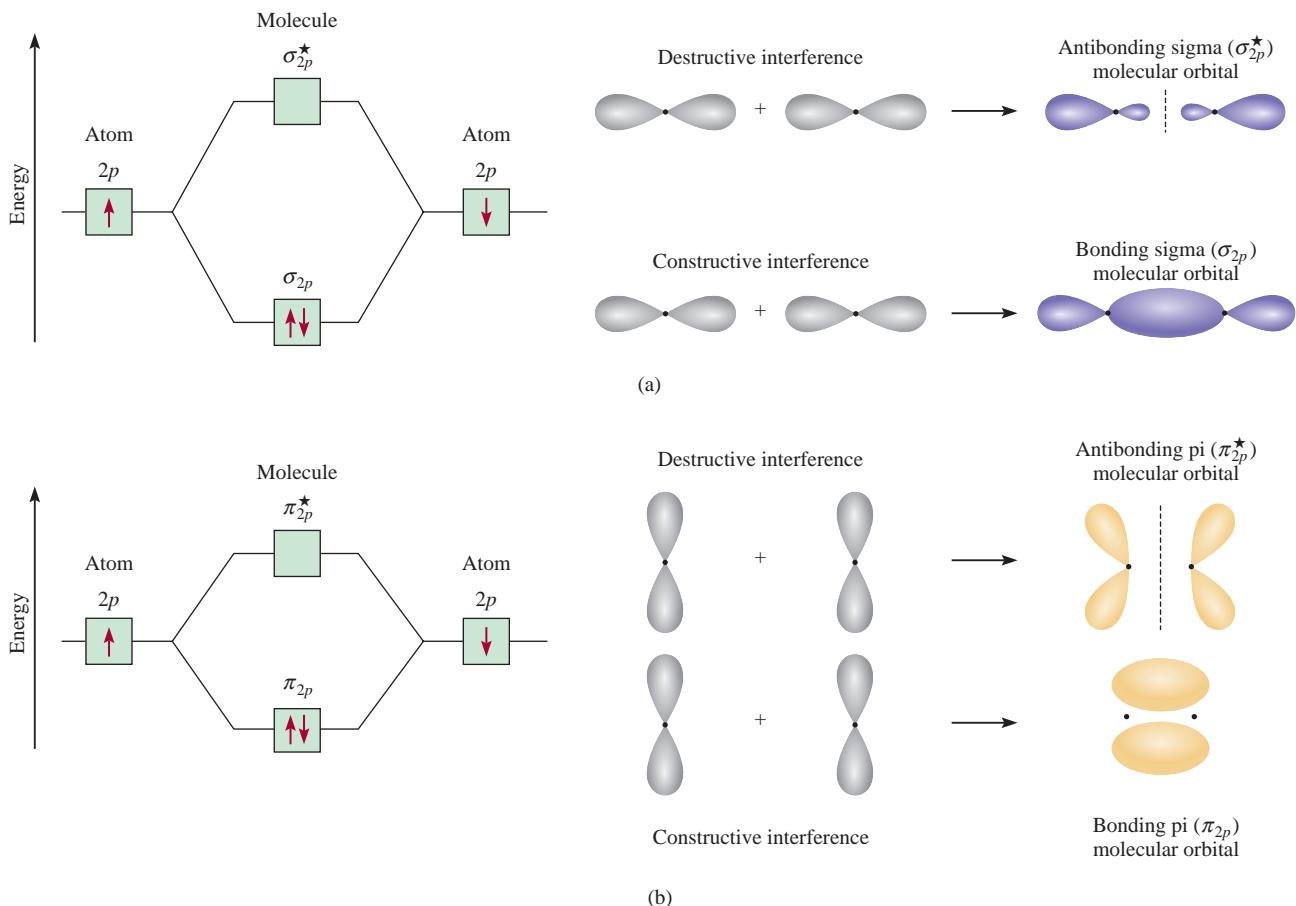
## Molecular Orbital Configurations

To understand properties of molecules, we must know how electrons are distributed among molecular orbitals. The procedure for determining the electron configuration of a molecule is analogous to the one we use to determine the electron configurations of atoms (see Section 7.8).

### Rules Governing Molecular Electron Configuration and Stability

To write the electron configuration of a molecule, we must first arrange the molecular orbitals in order of increasing energy. Then we can use the following guidelines to fill the molecular orbitals with electrons. The rules also help us understand the stabilities of the molecular orbitals.

1. The number of molecular orbitals formed is always equal to the number of atomic orbitals combined.
2. The more stable the bonding molecular orbital, the less stable the corresponding antibonding molecular orbital.
3. The filling of molecular orbitals proceeds from low to high energies. In a stable molecule, the number of electrons in bonding molecular orbitals is always greater than that in antibonding molecular orbitals because we place electrons first in the lower-energy bonding molecular orbitals.

**Figure 10.23**

Two possible interactions between two equivalent  $p$  orbitals and the corresponding molecular orbitals. (a) When the  $p$  orbitals overlap end-to-end, a sigma bonding and a sigma antibonding molecular orbital form. (b) When the  $p$  orbitals overlap side-to-side, a pi bonding and a pi antibonding molecular orbital form. Normally, a sigma bonding molecular orbital is more stable than a pi bonding molecular orbital, because side-to-side interaction leads to a smaller overlap of the  $p$  orbitals than does end-to-end interaction. We assume that the  $2p_x$  orbitals take part in the sigma molecular orbital formation. The  $2p_y$  and  $2p_z$  orbitals can interact to form only  $\pi$  molecular orbitals. The behavior shown in (b) represents the interaction between the  $2p_y$  orbitals or the  $2p_z$  orbitals.

- Like an atomic orbital, each molecular orbital can accommodate up to two electrons with opposite spins in accordance with the Pauli exclusion principle.
- When electrons are added to molecular orbitals of the same energy, the most stable arrangement is predicted by Hund's rule; that is, electrons enter these molecular orbitals with parallel spins.
- The number of electrons in the molecular orbitals is equal to the sum of all the electrons on the bonding atoms.

### Hydrogen and Helium Molecules

Later in this section we will study molecules formed by atoms of the second-period elements. Before we do, it will be instructive to predict the relative stabilities of the simple species  $H_2^+$ ,  $H_2$ ,  $He_2^+$ , and  $He_2$ , using the energy-level diagrams shown in

**Figure 10.24**

*Energy levels of the bonding and antibonding molecular orbitals in  $H_2^+$ ,  $H_2$ ,  $He_2^+$ , and  $He_2$ . In all these species, the molecular orbitals are formed by the interaction of two  $1s$  orbitals.*

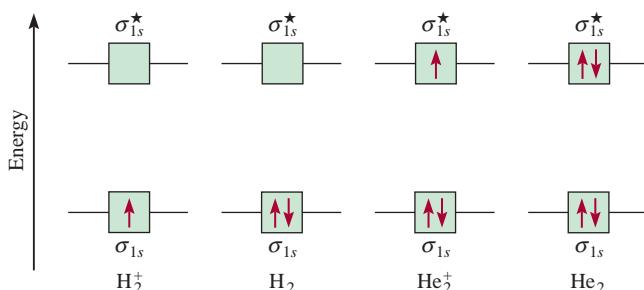


Figure 10.24. The  $\sigma_{1s}$  and  $\sigma_{1s}^*$  orbitals can accommodate a maximum of four electrons. The total number of electrons increases from one for  $H_2^+$  to four for  $He_2$ . The Pauli exclusion principle stipulates that each molecular orbital can accommodate a maximum of two electrons with opposite spins. We are concerned only with the ground-state electron configurations in these cases.

To evaluate the stabilities of these species we determine their **bond order**, defined as

$$\text{bond order} = \frac{1}{2} \left( \frac{\text{number of electrons}}{\text{in bonding MOs}} - \frac{\text{number of electrons}}{\text{in antibonding MOs}} \right) \quad (10.2)$$

The quantitative measure of the strength of a bond is bond enthalpy (Section 9.10).

The bond order indicates the strength of a bond. For example, if there are two electrons in the bonding molecular orbital and none in the antibonding molecular orbital, the bond order is one, which means that there is one covalent bond and that the molecule is stable. Note that the bond order can be a fraction, but a bond order of zero (or a negative value) means the bond has no stability and the molecule cannot exist. Bond order can be used only qualitatively for purposes of comparison. For example, a bonding sigma molecular orbital with two electrons and a bonding pi molecular orbital with two electrons would each have a bond order of one. Yet, these two bonds must differ in bond strength (and bond length) because of the differences in the extent of atomic orbital overlap.

We are ready now to make predictions about the stability of  $H_2^+$ ,  $H_2$ ,  $He_2^+$ , and  $He_2$  (see Figure 10.24). The  $H_2^+$  molecular ion has only one electron in the  $\sigma_{1s}$  orbital. Because a covalent bond consists of two electrons in a bonding molecular orbital,  $H_2^+$  has only half of one bond, or a bond order of  $\frac{1}{2}$ . Thus, we predict that the  $H_2^+$  molecule may be a stable species. The electron configuration of  $H_2^+$  is written as  $(\sigma_{1s})^1$ .

The  $H_2$  molecule has two electrons, both of which are in the  $\sigma_{1s}$  orbital. According to our scheme, two electrons equal one full bond; therefore, the  $H_2$  molecule has a bond order of one, or one full covalent bond. The electron configuration of  $H_2$  is  $(\sigma_{1s})^2$ .

As for the  $He_2^+$  molecular ion, we place the first two electrons in the  $\sigma_{1s}$  orbital and the third electron in the  $\sigma_{1s}^*$  orbital. Because the antibonding molecular orbital is destabilizing, we expect  $He_2^+$  to be less stable than  $H_2$ . Roughly speaking, the instability resulting from the electron in the  $\sigma_{1s}^*$  orbital is balanced by one of the  $\sigma_{1s}$  electrons. The bond order is  $\frac{1}{2}(2 - 1) = \frac{1}{2}$  and the overall stability of  $He_2^+$  is similar to that of the  $H_2^+$  molecule. The electron configuration of  $He_2^+$  is  $(\sigma_{1s})^2(\sigma_{1s}^*)^1$ .

In  $He_2$  there would be two electrons in the  $\sigma_{1s}$  orbital and two electrons in the  $\sigma_{1s}^*$  orbital, so the molecule would have a bond order of zero and no net stability. The electron configuration of  $He_2$  would be  $(\sigma_{1s})^2(\sigma_{1s}^*)^2$ .

The superscript in  $(\sigma_{1s})^1$  indicates that there is one electron in the sigma bonding molecular orbital.

To summarize, we can arrange our examples in order of decreasing stability:



We know that the hydrogen molecule is a stable species. Our simple molecular orbital method predicts that  $\text{H}_2^+$  and  $\text{He}_2^+$  also possess some stability, because both have bond orders of  $\frac{1}{2}$ . Indeed, their existence has been confirmed by experiment. It turns out that  $\text{H}_2^+$  is somewhat more stable than  $\text{He}_2^+$ , because there is only one electron in the hydrogen molecular ion and therefore it has no electron-electron repulsion. Furthermore,  $\text{H}_2^+$  also has less nuclear repulsion than  $\text{He}_2^+$ . Our prediction about  $\text{He}_2$  is that it would have no stability, but in 1993  $\text{He}_2$  gas was found to exist. The “molecule” is extremely unstable and has only a transient existence under specially created conditions.

### Homonuclear Diatomic Molecules of Second-Period Elements

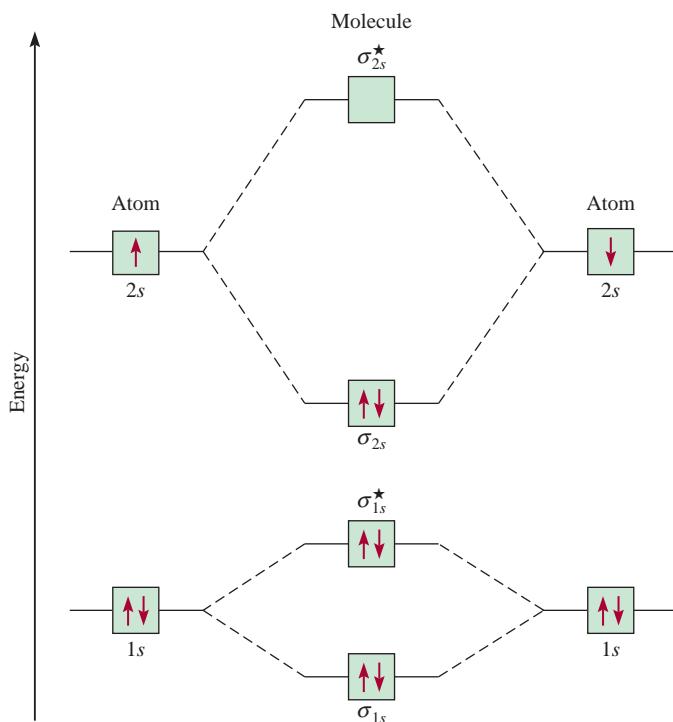
We are now ready to study the ground-state electron configuration of molecules containing second-period elements. We will consider only the simplest case, that of **homonuclear diatomic molecules**, or *diatomic molecules containing atoms of the same elements*.

Figure 10.25 shows the molecular orbital energy level diagram for the first member of the second period,  $\text{Li}_2$ . These molecular orbitals are formed by the overlap of  $1s$  and  $2s$  orbitals. We will use this diagram to build up all the diatomic molecules, as we will see shortly.

The situation is more complex when the bonding also involves  $p$  orbitals. Two  $p$  orbitals can form either a sigma bond or a pi bond. Because there are three  $p$  orbitals for each atom of a second-period element, we know that one sigma and two pi molecular orbitals will result from the constructive interaction. The sigma molecular orbital

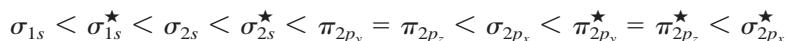


**Interactivity:**  
Energy Levels of Bonding—  
Homonuclear Diatomic  
Molecules  
ARIS, Interactives



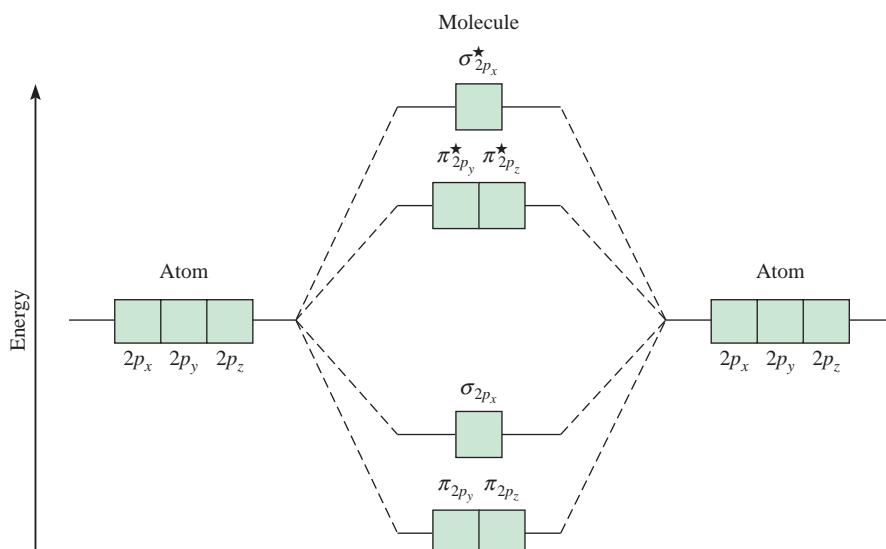
**Figure 10.25**  
Molecular orbital energy level diagram for the  $\text{Li}_2$  molecule. The six electrons in  $\text{Li}_2$  ( $\text{Li}$ 's electron configuration is  $1s^22s^1$ ) are in the  $\sigma_{1s}$ ,  $\sigma_{1s}^*$ , and  $\sigma_{2s}$  orbitals. Since there are two electrons each in  $\sigma_{1s}$  and  $\sigma_{1s}^*$  (just as in  $\text{He}_2$ ), there is no net bonding or antibonding effect. Therefore, the single covalent bond in  $\text{Li}_2$  is formed by the two electrons in the bonding molecular orbital  $\sigma_{2s}$ . Note that although the antibonding orbital ( $\sigma_{1s}^*$ ) has higher energy and is thus less stable than the bonding orbital ( $\sigma_{1s}$ ), this antibonding orbital has less energy and greater stability than the  $\sigma_{2s}$  bonding orbital.

is formed by the overlap of the  $2p_x$  orbitals along the internuclear axis, that is, the  $x$ -axis. The  $2p_y$  and  $2p_z$  orbitals are perpendicular to the  $x$ -axis, and they will overlap sideways to give two pi molecular orbitals. The molecular orbitals are called  $\sigma_{2p_x}$ ,  $\pi_{2p_y}$ , and  $\pi_{2p_z}$  orbitals, where the subscripts indicate which atomic orbitals take part in forming the molecular orbitals. As shown in Figure 10.23, overlap of the two  $p$  orbitals is normally greater in a  $\sigma$  molecular orbital than in a  $\pi$  molecular orbital, so we would expect the former to be lower in energy. However, the energies of molecular orbitals actually increase as follows:



The inversion of the  $\sigma_{2p_x}$  orbital and the  $\pi_{2p_y}$  and  $\pi_{2p_z}$  orbitals is due to the interaction between the  $2s$  orbital on one atom with the  $2p$  orbital on the other. In MO terminology, we say there is mixing between these orbitals. The condition for mixing is that the  $2s$  and  $2p$  orbitals must be close in energy. This condition is met for the lighter molecules  $B_2$ ,  $C_2$ , and  $N_2$  with the result that the  $\sigma_{2p_x}$  orbital is raised in energy relative to the  $\pi_{2p_y}$  and  $\pi_{2p_z}$  orbitals as already shown. The mixing is less pronounced for  $O_2$  and  $F_2$  so the  $\sigma_{2p_x}$  orbital lies lower in energy than the  $\pi_{2p_y}$  and  $\pi_{2p_z}$  orbitals in these molecules.

With these concepts and Figure 10.26, which shows the order of increasing energies for  $2p$  molecular orbitals, we can write the electron configurations and predict the magnetic properties and bond orders of second-period homonuclear diatomic molecules.



**Figure 10.26**

General molecular orbital energy level diagram for the second-period homonuclear diatomic molecules  $Li_2$ ,  $Be_2$ ,  $B_2$ ,  $C_2$ , and  $N_2$ . For simplicity, the  $\sigma_{1s}$  and  $\sigma_{2s}$  orbitals have been omitted. Note that in these molecules the  $\sigma_{2p_x}$  orbital is higher in energy than either the  $\pi_{2p_y}$  or the  $\pi_{2p_z}$  orbitals. This means that electrons in the  $\sigma_{2p_x}$  orbitals are less stable than those in  $\pi_{2p_y}$  and  $\pi_{2p_z}$ . For  $O_2$  and  $F_2$ , the  $\sigma_{2p_x}$  orbital is lower in energy than  $\pi_{2p_y}$  and  $\pi_{2p_z}$ .

### The Carbon Molecule ( $C_2$ )

The carbon atom has the electron configuration  $1s^2 2s^2 2p^2$ ; thus, there are 12 electrons in the  $C_2$  molecule. From the bonding scheme for  $Li_2$ , we place four additional carbon electrons in the  $\pi_{2p_y}$  and  $\pi_{2p_z}$  orbitals. Therefore,  $C_2$  has the electron configuration

$$(\sigma_{1s})^2 (\sigma_{1s}^\star)^2 (\sigma_{2s})^2 (\sigma_{2s}^\star)^2 (\pi_{2p_y})^2 (\pi_{2p_z})^2$$

Its bond order is 2, and the molecule has no unpaired electrons. Again, diamagnetic  $C_2$  molecules have been detected in the vapor state. Note that the double bonds in  $C_2$  are both pi bonds because of the four electrons in the two pi molecular orbitals. In most other molecules, a double bond is made up of a sigma bond and a pi bond.

### The Oxygen Molecule ( $O_2$ )

As we stated earlier, valence bond theory does not account for the magnetic properties of the oxygen molecule. To show the two unpaired electrons on  $O_2$ , we need to draw an alternative to the resonance structure present on p. 340:



This structure is unsatisfactory on at least two counts. First, it implies the presence of a single covalent bond, but experimental evidence strongly suggests that there is a double bond in this molecule. Second, it places seven valence electrons around each oxygen atom, a violation of the octet rule.

The ground-state electron configuration of O is  $1s^2 2s^2 2p^4$ ; thus, there are 16 electrons in  $O_2$ . Using the order of increasing energies of the molecular orbitals discussed above, we write the ground-state electron configuration of  $O_2$  as

$$(\sigma_{1s})^2 (\sigma_{1s}^\star)^2 (\sigma_{2s})^2 (\sigma_{2s}^\star)^2 (\sigma_{2p_x})^2 (\pi_{2p_y})^2 (\pi_{2p_z})^2 (\pi_{2p_y}^\star)^1 (\pi_{2p_z}^\star)^1$$

According to Hund's rule, the last two electrons enter the  $\pi_{2p_y}^\star$  and  $\pi_{2p_z}^\star$  orbitals with parallel spins. Ignoring the  $\sigma_{1s}$  and  $\sigma_{2s}$  orbitals (because their net effects on bonding are zero), we calculate the bond order of  $O_2$  using Equation (10.2):

$$\text{bond order} = \frac{1}{2}(6 - 2) = 2$$

Therefore, the  $O_2$  molecule has a bond order of 2 and oxygen is paramagnetic, a prediction that corresponds to experimental observations.

Table 10.5 summarizes the general properties of the stable diatomic molecules of the second period.

### Example 10.6

The  $N_2^+$  ion can be prepared by bombarding the  $N_2$  molecule with fast-moving electrons. Predict the following properties of  $N_2^+$ : (a) electron configuration, (b) bond order, (c) magnetic properties, and (d) bond length relative to the bond length of  $N_2$  (is it longer or shorter?).

**Strategy** From Table 10.5 we can deduce the properties of ions generated from the homonuclear molecules. How does the stability of a molecule depend on the number of electrons in bonding and antibonding molecular orbitals? From what molecular orbital is an electron removed to form the  $N_2^+$  ion from  $N_2$ ? What properties determine whether a species is diamagnetic or paramagnetic?

(Continued)

**TABLE 10.5** Properties of Homonuclear Diatomic Molecules of the Second-Period Elements\*

	Li <sub>2</sub>	B <sub>2</sub>	C <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	F <sub>2</sub>	
$\sigma_{2p_x}^{\star}$	□	□	□	□	□	□	$\sigma_{2p_x}^{\star}$
$\pi_{2p_y}^{\star}, \pi_{2p_z}^{\star}$	□□	□□	□□	□□	↑↑	↓↑↓	$\pi_{2p_y}^{\star}, \pi_{2p_z}^{\star}$
$\sigma_{2p_x}$	□	□	□	↑↓	↑↓↑↓	↑↓↑↓	$\pi_{2p_y}, \pi_{2p_z}$
$\pi_{2p_y}, \pi_{2p_z}$	□□	↑↑	↑↓↑↓	↑↓↑↓	↑↓	↑↓	$\sigma_{2p_x}$
$\sigma_{2s}^{\star}$	□	↑↓	↑↓	↑↓	↑↓	↑↓	$\sigma_{2s}^{\star}$
$\sigma_{2s}$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	$\sigma_{2s}$
Bond order	1	1	2	3	2	1	
Bond length (pm)	267	159	131	110	121	142	
Bond enthalpy (kJ/mol)	104.6	288.7	627.6	941.4	498.7	156.9	
Magnetic properties	Diamagnetic	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	

\*For simplicity the  $\sigma_{1s}$  and  $\sigma_{1s}^{\star}$  orbitals are omitted. These two orbitals hold a total of four electrons. Remember that for O<sub>2</sub> and F<sub>2</sub>,  $\sigma_{2p_x}$  is lower in energy than  $\pi_{2p_y}$  and  $\pi_{2p_z}$ .

**Solution** From Table 10.5 we can deduce the properties of ions generated from the homonuclear diatomic molecules.

(a) Because N<sub>2</sub><sup>+</sup> has one fewer electron than N<sub>2</sub>, its electron configuration is

$$(\sigma_{1s})^2 (\sigma_{1s}^{\star})^2 (\sigma_{2s})^2 (\sigma_{2s}^{\star})^2 (\pi_{2p_y})^2 (\pi_{2p_z})^2 (\sigma_{2p_x})^1$$

(b) The bond order of N<sub>2</sub><sup>+</sup> is found by using Equation (10.2):

$$\text{bond order} = \frac{1}{2}(9 - 4) = 2.5$$

(c) N<sub>2</sub><sup>+</sup> has one unpaired electron, so it is paramagnetic.

(d) Because the electrons in the bonding molecular orbitals are responsible for holding the atoms together, N<sub>2</sub><sup>+</sup> should have a weaker and, therefore, longer bond than N<sub>2</sub>. (In fact, the bond length of N<sub>2</sub><sup>+</sup> is 112 pm, compared with 110 pm for N<sub>2</sub>.)

**Check** Because an electron is removed from a bonding molecular orbital, we expect the bond order to decrease. The N<sub>2</sub><sup>+</sup> ion has an odd number of electrons (13), so it should be paramagnetic.

Similar problems: 10.55, 10.57.

**Practice Exercise** Which of the following species has a longer bond length: F<sub>2</sub>, F<sub>2</sub><sup>+</sup>, or F<sub>2</sub><sup>-</sup>?

## KEY EQUATIONS

$$\mu = Q \times r \quad (10.1) \quad \begin{array}{l} \text{Expressing dipole moment in terms of charge } (Q) \\ \text{and distance of separation } (r) \text{ between charges.} \end{array}$$

$$\text{bond order} = \frac{1}{2} \left( \frac{\text{number of electrons}}{\text{in bonding MOs}} - \frac{\text{number of electrons}}{\text{in antibonding MOs}} \right) \quad (10.2)$$

## SUMMARY OF FACTS AND CONCEPTS

- The VSEPR model for predicting molecular geometry is based on the assumption that valence-shell electron pairs repel one another and tend to stay as far apart as possible. According to the VSEPR model, molecular geometry can be predicted from the number of bonding electron pairs and lone pairs. Lone pairs repel other pairs more strongly than bonding pairs do and thus distort bond angles from those of the ideal geometry.
- The dipole moment is a measure of the charge separation in molecules containing atoms of different electronegativities. The dipole moment of a molecule is the resultant of whatever bond moments are present in a molecule. Information about molecular geometry can be obtained from dipole moment measurements.
- In valence bond theory, hybridized atomic orbitals are formed by the combination and rearrangement of orbitals of the same atom. The hybridized orbitals are all of equal energy and electron density, and the number of hybridized orbitals is equal to the number of pure atomic orbitals that combine. Valence-shell expansion can be explained by assuming hybridization of  $s$ ,  $p$ , and  $d$  orbitals.
- In  $sp$  hybridization, the two hybrid orbitals lie in a straight line; in  $sp^2$  hybridization, the three hybrid orbitals are directed toward the corners of a triangle; in  $sp^3$  hybridization, the four hybrid orbitals are directed toward the corners of a tetrahedron; in  $sp^3d$  hybridiza-
- tion, the five hybrid orbitals are directed toward the corners of a trigonal bipyramidal; in  $sp^3d^2$  hybridization, the six hybrid orbitals are directed toward the corners of an octahedron.
- In an  $sp^2$ -hybridized atom (for example, carbon), the one unhybridized  $p$  orbital can form a pi bond with another  $p$  orbital. A carbon-carbon double bond consists of a sigma bond and a pi bond. In an  $sp$ -hybridized carbon atom, the two unhybridized  $p$  orbitals can form two pi bonds with two  $p$  orbitals on another atom (or atoms). A carbon-carbon triple bond consists of one sigma bond and two pi bonds.
- Molecular orbital theory describes bonding in terms of the combination and rearrangement of atomic orbitals to form orbitals that are associated with the molecule as a whole. Bonding molecular orbitals increase electron density between the nuclei and are lower in energy than individual atomic orbitals. Antibonding molecular orbitals have a region of zero electron density between the nuclei, and an energy level higher than that of the individual atomic orbitals. Molecules are stable if the number of electrons in bonding molecular orbitals is greater than that in antibonding molecular orbitals.
- We write electron configurations for molecular orbitals as we do for atomic orbitals, referring to the Pauli exclusion principle and Hund's rule.

## KEY WORDS

Antibonding molecular orbital, p. 340

Bond order, p. 344

Bonding molecular orbital, p. 340

Dipole moment ( $\mu$ ), p. 323

Homonuclear diatomic molecule, p. 345

Hybrid orbital, p. 328

Hybridization, p. 328

Molecular orbital, p. 340

Nonpolar molecule, p. 323

Pi bond ( $\pi$  bond), p. 337

Pi molecular orbital, p. 342

Polar molecule, p. 323

Sigma bond ( $\sigma$  bond), p. 337

Sigma molecular orbital, p. 341

Valence shell, p. 313

Valence-shell electron-pair repulsion (VSEPR) model, p. 313

## QUESTIONS AND PROBLEMS

### Molecular Geometry

#### Review Questions

- How is the geometry of a molecule defined and why is the study of molecular geometry important?
- Sketch the shape of a linear triatomic molecule, a trigonal planar molecule containing four atoms, a tetrahedral molecule, a trigonal bipyramidal molecule, and

an octahedral molecule. Give the bond angles in each case.

- How many atoms are directly bonded to the central atom in a tetrahedral molecule, a trigonal bipyramidal molecule, and an octahedral molecule?
- Discuss the basic features of the VSEPR model. Explain why the magnitude of repulsion decreases in

this order: lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair.

- 10.5 In the trigonal bipyramidal arrangement, why does a lone pair occupy an equatorial position rather than an axial position?
- 10.6 The geometry of  $\text{CH}_4$  could be square planar, with the four H atoms at the corners of a square and the C atom at the center of the square. Sketch this geometry and compare its stability with that of a tetrahedral  $\text{CH}_4$  molecule.

### Problems

- 10.7 Predict the geometries of these species using the VSEPR method: (a)  $\text{PCl}_3$ , (b)  $\text{CHCl}_3$ , (c)  $\text{SiH}_4$ , (d)  $\text{TeCl}_4$ .
- 10.8 Predict the geometries of these species: (a)  $\text{AlCl}_3$ , (b)  $\text{ZnCl}_2$ , (c)  $\text{ZnCl}_4^{2-}$ .
- 10.9 Predict the geometry of these molecules and ion using the VSEPR method: (a)  $\text{HgBr}_2$ , (b)  $\text{N}_2\text{O}$  (arrangement of atoms is NNO), (c)  $\text{SCN}^-$  (arrangement of atoms is SCN).
- 10.10 Predict the geometries of these ions: (a)  $\text{NH}_4^+$ , (b)  $\text{NH}_2^-$ , (c)  $\text{CO}_3^{2-}$ , (d)  $\text{ICl}_2^-$ , (e)  $\text{ICl}_4^-$ , (f)  $\text{AlH}_4^-$ , (g)  $\text{SnCl}_5^-$  (h)  $\text{H}_3\text{O}^+$ , (i)  $\text{BeF}_4^{2-}$ .
- 10.11 Describe the geometry around each of the three central atoms in the  $\text{CH}_3\text{COOH}$  molecule.
- 10.12 Which of these species are tetrahedral?  $\text{SiCl}_4$ ,  $\text{SeF}_4$ ,  $\text{XeF}_4$ ,  $\text{Cl}_4$ ,  $\text{CdCl}_4^{2-}$ .

### Dipole Moments

#### Review Questions

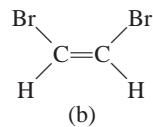
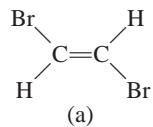
- 10.13 Define dipole moment. What are the units and symbol for dipole moment?
- 10.14 What is the relationship between the dipole moment and bond moment? How is it possible for a molecule to have bond moments and yet be nonpolar?
- 10.15 Explain why an atom cannot have a permanent dipole moment.
- 10.16 The bonds in beryllium hydride ( $\text{BeH}_2$ ) molecules are polar, and yet the dipole moment of the molecule is zero. Explain.

### Problems

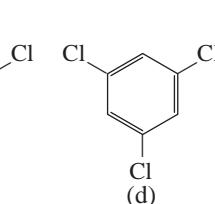
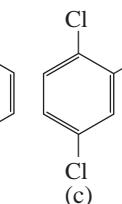
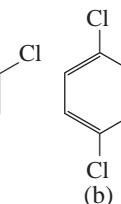
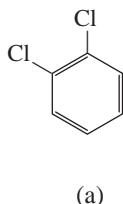
- 10.17 Referring to Table 10.3, arrange the following molecules in order of increasing dipole moment:  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Te}$ ,  $\text{H}_2\text{Se}$ .
- 10.18 The dipole moments of the hydrogen halides decrease from HF to HI (see Table 10.3). Explain this trend.
- 10.19 List these molecules in order of increasing dipole moment:  $\text{H}_2\text{O}$ ,  $\text{CBr}_4$ ,  $\text{H}_2\text{S}$ , HF,  $\text{NH}_3$ ,  $\text{CO}_2$ .

- 10.20 Does the molecule OCS have a higher or lower dipole moment than  $\text{CS}_2$ ?

- 10.21 Which of these molecules has a higher dipole moment?



- 10.22 Arrange these compounds in order of increasing dipole moment:



### Valence Bond Theory

#### Review Questions

- 10.23 What is valence bond theory? How does it differ from the Lewis concept of chemical bonding?
- 10.24 Use valence bond theory to explain the bonding in  $\text{Cl}_2$  and  $\text{HCl}$ . Show how the atomic orbitals overlap when a bond is formed.
- 10.25 Draw a potential energy curve for the bond formation in  $\text{F}_2$ .

### Hybridization

#### Review Questions

- 10.26 What is the hybridization of atomic orbitals? Why is it impossible for an isolated atom to exist in the hybridized state?
- 10.27 How does a hybrid orbital differ from a pure atomic orbital? Can two  $2p$  orbitals of an atom hybridize to give two hybridized orbitals?
- 10.28 What is the angle between these two hybrid orbitals on the same atom? (a)  $sp$  and  $sp$  hybrid orbitals, (b)  $sp^2$  and  $sp^2$  hybrid orbitals, (c)  $sp^3$  and  $sp^3$  hybrid orbitals.
- 10.29 How would you distinguish between a sigma bond and a pi bond?
- 10.30 Which of these pairs of atomic orbitals of adjacent nuclei can overlap to form a sigma bond? Which overlap to form a pi bond? Which cannot overlap (no bond)? Consider the  $x$ -axis to be the internuclear axis, that is, the line joining the nuclei of the two atoms. (a)  $1s$  and  $1s$ , (b)  $1s$  and  $2p_x$ , (c)  $2p_x$  and  $2p_y$ , (d)  $3p_y$  and  $3p_y$ , (e)  $2p_x$  and  $2p_x$ , (f)  $1s$  and  $2s$ .

### Problems

- 10.31 Describe the bonding scheme of the  $\text{AsH}_3$  molecule in terms of hybridization.
- 10.32** What is the hybridization state of Si in  $\text{SiH}_4$  and in  $\text{H}_3\text{Si}—\text{SiH}_3$ ?
- 10.33 Describe the change in hybridization (if any) of the Al atom in this reaction:

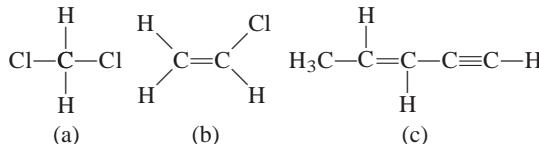


- 10.34** Consider the reaction

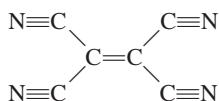


Describe the changes in hybridization (if any) of the B and N atoms as a result of this reaction.

- 10.35 What hybrid orbitals are used by nitrogen atoms in these species? (a)  $\text{NH}_3$ , (b)  $\text{H}_2\text{N}—\text{NH}_2$ , (c)  $\text{NO}_3^-$ .
- 10.36** What are the hybrid orbitals of the carbon atoms in these molecules?
- $\text{H}_3\text{C}—\text{CH}_3$
  - $\text{H}_3\text{C}—\text{CH}=\text{CH}_2$
  - $\text{CH}_3—\text{C}\equiv\text{C}—\text{CH}_2\text{OH}$
  - $\text{CH}_3\text{CH}=\text{O}$
  - $\text{CH}_3\text{COOH}$ .
- 10.37 Specify which hybrid orbitals are used by carbon atoms in these species: (a)  $\text{CO}$ , (b)  $\text{CO}_2$ , (c)  $\text{CN}^-$ .
- 10.38** What is the hybridization state of the central N atom in the azide ion,  $\text{N}_3^-$ ? (Arrangement of atoms: NNN.)
- 10.39 The allene molecule  $\text{H}_2\text{C}=\text{C}=\text{CH}_2$  is linear (the three C atoms lie on a straight line). What are the hybridization states of the carbon atoms? Draw diagrams to show the formation of sigma bonds and pi bonds in allene.
- 10.40** Describe the hybridization of phosphorus in  $\text{PF}_5$ .
- 10.41 How many sigma bonds and pi bonds are there in each of these molecules?



- 10.42** How many pi bonds and sigma bonds are there in the tetracyanoethylene molecule?



### Molecular Orbital Theory

#### Review Questions

- 10.43 What is molecular orbital theory? How does it differ from valence bond theory?

- 10.44 Define these terms: bonding molecular orbital, anti-bonding molecular orbital, pi molecular orbital, sigma molecular orbital.
- 10.45 Sketch the shapes of these molecular orbitals:  $\sigma_{1s}$ ,  $\sigma_{1s}^*$ ,  $\pi_{2p}$ , and  $\pi_{2p}^*$ . How do their energies compare?
- 10.46 Explain the significance of bond order. Can bond order be used for quantitative comparisons of the strengths of chemical bonds?

### Problems

- 10.47 Explain in molecular orbital terms the changes in H—H internuclear distance that occur as the molecular  $\text{H}_2$  is ionized first to  $\text{H}_2^+$  and then to  $\text{H}_2^{2+}$ .
- 10.48** The formation of  $\text{H}^+$  from two H atoms is an energetically favorable process. Yet statistically there is less than a 100 percent chance that any two H atoms will undergo the reaction. Apart from energy considerations, how would you account for this observation based on the electron spins in the two H atoms?
- 10.49 Draw a molecular orbital energy level diagram for each of these species:  $\text{He}_2$ ,  $\text{HHe}$ ,  $\text{He}_2^+$ . Compare their relative stabilities in terms of bond orders. (Treat  $\text{HHe}$  as a diatomic molecule with three electrons.)
- 10.50** Arrange these species in order of increasing stability:  $\text{Li}_2$ ,  $\text{Li}_2^+$ ,  $\text{Li}_2^-$ . Justify your choice with a molecular orbital energy level diagram.
- 10.51 Use molecular orbital theory to explain why the  $\text{Be}_2$  molecule does not exist.
- 10.52** Which of these species has a longer bond,  $\text{B}_2$  or  $\text{B}_2^+$ ? Explain in terms of molecular orbital theory.
- 10.53 Acetylene ( $\text{C}_2\text{H}_2$ ) has a tendency to lose two protons ( $\text{H}^+$ ) and form the carbide ion ( $\text{C}_2^{2-}$ ), which is present in a number of ionic compounds, such as  $\text{CaC}_2$  and  $\text{MgC}_2$ . Describe the bonding scheme in the  $\text{C}_2^{2-}$  ion in terms of molecular orbital theory. Compare the bond order in  $\text{C}_2^{2-}$  with that in  $\text{C}_2$ .
- 10.54** Compare the Lewis and molecular orbital treatments of the oxygen molecule.
- 10.55 Explain why the bond order of  $\text{N}_2$  is greater than that of  $\text{N}_2^+$ , but the bond order of  $\text{O}_2$  is less than that of  $\text{O}_2^+$ .
- 10.56** Compare the relative stability of these species and indicate their magnetic properties (that is, diamagnetic or paramagnetic):  $\text{O}_2$ ,  $\text{O}_2^+$ ,  $\text{O}_2^-$  (superoxide ion),  $\text{O}_2^{2-}$  (peroxide ion).
- 10.57 Use molecular orbital theory to compare the relative stabilities of  $\text{F}_2$  and  $\text{F}_2^+$ .
- 10.58** A single bond is almost always a sigma bond, and a double bond is almost always made up of a sigma bond and a pi bond. There are very few exceptions to this rule. Show that the  $\text{B}_2$  and  $\text{C}_2$  molecules are examples of the exceptions.

### Additional Problems

**10.59** Which of these species is not likely to have a tetrahedral shape? (a)  $\text{SiBr}_4$ , (b)  $\text{NF}_4^+$ , (c)  $\text{SF}_4$ , (d)  $\text{BeCl}_4^{2-}$ , (e)  $\text{BF}_4^-$ , (f)  $\text{AlCl}_4^-$ .

**10.60** Draw the Lewis structure of mercury(II) bromide. Is this molecule linear or bent? How would you establish its geometry?

**10.61** Sketch the bond moments and resultant dipole moments for these molecules:  $\text{H}_2\text{O}$ ,  $\text{PCl}_3$ ,  $\text{XeF}_4$ ,  $\text{PCl}_5$ ,  $\text{SF}_6$ .

**10.62** Although both carbon and silicon are in Group 4A, very few  $\text{Si}=\text{Si}$  bonds are known. Account for the instability of silicon-to-silicon double bonds in general. (*Hint:* Compare the atomic radii of C and Si in Figure 8.4. What effect would the larger size have on pi bond formation?)

**10.63** Predict the geometry of sulfur dichloride ( $\text{SCl}_2$ ) and the hybridization of the sulfur atom.

**10.64** Antimony pentafluoride,  $\text{SbF}_5$ , reacts with  $\text{XeF}_4$  and  $\text{XeF}_6$  to form ionic compounds,  $\text{XeF}_3^+\text{SbF}_6^-$  and  $\text{XeF}_5^+\text{SbF}_6^-$ . Describe the geometries of the cations and anion in these two compounds.

**10.65** Draw Lewis structures and give the other information requested for the following molecules: (a)  $\text{BF}_3$ . Shape: planar or nonplanar? (b)  $\text{ClO}_3^-$ . Shape: planar or nonplanar? (c)  $\text{H}_2\text{O}$ . Show the direction of the resultant dipole moment. (d)  $\text{OF}_2$ . Polar or nonpolar molecule? (e)  $\text{SeO}_2$ . Estimate the OSeO bond angle.

**10.66** Predict the bond angles for these molecules: (a)  $\text{BeCl}_2$ , (b)  $\text{BCl}_3$ , (c)  $\text{CCl}_4$ , (d)  $\text{CH}_3\text{Cl}$ , (e)  $\text{Hg}_2\text{Cl}_2$  (arrangement of atoms: ClHgHgCl), (f)  $\text{SnCl}_2$ , (g)  $\text{H}_2\text{O}_2$ , (h)  $\text{SnH}_4$ .

**10.67** Briefly compare the VSEPR and hybridization approaches to the study of molecular geometry.

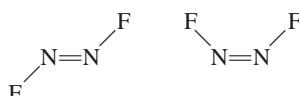
**10.68** Describe the hybridization state of arsenic in arsenic pentafluoride ( $\text{AsF}_5$ ).

**10.69** Draw Lewis structures and give the other information requested for these: (a)  $\text{SO}_3$ . Polar or nonpolar molecule? (b)  $\text{PF}_3$ . Polar or nonpolar molecule? (c)  $\text{F}_3\text{SiH}$ . Show the direction of the resultant dipole moment. (d)  $\text{SiH}_3^-$ . Planar or pyramidal shape? (e)  $\text{Br}_2\text{CH}_2$ . Polar or nonpolar molecule?

**10.70** Which of these molecules are linear?  $\text{ICl}_2^-$ ,  $\text{IF}_2^+$ ,  $\text{OF}_2$ ,  $\text{SnI}_2$ ,  $\text{CdBr}_2$ .

**10.71** Draw the Lewis structure for the  $\text{BeCl}_4^{2-}$  ion. Predict its geometry and describe the hybridization state of the Be atom.

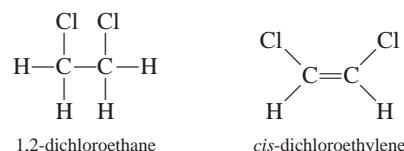
**10.72** The  $\text{N}_2\text{F}_2$  molecule can exist in either of these two forms:



- (a) What is the hybridization of N in the molecule?  
 (b) Which structure has a dipole moment?

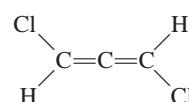
**10.73** Cyclopropane ( $\text{C}_3\text{H}_6$ ) has the shape of a triangle in which a C atom is bonded to two H atoms and two other C atoms at each corner. Cubane ( $\text{C}_8\text{H}_8$ ) has the shape of a cube in which a C atom is bonded to one H atom and three other C atoms at each corner.  
 (a) Draw Lewis structures of these molecules.  
 (b) Compare the CCC angles in these molecules with those predicted for an  $sp^3$ -hybridized C atom.  
 (c) Would you expect these molecules to be easy to make?

**10.74** The compound 1,2-dichloroethane ( $\text{C}_2\text{H}_4\text{Cl}_2$ ) is nonpolar, while *cis*-dichloroethylene ( $\text{C}_2\text{H}_2\text{Cl}_2$ ) has a dipole moment:



The reason for the difference is that groups connected by a single bond can rotate with respect to each other, but no rotation occurs when a double bond connects the groups. On the basis of bonding considerations, explain why rotation occurs in 1,2-dichloroethane but not in *cis*-dichloroethylene.

**10.75** Does the following molecule have a dipole moment?

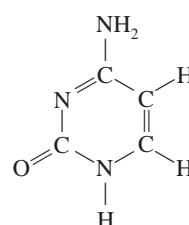


(*Hint:* See the answer to Problem 10.39.)

**10.76** The compounds carbon tetrachloride ( $\text{CCl}_4$ ) and silicon tetrachloride ( $\text{SiCl}_4$ ) are similar both in geometry and hybridization. However,  $\text{CCl}_4$  does not react with water but  $\text{SiCl}_4$  does. Explain the difference in their chemical reactivities. (*Hint:* The first step of the reaction is believed to be the addition of a water molecule to the Si atom in  $\text{SiCl}_4$ .)

**10.77** Write the ground-state electron configuration for  $\text{B}_2$ . Is the molecule diamagnetic or paramagnetic?

**10.78** What are the hybridization states of the C and N atoms in this molecule?



- 10.79 Use molecular orbital theory to explain the difference between the bond enthalpies of  $F_2$  and  $F_2^-$  (see Problem 9.105).

- 10.80** The ionic character of the bond in a diatomic molecule can be estimated by the formula

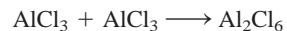
$$\frac{\mu}{ed} \times 100\%$$

where  $\mu$  is the experimentally measured dipole moment (in C m),  $e$  is the electronic charge ( $1.6022 \times 10^{-19}$  C), and  $d$  is the bond length in meters. (The quantity  $ed$  is the hypothetical dipole moment for the case in which the transfer of an electron from the less electronegative to the more electronegative atom is complete.) Given that the dipole moment and bond length of HF are 1.92 D and 91.7 pm, respectively, calculate the percent ionic character of the molecule.

- 10.81 The geometries discussed in this chapter all lend themselves to fairly straightforward elucidation of bond angles. The exception is the tetrahedron, because its bond angles are hard to visualize. Consider

the  $CCl_4$  molecule, which has a tetrahedral geometry and is nonpolar. By equating the bond moment of a particular C—Cl bond to the resultant bond moments of the other three C—Cl bonds in opposite directions, show that the bond angles are all equal to  $109.5^\circ$ .

- 10.82** Aluminum trichloride ( $AlCl_3$ ) is an electron-deficient molecule. It has a tendency to form a dimer (a molecule made of two  $AlCl_3$  units):

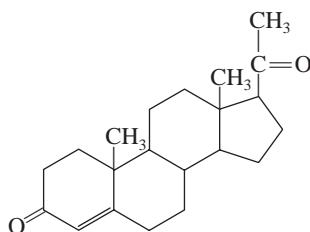


(a) Draw a Lewis structure for the dimer. (b) Describe the hybridization state of Al in  $AlCl_3$  and  $Al_2Cl_6$ . (c) Sketch the geometry of the dimer. (d) Do these molecules possess a dipole moment?

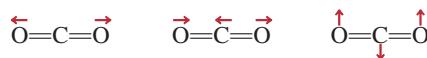
- 10.83 Assume that the third-period element phosphorus forms a diatomic molecule,  $P_2$ , in an analogous way as nitrogen does to form  $N_2$ . (a) Write the electronic configuration for  $P_2$ . Use  $[Ne_2]$  to represent the electron configuration for the first two periods. (b) Calculate its bond order. (c) What are its magnetic properties (diamagnetic or paramagnetic)?

## SPECIAL PROBLEMS

- 10.84** Progesterone is a hormone responsible for female sex characteristics. In the usual shorthand structure, each point where lines meet represents a C atom, and most H atoms are not shown. Draw the complete structure of the molecule, showing all C and H atoms. Indicate which C atoms are  $sp^2$ - and  $sp^3$ -hybridized.



- 10.85 Greenhouse gases absorb (and trap) outgoing infrared radiation (heat) from Earth and contribute to global warming. The molecule of a greenhouse gas either possesses a permanent dipole moment or has a changing dipole moment during its vibrational motions. Consider three of the vibrational modes of carbon dioxide



where the arrows indicate the movement of the atoms. (During a complete cycle of vibration, the atoms move toward one extreme position and then reverse their direction to the other extreme position.) Which of the preceding vibrations are responsible for  $CO_2$  behaving as a greenhouse gas? Which of the following molecules can act as a greenhouse gas:  $N_2$ ,  $O_2$ ,  $CO$ ,  $NO_2$ , and  $N_2O$ ?

- 10.86** The molecules *cis*-dichloroethylene and *trans*-dichloroethylene shown on p. 324 can be interconverted by heating or irradiation. (a) Starting with *cis*-dichloroethylene, show that rotating the  $C=C$  bond by  $180^\circ$  will break only the pi bond but will leave the sigma bond intact. Explain the formation of *trans*-dichloroethylene from this process. (Treat the rotation as two, stepwise  $90^\circ$  rotations.) (b) Account for the difference in the bond enthalpies for the pi bond (about 270 kJ/mol) and the sigma bond (about 350 kJ/mol). (c) Calculate the longest wavelength of light needed to bring about this conversion.

- 10.87 For each pair listed here, state which one has a higher first ionization energy and explain your choice: (a) H or  $H_2$ , (b) N or  $N_2$ , (c) O or  $O_2$ , (d) F or  $F_2$ .

- 10.88** The molecule benzyne ( $C_6H_4$ ) is a very reactive species. It resembles benzene in that it has a six-membered ring of carbon atoms. Draw a Lewis

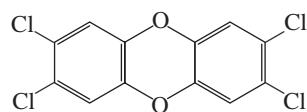
structure of the molecule and account for the molecule's high reactivity.

- 10.89** Consider a  $\text{N}_2$  molecule in its first excited electronic state; that is, when an electron in the highest occupied molecular orbital is promoted to the lowest empty molecular orbital. (a) Identify the molecular orbitals involved and sketch a diagram to show the transition. (b) Compare the bond order and bond length of  $\text{N}_2^*$  with  $\text{N}_2$ , where the asterisk denotes the excited molecule. (c) Is  $\text{N}_2^*$  diamagnetic or paramagnetic? (d) When  $\text{N}_2^*$  loses its excess energy and converts to the ground state  $\text{N}_2$ , it emits a photon of wavelength 470 nm, which makes up part of the auroras lights. Calculate the energy difference between these levels.
- 10.90** As mentioned in the chapter, the Lewis structure for  $\text{O}_2$  is



Use the molecular orbital theory to show that the structure actually corresponds to an excited state of the oxygen molecule.

- 10.91** Draw the Lewis structure of ketene ( $\text{C}_2\text{H}_2\text{O}$ ) and describe the hybridization states of the C atoms. The molecule does not contain O—H bonds. On separate diagrams, sketch the formation of sigma and pi bonds.
- 10.92** TCDD, or 2,3,7,8-tetrachlorodibenzo-p-dioxin, is a highly toxic compound



It gained considerable notoriety in 2004 when it was implicated in the murder plot of a Ukrainian politician. (a) Describe its geometry and state whether the molecule has a dipole moment. (b) How many pi bonds and sigma bonds are there in the molecule?

## ANSWERS TO PRACTICE EXERCISES

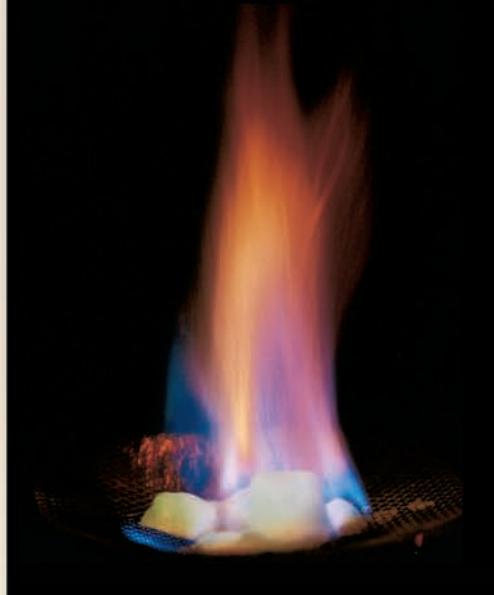
**10.1** (a) Tetrahedral, (b) linear, (c) trigonal planar.

**10.2** No. **10.3** (a)  $sp^3$ , (b)  $sp^2$ . **10.4**  $sp^3d^2$ .

**10.5** The C atom is  $sp$ -hybridized. It forms a sigma bond with the H atom and another sigma bond with the N atom.

The two unhybridized  $p$  orbitals on the C atom are used to form two pi bonds with the N atom. The lone pair on the N atom is placed in the  $sp$  orbital. **10.6**  $\text{F}_2^-$ .

Methane hydrate (methane trapped in a cage of frozen water) burning in air.



## Introduction to Organic Chemistry

### CHAPTER OUTLINE

- 11.1 Classes of Organic Compounds 356
- 11.2 Aliphatic Hydrocarbons 356
  - Alkanes • Cycloalkanes • Alkenes • Alkynes
- 11.3 Aromatic Hydrocarbons 370
  - Nomenclature of Aromatic Compounds • Properties and Reactions of Aromatic Compounds
- 11.4 Chemistry of the Functional Groups 374
  - Alcohols • Ethers • Aldehydes and Ketones • Carboxylic Acids • Esters • Amines • Summary of Functional Groups
- 11.5 Chirality—The Handedness of Molecules 381

### ESSENTIAL CONCEPTS

**Organic Compounds** Organic compounds contain primarily carbon and hydrogen atoms, plus nitrogen, oxygen, sulfur, and atoms of other elements. The parent compounds of all organic compounds are the hydrocarbons—the alkanes (containing only single bonds), the alkenes (containing carbon–carbon double bonds), the alkynes (containing carbon–carbon triple bonds), and the aromatic hydrocarbons (containing the benzene ring).

**Functional Groups** The reactivity of organic compounds can be reliably predicted by the presence of functional groups, which are groups of atoms that are largely responsible for the chemical behavior of the compounds.

**Chirality** Certain organic compounds can exist as nonsuperimposable mirror-image twins. These compounds are said to be chiral. The pure enantiomer of a compound can rotate plane-polarized light. Enantiomers have identical physical properties but exhibit different chemical properties toward another chiral substance.



### Activity Summary

- 1. Interactivity: Aliphatic Hydrocarbons (11.2)
- 2. Interactivity: Cyclohexane—Boat and Chair Formations (11.2)
- 3. Animations: Chirality (11.5)

Common elements in organic compounds.

## 11.1 Classes of Organic Compounds

Carbon can form more compounds than most other elements because carbon atoms are able not only to form single, double, and triple carbon-carbon bonds, but also to link up with each other in chains and ring structures. *The branch of chemistry that deals with carbon compounds is organic chemistry.*

Classes of organic compounds can be distinguished according to functional groups they contain. A ***functional group*** is a group of atoms that is largely responsible for the chemical behavior of the parent molecule. Different molecules containing the same kind of functional group or groups undergo similar reactions. Thus, by learning the characteristic properties of a few functional groups, we can study and understand the properties of many organic compounds. In the second half of this chapter we will discuss the functional groups known as alcohols, ethers, aldehydes and ketones, carboxylic acids, and amines.

All organic compounds are derived from a group of compounds known as **hydrocarbons** because they are *made up of only hydrogen and carbon*. On the basis of structure, hydrocarbons are divided into two main classes—aliphatic and aromatic. *Aliphatic hydrocarbons do not contain the benzene group, or the benzene ring*, whereas *aromatic hydrocarbons contain one or more benzene rings*.

## 11.2 Aliphatic Hydrocarbons

Aliphatic hydrocarbons are divided into alkanes, alkenes, and alkynes, discussed in this section (Figure 11.1).

## Alkanes



**Interactivity:**  
Aliphatic Hydrocarbons  
**ARIS Interactives**

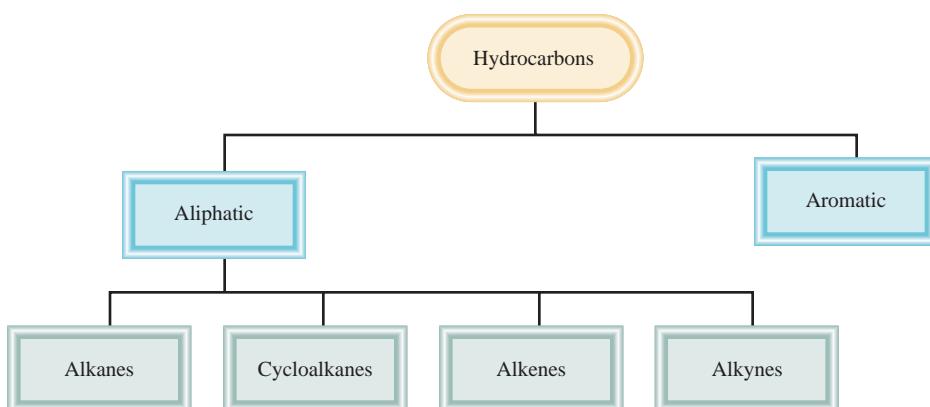
**For a given number of carbon atoms, the saturated hydrocarbon contains the largest number of hydrogen atoms.**

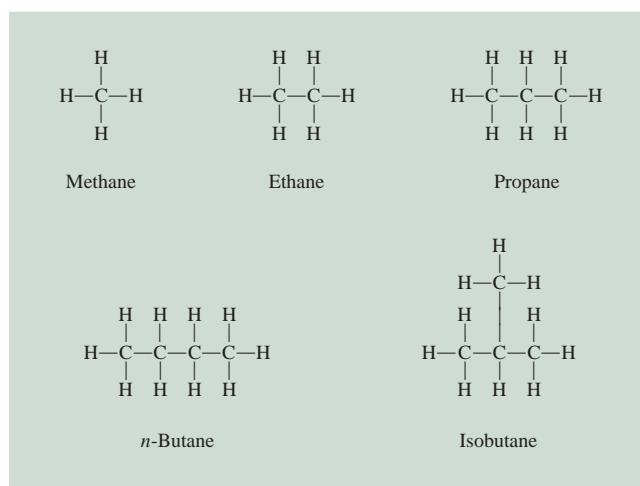
**Alkanes** are hydrocarbons that have the general formula  $C_nH_{2n+2}$ , where  $n = 1, 2, \dots$ . The essential characteristic of alkanes is that *only single covalent bonds are present*. The alkanes are known as **saturated hydrocarbons** because they *contain the maximum number of hydrogen atoms that can bond with the number of carbon atoms present*.

The simplest alkane (that is, with  $n = 1$ ) is methane  $\text{CH}_4$ , which is a natural product of the anaerobic bacterial decomposition of vegetable matter under water. Because it was first collected in marshes, methane became known as "marsh gas." A

## **Figure 11.1**

### *Classification of hydrocarbons*



**Figure 11.2**

Structures of the first four alkanes. Note that butane can exist in two structurally different forms, called structural isomers.

rather improbable but proven source of methane is termites. When these voracious insects consume wood, the microorganisms that inhabit their digestive system break down cellulose (the major component of wood) into methane, carbon dioxide, and other compounds. An estimated 170 million tons of methane are produced annually by termites! It is also produced in some sewage treatment processes. Commercially, methane is obtained from natural gas.

Figure 11.2 shows the structures of the first four alkanes ( $n = 1$  to  $n = 4$ ). Natural gas is a mixture of methane, ethane, and a small amount of propane. We discussed the bonding scheme of methane in Chapter 10. The carbon atoms in all the alkanes can be assumed to be  $sp^3$ -hybridized. The structures of ethane and propane are straightforward, for there is only one way to join the carbon atoms in these molecules. Butane, however, has two possible bonding schemes resulting in different compounds called *n*-butane (*n* stands for normal) and isobutane. *n*-Butane is a straight-chain alkane because the carbon atoms are joined in a continuous chain. In a branched-chain alkane like isobutane, one or more carbon atoms are bonded to a nonterminal carbon atom. *Isomers that differ in the order in which atoms are connected* are called **structural isomers**.

In the alkane series, as the number of carbon atoms increases, the number of structural isomers increases rapidly. For example,  $C_4H_{10}$  has two isomers;  $C_{10}H_{22}$  has 75 isomers; and  $C_{30}H_{62}$  has over 400 million possible isomers! Obviously, most of these isomers do not exist in nature nor have they been synthesized. Nevertheless, the numbers help to explain why carbon is found in so many more compounds than any other element.



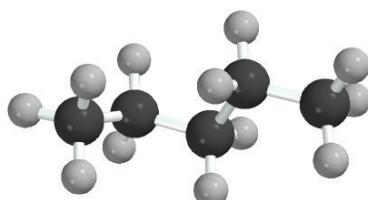
Termites are a natural source of methane.

### Example 11.1

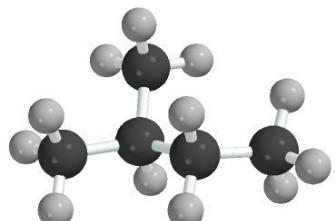
How many structural isomers can be identified for pentane,  $C_5H_{12}$ ?

**Strategy** For small hydrocarbon molecules (eight or fewer C atoms), it is relatively easy to determine the number of structural isomers by trial and error.

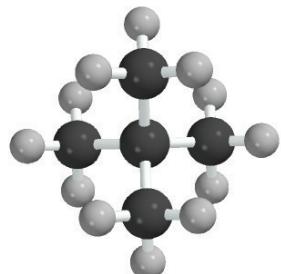
(Continued)



n-pentane



2-methylbutane



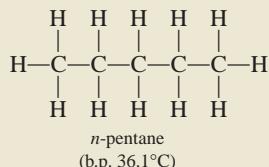
2,2-dimethylpropane

**Similar problems:** 11.11, 11.12.

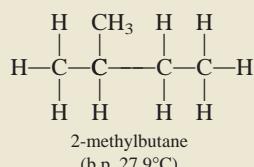


Crude oil is the source of many hydrocarbons.

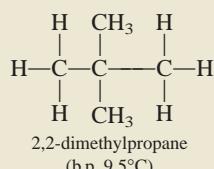
**Solution** The first step is to write the straight-chain structure:



The second structure, by necessity, must be a branched chain:



Yet another branched-chain structure is possible:



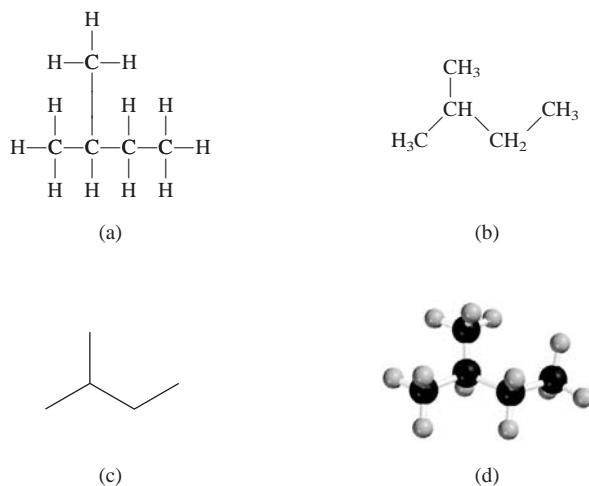
We can draw no other structure for an alkane having the molecular formula C<sub>5</sub>H<sub>12</sub>. Thus, pentane has three structural isomers, in which the numbers of carbon and hydrogen atoms remain unchanged despite the differences in structure.

**Practice Exercise** How many structural isomers are there in the alkane C<sub>6</sub>H<sub>14</sub>?

Table 11.1 shows the melting and boiling points of the straight-chain isomers of the first 10 alkanes. The first four are gases at room temperature; and pentane through decane are liquids. As molecular size increases, so does the boiling point.

**TABLE 11.1** The First 10 Straight-Chain Alkanes

Name of Hydrocarbon	Molecular Formula	Number of Carbon Atoms	Melting Point (°C)	Boiling Point (°C)
Methane	CH <sub>4</sub>	1	-182.5	-161.6
Ethane	CH <sub>3</sub> -CH <sub>3</sub>	2	-183.3	-88.6
Propane	CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>3</sub>	3	-189.7	-42.1
Butane	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>2</sub> -CH <sub>3</sub>	4	-138.3	-0.5
Pentane	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>3</sub> -CH <sub>3</sub>	5	-129.8	36.1
Hexane	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>4</sub> -CH <sub>3</sub>	6	-95.3	68.7
Heptane	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>5</sub> -CH <sub>3</sub>	7	-90.6	98.4
Octane	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>6</sub> -CH <sub>3</sub>	8	-56.8	125.7
Nonane	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>7</sub> -CH <sub>3</sub>	9	-53.5	150.8
Decane	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>8</sub> -CH <sub>3</sub>	10	-29.7	174.0



**Figure 11.3**  
*Different representations of 2-methylbutane. (a) Structural formula. (b) Abbreviated formula. (c) Skeletal formula. (d) Molecular model.*

## *Drawing Chemical Structures*

Before proceeding further, it is useful to learn different ways of drawing the structure of organic compounds. Consider the alkane 2-methylbutane ( $C_5H_{12}$ ). To see how atoms are connected in this molecule, we need to first write a more detailed molecular formula,  $CH_3CH(CH_3)CH_2CH_3$ , and then draw its structural formula, shown in Figure 11.3(a). While informative, this structure is time-consuming to draw. Therefore, chemists have devised ways to simplify the representation. Figure 11.3(b) is an abbreviated version and the structure shown in Figure 11.3(c) is called the *skeletal structure* in which all the C and H letters are omitted. A carbon atom is assumed to be at each intersection of two lines (bonds) and at the end of each line. Because every C atom forms four bonds, we can always deduce the number of H atoms bonded to any C atom. One of the two end  $CH_3$  groups is represented by a vertical line. What is lacking in these structures, however, is the three-dimensionality of the molecule, which is shown by the molecular model in Figure 11.3(d). Depending on the purpose of discussion, any of these representations can be used to describe the properties of the molecule.

**Shortly we will discuss the nomenclature of alkanes.**

**Skeletal structure is the simplest structure. Atoms other than C and H must be shown explicitly in a skeletal structure.**

## *Conformation of Ethane*

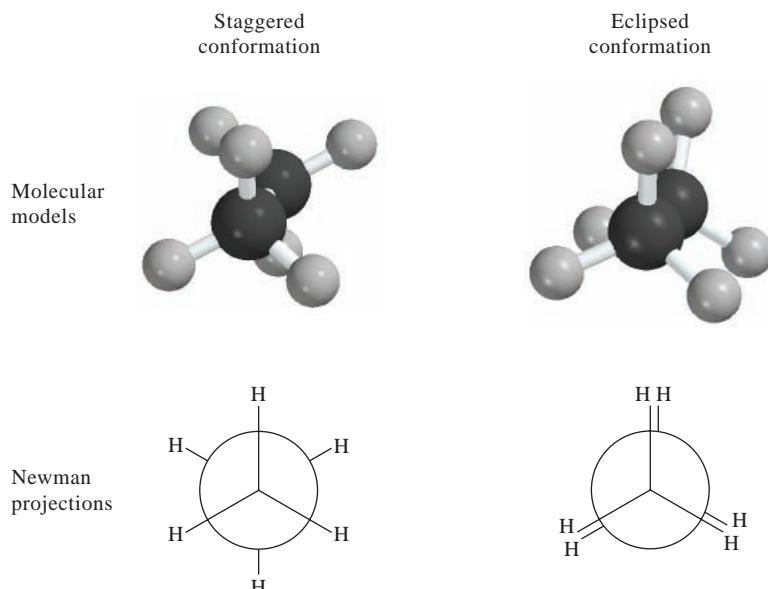
Molecular geometry gives the spatial arrangement of atoms in a molecule. However, atoms are not held rigidly in position because of internal molecular motions. For this reason, even a simple molecule like ethane may be structurally more complicated than we think.

The two C atoms in ethane are  $sp^3$ -hybridized and they are joined by a sigma bond (see Section 10.5). Sigma bonds have cylindrical symmetry, that is, the overlap of the  $sp^3$  orbitals is the same regardless of the rotation of the C—C bond. Yet this bond rotation is not totally free because of the interactions between the H atoms on different C atoms. Figure 11.4 shows the two extreme *conformations* of ethane. **Conformations** are *different spatial arrangements of a molecule that are generated by rotation about single bonds*. In the staggered conformation, the three H atoms on one C atom are pointing away from the three H atoms on the other C atom, whereas in the eclipsed conformation the two groups of H atoms are aligned parallel to one another.

A simpler and effective way of viewing these two conformations is by using the Newman projection, also shown in Figure 11.4. Look at the C—C bond end-on. The two C atoms are represented by a circle. The C—H bonds attached to the front

**Figure 11.4**

Molecular models and Newman projections of the staggered and eclipsed conformations of ethane. The dihedral angle in the staggered form is  $60^\circ$  and that in the eclipsed form is  $0^\circ$ . The C—C bond is rotated slightly in the Newman projection of the eclipsed form in order to show the H atoms attached to the back C atom. The proximity of the H atoms on the two C atoms in the eclipsed form results in a greater repulsion, and hence its instability relative to the staggered form.

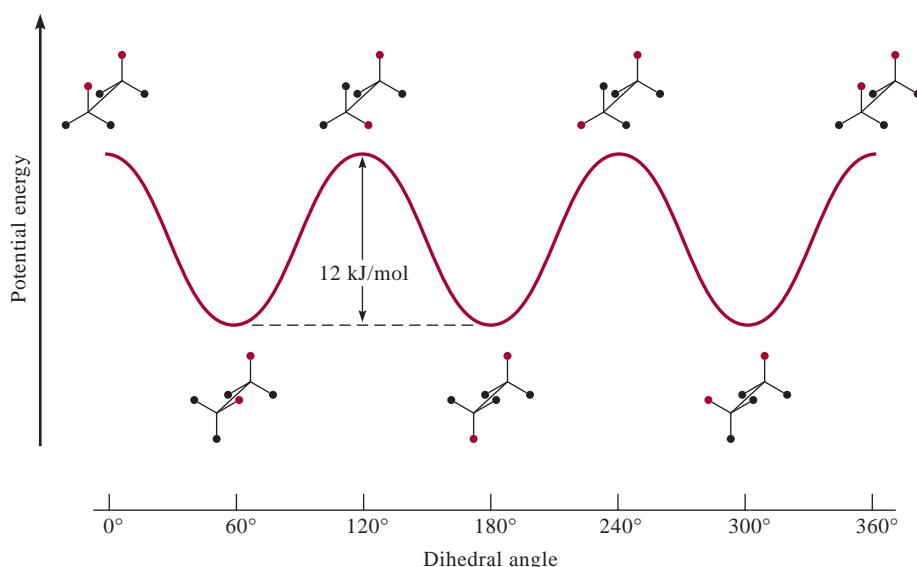


C atom are the lines going to the center of the circle, and the C—H bonds attached to the rear C atom appear as lines going to the edge of the circle. The eclipsed form of ethane is less stable than the staggered form. Figure 11.5 shows the variation in the potential energy of ethane as a function of rotation. The rotation of one  $\text{CH}_3$  group relative to the other is described in terms of the angle between the C—H bonds on front and back carbons, called the *dihedral angle*. The dihedral angle for the first eclipsed conformation is zero. A clockwise rotation of  $60^\circ$  about the C—C bond generates a staggered conformation, which is converted to another eclipsed conformation by a similar rotation and so on.

Conformational analysis of molecules is of great importance in understanding the details of reactions ranging from simple hydrocarbons to proteins and DNAs.

**Figure 11.5**

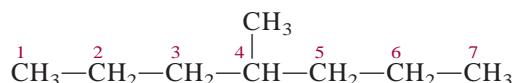
Potential energy diagram for the internal rotation in ethane. Here the dihedral angle is defined by the angle between the two C—H bonds (with the red spheres representing the H atoms). Dihedral angles of  $0^\circ$ ,  $120^\circ$ ,  $240^\circ$ , and  $360^\circ$  represent the eclipsed conformation, while those of  $60^\circ$ ,  $180^\circ$ , and  $300^\circ$  represent the staggered conformation. Thus, a rotation of  $60^\circ$  changes the eclipsed conformation to the staggered one and vice versa. The staggered conformation is more stable than the eclipsed conformation by 12 kJ/mol. However, these two forms interconvert rapidly and cannot be separated from each other.



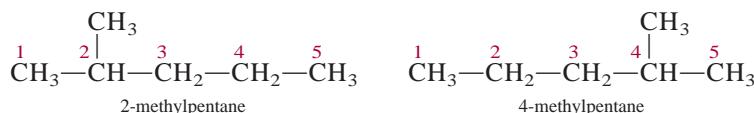
### Alkane Nomenclature

The nomenclature of alkanes and all other organic compounds is based on the recommendations of the International Union of Pure and Applied Chemistry (IUPAC). The first four alkanes (methane, ethane, propane, and butane) have nonsystematic names. As Table 11.1 shows, the number of carbon atoms is reflected in the Greek prefixes for the alkanes containing 5 to 10 carbons. We now apply the IUPAC rules to the following examples:

1. The parent name of the hydrocarbon is that given to the longest continuous chain of carbon atoms in the molecule. Thus, the parent name of the following compound is heptane because there are seven carbon atoms in the longest chain

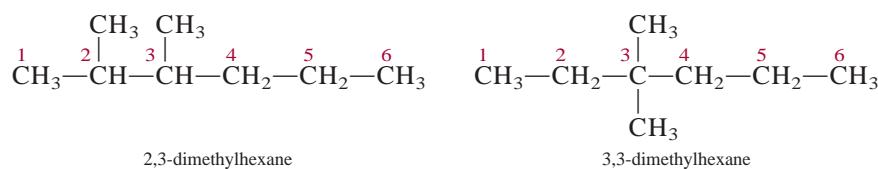


2. An alkane less one hydrogen atom is an *alkyl* group. For example, when a hydrogen atom is removed from methane, we are left with the  $\text{CH}_3$  fragment, which is called a *methyl* group. Similarly, removing a hydrogen atom from the ethane molecule gives an *ethyl* group, or  $\text{C}_2\text{H}_5$ . Table 11.2 lists the names of several common alkyl groups. Any chain branching off the longest chain is named as an alkyl group.
3. When one or more hydrogen atoms are replaced by other groups, the name of the compound must indicate the locations of carbon atoms where replacements are made. The procedure is to number each carbon atom on the longest chain in the direction that gives the smaller numbers for the locations of all branches. Consider the two different systems for the *same* compound shown below:

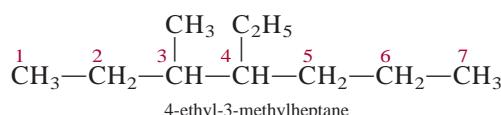


The compound on the left is numbered correctly because the methyl group is located at carbon 2 of the pentane chain; in the compound on the right, the methyl group is located at carbon 4. Thus, the name of the compound is 2-methylpentane, and not 4-methylpentane. Note that the branch name and the parent name are written as a single word, and a hyphen follows the number.

4. When there is more than one alkyl branch of the same kind present, we use a prefix such as *di-*, *tri-*, or *tetra-* with the name of the alkyl group. Consider the following examples:



When there are two or more different alkyl groups, the names of the groups are listed alphabetically. For example,



**TABLE 11.2**

### Common Alkyl Groups

Name	Formula
Methyl	$-\text{CH}_3$
Ethyl	$-\text{CH}_2-\text{CH}_3$
n-Propyl	$-(\text{CH}_2)_2-\text{CH}_3$
n-Butyl	$-(\text{CH}_2)_3-\text{CH}_3$
Isopropyl	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{C}-\text{H} \\   \\ \text{CH}_3 \end{array}$
<i>t</i> -Butyl*	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{C}-\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$

\*The letter *t* stands for tertiary.

**TABLE 11.3****Names of Common Substituent Groups**

Functional Group	Name
$-\text{NH}_2$	Amino
$-\text{F}$	Fluoro
$-\text{Cl}$	Chloro
$-\text{Br}$	Bromo
$-\text{I}$	Iodo
$-\text{NO}_2$	Nitro
$-\text{CH}=\text{CH}_2$	Vinyl

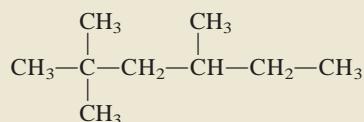
5. Of course, alkanes can have many different types of substituents. Table 11.3 lists the names of some substituents, including bromo and nitro. Thus, the compound



is called 3-bromo-2-nitrohexane. Note that the substituent groups are listed alphabetically in the name, and the chain is numbered in the direction that gives the lowest number to the first substituted carbon atom.

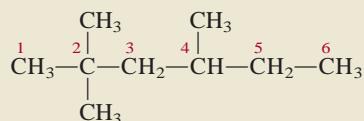
**Example 11.2**

Give the IUPAC name of the following compound:



**Strategy** We follow the IUPAC rules and use the information in Table 11.2 to name the compound. How many C atoms are there in the longest chain?

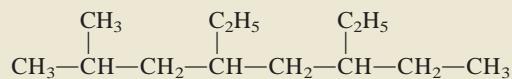
**Solution** The longest chain has six C atoms so the parent compound is called hexane. Note that there are two methyl groups attached to carbon number 2 and one methyl group attached to carbon number 4.



**Similar problems:** 11.28(a), (b), (c).

Therefore, we call the compound 2,2,4-trimethylhexane.

**Practice Exercise** Give the IUPAC name of the following compound:



Example 11.3 shows that prefixes such as di-, tri-, and tetra- are used as needed, but are ignored when alphabetizing.

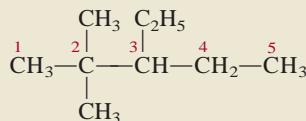
**Example 11.3**

Write the structural formula of 3-ethyl-2,2-dimethylpentane.

**Strategy** We follow the preceding procedure and the information in Table 11.2 to write the structural formula of the compound. How many C atoms are there in the longest chain?

(Continued)

**Solution** The parent compound is pentane, so the longest chain has five C atoms. There are two methyl groups attached to carbon number 2 and one ethyl group attached to carbon number 3. Therefore, the structure of the compound is

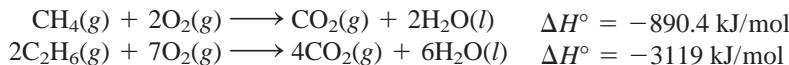


Similar problems: 11.27(a), (c), (e).

**Practice Exercise** Write the structural formula of 5-ethyl-2,6-dimethyloctane.

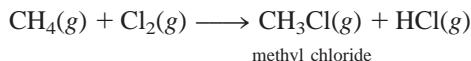
### Reactions of Alkanes

Alkanes are generally not considered to be very reactive substances. However, under suitable conditions they do react. For example, natural gas, gasoline, and fuel oil are alkanes that undergo highly exothermic combustion reactions:

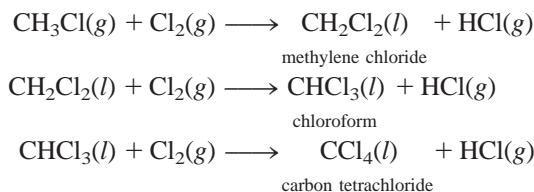


These, and similar combustion reactions, have long been utilized in industrial processes and in domestic heating and cooking.

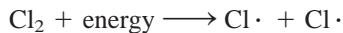
*Halogenation* of alkanes—that is, the replacement of one or more hydrogen atoms by halogen atoms—is another type of reaction that alkanes undergo. When a mixture of methane and chlorine is heated above 100°C or irradiated with light of a suitable wavelength, methyl chloride is produced:



If an excess of chlorine gas is present, the reaction can proceed further:

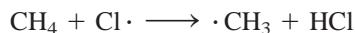


A great deal of experimental evidence suggests that the initial step of the first halogenation reaction occurs as follows:

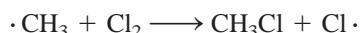


Thus, the covalent bond in  $\text{Cl}_2$  breaks and two chlorine atoms form. We know it is the Cl—Cl bond that breaks when the mixture is heated or irradiated because the bond enthalpy of  $\text{Cl}_2$  is 242.7 kJ/mol, whereas about 414 kJ/mol are needed to break C—H bonds in  $\text{CH}_4$ .

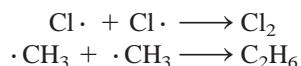
A chlorine atom is a **radical**, which *contains an unpaired electron* (shown by a single dot). Chlorine atoms are highly reactive and attack methane molecules according to the equation



This reaction produces hydrogen chloride and the methyl radical  $\cdot\text{CH}_3$ . The methyl radical is another reactive species; it combines with molecular chlorine to give methyl chloride and a chlorine atom:



The production of methylene chloride from methyl chloride and any further reactions can be explained in the same way. The actual mechanism is more complex than the scheme we have shown because “side reactions” that do not lead to the desired products often take place, such as



**The systematic names of methyl chloride, methylene chloride, and chloroform are chloromethane, dichloromethane, and trichloromethane, respectively.**

Alkanes in which one or more hydrogen atoms have been replaced by a halogen atom are called *alkyl halides*. Among the large number of alkyl halides, the best known are chloroform ( $\text{CHCl}_3$ ), carbon tetrachloride ( $\text{CCl}_4$ ), methylene chloride ( $\text{CH}_2\text{Cl}_2$ ), and the chlorofluorohydrocarbons.

Chloroform is a volatile, sweet-tasting liquid that was used for many years as anesthetic. However, because of its toxicity (it can severely damage the liver, kidneys, and heart) it has been replaced by other compounds. Carbon tetrachloride, also a toxic substance, serves as a cleaning liquid, for it removes grease stains from clothing. Methylene chloride is used as a solvent to decaffeinate coffee and as a paint remover.



**Interactivity:**  
Cyclohexane—Boat and Chair  
Formations  
ARIS, Interactives

In addition to C, atoms such as N, O, and S may also occupy the ring positions in these compounds.<sup>3</sup>

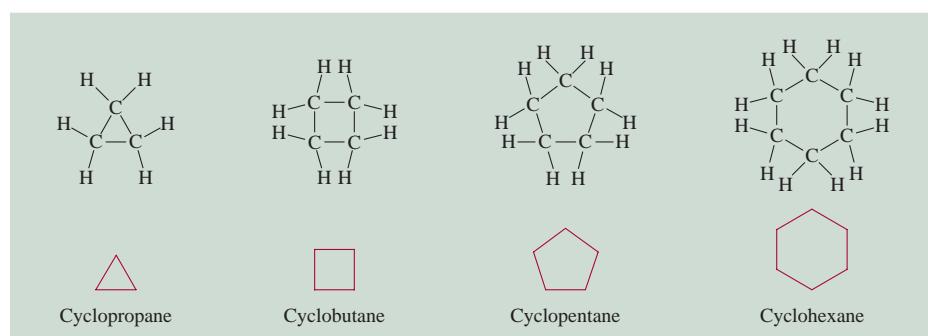
## Cycloalkanes

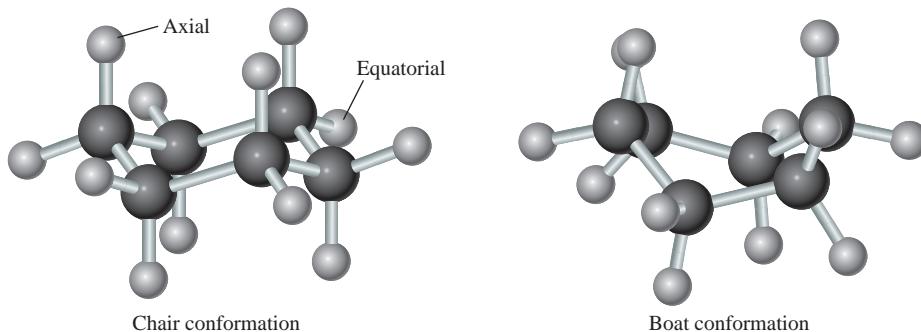
Alkanes whose carbon atoms are joined in rings are known as *cycloalkanes*. They have the general formula  $\text{C}_n\text{H}_{2n}$ , where  $n = 3, 4, \dots$ . The simplest cycloalkane is cyclopropane,  $\text{C}_3\text{H}_6$  (Figure 11.6). Many biologically significant substances such as antibiotics, sugars, cholesterol, and hormones contain one or more such ring systems. Cyclohexane can assume two different conformations called the chair and boat that are relatively free of angle strain (Figure 11.7). By “angle strain” we mean that the bond angles at each carbon atom deviate from the tetrahedral value of  $109.5^\circ$  required for  $sp^3$  hybridization.

## Alkenes

The *alkenes* (also called *olefins*) contain at least one carbon-carbon double bond. Alkenes have the general formula  $\text{C}_n\text{H}_{2n}$ , where  $n = 2, 3, \dots$ . The simplest alkene is  $\text{C}_2\text{H}_4$ , ethylene, in which both carbon atoms are  $sp^2$ -hybridized and the double bond is made up of a sigma bond and a pi bond (see Section 10.5).

**Figure 11.6**  
Structures of the first four cycloalkanes and their simplified forms.



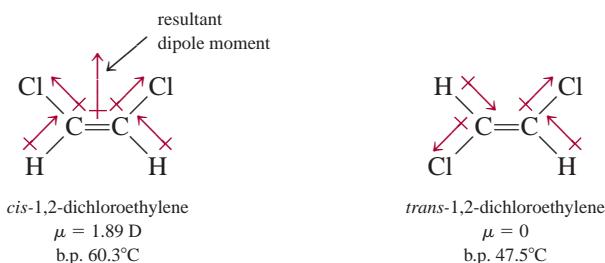
**Figure 11.7**

The cyclohexane molecule can exist in various shapes. The most stable shape is the chair conformation and a less stable one is the boat conformation. Two types of H atoms are labeled axial and equatorial, respectively.

### Geometric Isomers of Alkenes

In a compound such as ethane,  $C_2H_6$ , the rotation of the two methyl groups about the carbon-carbon single bond (which is a sigma bond) is quite free. The situation is different for molecules that contain carbon-carbon double bonds, such as ethylene,  $C_2H_4$ . In addition to the sigma bond, there is a pi bond between the two carbon atoms. Rotation about the carbon-carbon linkage does not affect the sigma bond, but it does move the two  $2p_z$  orbitals out of alignment for overlap and, hence, partially or totally destroys the pi bond (see Figure 10.15). This process requires an input of energy on the order of 270 kJ/mol. For this reason, the rotation of a carbon-carbon double bond is considerably restricted, but not impossible. Consequently, molecules containing carbon-carbon double bonds (that is, the alkenes) may have **geometric isomers**, which have the same type and number of atoms and the same chemical bonds but different spatial arrangements. Such isomers cannot be interconverted without breaking a chemical bond.

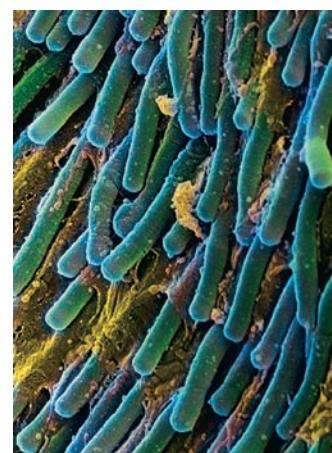
The molecule dichloroethylene,  $ClHC=CHCl$ , can exist as one of the two geometric isomers called *cis*-1,2-dichloroethylene and *trans*-1,2-dichloroethylene:



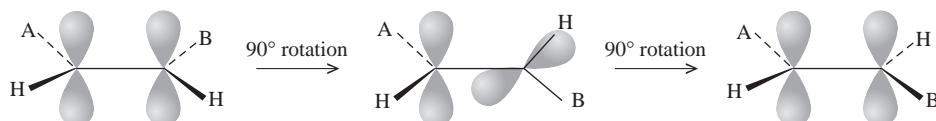
where the term *cis* means that two particular atoms (or groups of atoms) are adjacent to each other, and *trans* means that the two atoms (or groups of atoms) are across from each other. Generally, *cis* and *trans* isomers have distinctly different physical and chemical properties. Heat or irradiation with light is commonly used to bring about the conversion of one geometric isomer to another, a process called *cis-trans isomerization*, or geometric isomerization (Figure 11.8).

### *Cis-trans* Isomerization in the Vision Process

The molecules in the retina that respond to light are rhodopsin, which has two components called 11-*cis* retinal and opsin (Figure 11.9). Retinal is the light-sensitive component and opsin is a protein molecule. Upon receiving a photon in the visible region the 11-*cis* retinal isomerizes to the all-*trans* retinal by breaking a carbon-carbon pi bond. With the pi bond broken, the remaining carbon-carbon sigma bond is free to rotate and transforms into the all-*trans* retinal. At this point an electrical impulse is generated and transmitted to the brain, which forms a visual image. The all-*trans*



An electron micrograph of rod-shaped cells (containing rhodopsins) in the retina.

**Figure 11.8**

*Breaking and remaking the pi bond.* When a compound containing a C=C bond is heated or excited by light, the weaker pi bond is broken. This allows the free rotation of the single carbon-to-carbon sigma bond. A rotation of 180° converts a *cis* isomer to a *trans* isomer or the other way around. Note that a dashed line represents a bond axis behind the plane of the paper, the wedged line represents a bond axis in front of the paper, and the solid line represents bonds in the plane of the paper. The letters A and B represent atoms (other than H) or groups of atoms. Here we have a *cis*-to-*trans* isomerization.

retinal does not fit into the binding site on opsin and eventually separates from the protein. In time, the *trans* isomer is converted back to 11-*cis* retinal by an enzyme (in the absence of light) and rhodopsin is regenerated by the binding of the *cis* isomer to opsin and the visual cycle can begin again.

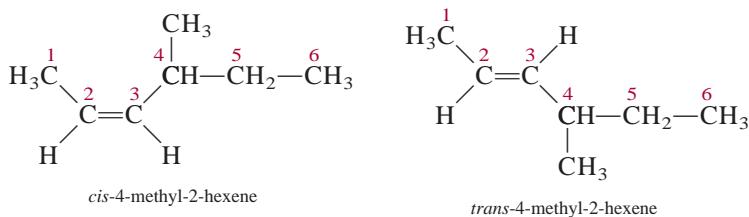
### Alkene Nomenclature

In naming alkenes we indicate the positions of the carbon-carbon double bonds. The names of compounds containing C=C bonds end with *-ene*. As with the alkanes, the name of the parent compound is determined by the number of carbon atoms in the longest chain (see Table 11.1), as shown here:

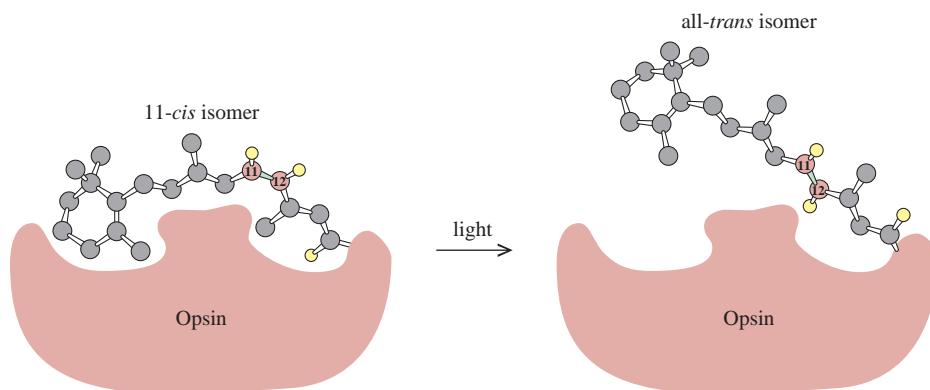


The numbers in the names of alkenes refer to the lowest numbered carbon atom in the chain that is part of the C=C bond of the alkene. The name “butene” means that there are four carbon atoms in the longest chain. Alkene nomenclature must specify whether a given molecule is *cis* or *trans* if it is a geometric isomer, such as

Note that geometric isomers are always structural isomers but the reverse is not true.

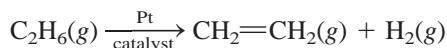
**Figure 11.9**

The primary event in the vision process is the conversion of 11-*cis* retinal to the all-*trans* isomer on rhodopsin. The double bond at which the isomerization occurs is between carbon-11 and carbon-12. For simplicity, most of the H atoms are omitted. In the absence of light, this transformation takes place about once in a thousand years!



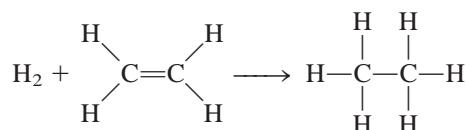
### Properties and Reactions of Alkenes

Ethylene is an extremely important substance because it is used in large quantities in manufacturing organic polymers (very large molecules) and in preparing many other organic chemicals. Ethylene and other alkenes are prepared industrially by the *cracking* process, that is, the thermal decomposition of a large hydrocarbon into smaller molecules. When ethane is heated to about 800°C in the presence of platinum, it undergoes the following reaction:

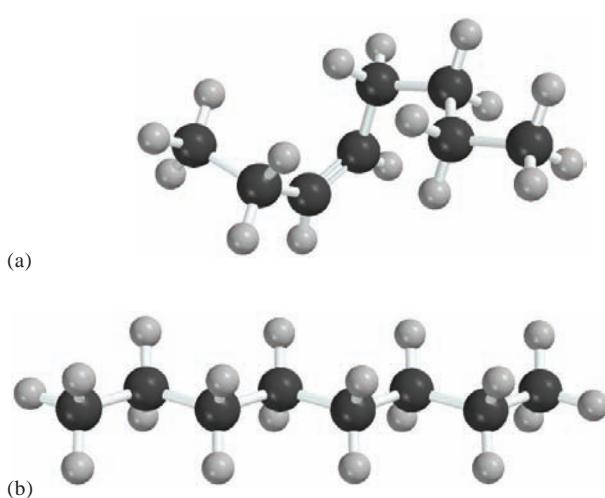


The platinum acts as a *catalyst*, a substance that speeds up a reaction without being used up in the process and therefore does not appear on either side of the equation. Other alkenes can be prepared by cracking the higher members of the alkane family.

Alkenes are classified as *unsaturated hydrocarbons*, compounds with double or triple carbon–carbon bonds. Unsaturated hydrocarbons commonly undergo *addition reactions* in which one molecule adds to another to form a single product. An example of an addition reaction is *hydrogenation*, which is the addition of molecular hydrogen to compounds containing C=C and C≡C bonds



Hydrogenation is an important process in the food industry. Vegetable oils have considerable nutritional value, but many oils must be hydrogenated to eliminate some of the C=C bonds before they can be used to prepare food. Upon exposure to air, *polyunsaturated* molecules—molecules with many C=C bonds—undergo oxidation to yield unpleasant-tasting products (vegetable oil that has oxidized is said to be rancid). In the hydrogenation process, a small amount of nickel catalyst is added to the oil and the mixture is exposed to hydrogen gas at high temperature and pressure. Afterward, the nickel is removed by filtration. Hydrogenation reduces the number of double bonds in the molecule but does not completely eliminate them. If all the double bonds are eliminated, the oil becomes hard and brittle (Figure 11.10).



**Figure 11.10**  
Oils and fats have side chains that resemble hydrocarbons.  
(a) The side chains of oils contain one or more C=C bonds. The *cis* form of the hydrocarbon chains prevents close packing of the molecules. Therefore, oils are liquids.  
(b) Upon hydrogenation, the saturated hydrocarbon chains stack well together. As a result, fats have higher density than oils and are solids at room temperature.

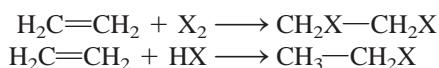
**Figure 11.11**

When ethylene gas is bubbled through an aqueous bromine solution, the reddish brown color gradually disappears due to the formation of 1,2-dibromoethane, which is colorless.

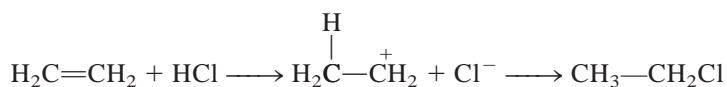


Under controlled conditions, suitable cooking oils and margarine may be prepared by hydrogenation from vegetable oils extracted from cottonseed, corn, and soybeans.

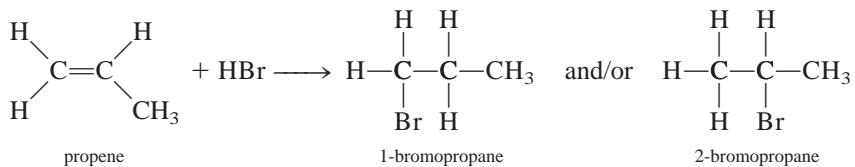
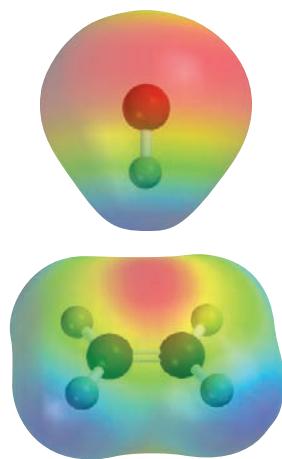
Other addition reactions to the C=C bond involve the hydrogen halides and halogens (Figure 11.11):



in which X represents a halogen atom. Figure 11.12 shows the electron density maps of HCl and ethylene. When the two molecules react, the interaction is between the electron-rich region (pi electrons of the double bond) and the electron-poor region of HCl, which is the H atom. The steps are



The addition of a hydrogen halide to an unsymmetrical alkene such as propene is more complicated because two products are possible:

**Figure 11.12**

The addition reaction between HCl and ethylene. The initial interaction is between the positive end of HCl (blue) and the electron-rich region of ethylene (red), which is associated with the pi electrons of the C=C bond.

In reality, however, only 2-bromopropane is formed. This phenomenon was observed in all reactions between unsymmetrical reagents and alkenes. In 1871 the Russian chemist Vladimir Markovnikov postulated a generalization that enables us to predict the outcome of such an addition reaction. This generalization, now known as *Markovnikov's rule*, states that in the addition of unsymmetrical (that is, polar) reagents to alkenes, the positive portion of the reagent (usually hydrogen) adds to the carbon atom in the double bond that already has the most hydrogen atoms. As the marginal figure on p. 369 shows, the C atom to which the two H atoms are attached



**Figure 11.13**  
Structure of polyethylene. Each carbon atom is  $sp^3$ -hybridized.

has a higher electron density. Therefore, this is the site for the  $H^+$  ion (from  $HBr$ ) to form a C—H bond, followed by the formation of the C—Br bond on the other C atom.

Finally we note that ethylene undergoes a different type of addition reaction that leads to the formation of a polymer. In this process, first an *initiator* molecule ( $R_2$ ) is heated to produce two radicals:



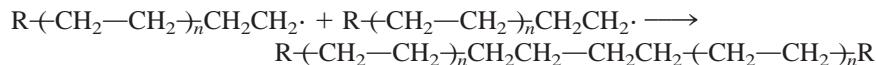
The reactive radical attacks an ethylene molecule to generate a new radical (it is the pi bond that is broken in the polymerization of ethylene):



which further reacts with another ethylene molecule, and so on:

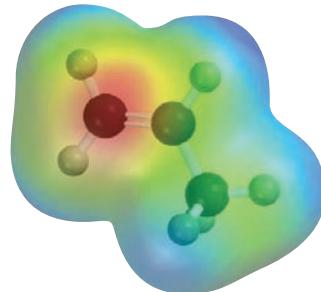


Very quickly a long chain of  $CH_2$  groups is built. Eventually, this process is terminated by the combination of two long-chain radicals to give the polymer called polyethylene (Figure 11.13):



where  $-(CH_2-CH_2)_n$  is a convenient shorthand convention for representing the repeating unit in the polymer. The value of  $n$  is understood to be very large, on the order of thousands.

Under different conditions, it is possible to prepare polyethylene with branched chains. Today, many different forms of polyethylene with widely different physical properties are known. Polyethylene is mainly used in films in frozen food packaging and other product wrappings. A specially treated type of polyethylene, called Tyvek, is used in home construction and mailer envelopes.



The electron density is higher on the carbon atom in the  $CH_2$  group in propene. This is the site of hydrogen addition by hydrogen halides.



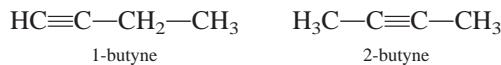
Common mailing envelopes made of Tyvek.

## Alkynes

Alkynes contain at least one carbon–carbon triple bond. They have the general formula  $C_nH_{2n-2}$ , where  $n = 2, 3, \dots$ .

### Alkyne Nomenclature

Names of compounds containing  $C\equiv C$  bonds end with *-yne*. Again the name of the parent compound is determined by the number of carbon atoms in the longest chain (see Table 11.1 for names of alkane counterparts). As in the case of alkenes, the names of alkynes indicate the position of the carbon–carbon triple bond, as, for example, in

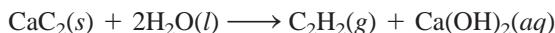




The reaction of calcium carbide with water produces acetylene, a flammable gas.

### Properties and Reactions of Alkynes

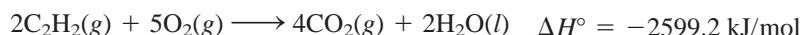
The simplest alkyne is ethyne, better known as acetylene ( $C_2H_2$ ). The structure and bonding of  $C_2H_2$  were discussed in Section 10.5. Acetylene is a colorless gas (b.p.  $-84^\circ C$ ) prepared in the laboratory by the reaction between calcium carbide and water:



Industrially, it is prepared by the thermal decomposition of ethylene at about  $1100^\circ C$ :

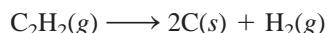


Acetylene has many important uses in industry. Because of its high heat of combustion



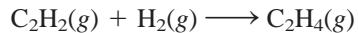
acetylene burned in an “oxyacetylene torch” gives an extremely hot flame (about  $3000^\circ C$ ). Thus, oxyacetylene torches are used to weld metals (see p. 195).

Acetylene is unstable and has a tendency to decompose:

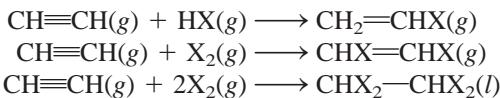


In the presence of a suitable catalyst or when the gas is kept under pressure, this reaction can occur with explosive violence. To be transported safely, it must be dissolved in an inert organic solvent such as acetone at moderate pressure. In the liquid state, acetylene is very sensitive to shock and is highly explosive.

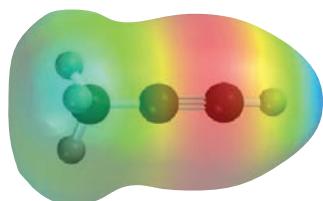
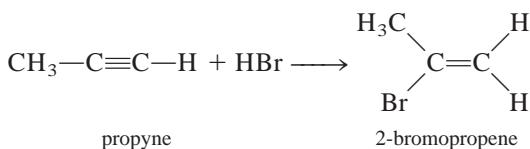
Being an unsaturated hydrocarbon, acetylene can be hydrogenated to yield ethylene:



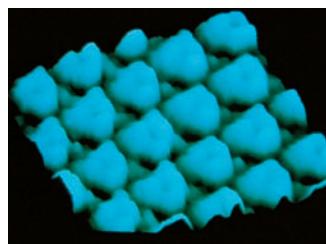
It undergoes these addition reactions with hydrogen halides and halogens:



Methylacetylene (propyne),  $CH_3—C\equiv C—H$ , is the next member in the alkyne family. It undergoes reactions similar to those of acetylene. The addition reactions of propyne also obey Markovnikov’s rule:



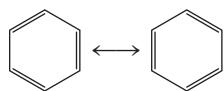
Propyne. Can you account for Markovnikov’s rule in this molecule?



An electron micrograph of benzene molecule, which shows clearly the ring structure.

### 11.3 Aromatic Hydrocarbons

Benzene ( $C_6H_6$ ) is the parent compound of this large family of organic substances. As we saw in Section 9.8, the properties of benzene are best represented by both of the following resonance structures (p. 297):



Benzene is a planar hexagonal molecule with carbon atoms situated at the six corners. All carbon-carbon bonds are equal in length and strength, as are all carbon-hydrogen bonds, and the CCC and HCC angles are all  $120^\circ$ . Therefore, each carbon atom is  $sp^2$ -hybridized; it forms three sigma bonds with two adjacent carbon atoms and a hydrogen atom (Figure 11.14). This arrangement leaves an unhybridized  $2p_z$  orbital on each carbon atom, perpendicular to the plane of the benzene molecule, or *benzene ring*, as it is often called. So far the description resembles the configuration of ethylene ( $C_2H_4$ ), discussed in Section 10.5, except that in this case there are six unhybridized  $2p_z$  orbitals in a cyclic arrangement.

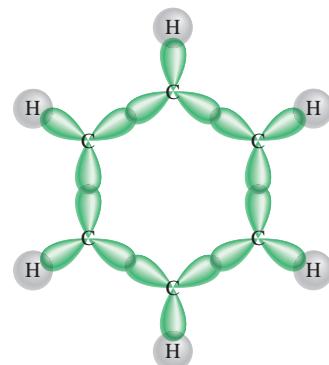
Because of their similar shape and orientation, each  $2p_z$  orbital overlaps two others, one on each adjacent carbon atom. According to the rules listed on p. 342, the interaction of six  $2p_z$  orbitals leads to the formation of six pi molecular orbitals, of which three are bonding and three antibonding. A benzene molecule in the ground state therefore has six electrons in the three pi bonding molecular orbitals, two electrons with paired spins in each orbital (Figure 11.15).

In the ethylene molecule, the overlap of the two  $2p_z$  orbitals gives rise to a bonding and an antibonding molecular orbital, which are localized over the two C atoms. The interaction of the  $2p_z$  orbitals in benzene, however, leads to the formation of **delocalized molecular orbitals**, which are not confined between two adjacent bonding atoms, but actually extend over three or more atoms. Therefore, electrons residing in any of these orbitals are free to move around the benzene ring. For this reason, the structure of benzene is sometimes represented as

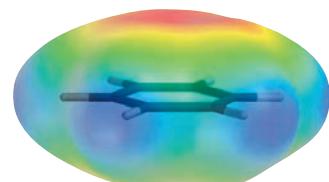


in which the circle indicates that the pi bonds between carbon atoms are not confined to individual pairs of atoms; rather, the pi electron densities are evenly distributed throughout the benzene molecule. As we will see shortly, electron delocalization imparts extra stability to aromatic hydrocarbons.

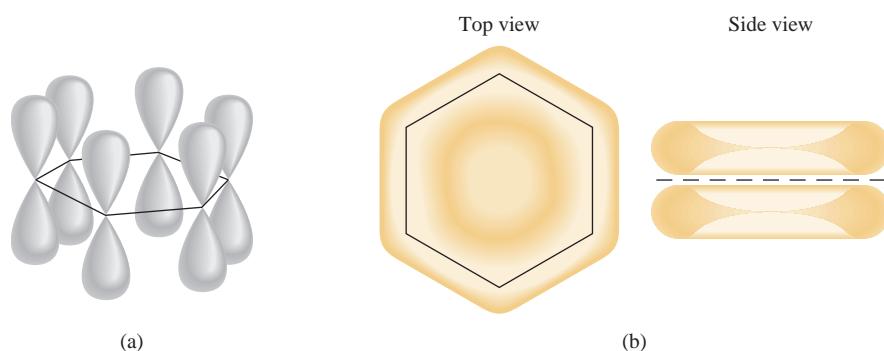
We can now state that each carbon-to-carbon linkage in benzene contains a sigma bond and a “partial” pi bond. The bond order between any two adjacent carbon atoms



**Figure 11.14**  
The sigma bond framework in the benzene molecule. Each C atom is  $sp^2$ -hybridized and forms sigma bonds with two adjacent C atoms and another sigma bond with an H atom.



Electrostatic potential map of benzene shows the electron density (red color) above and below the plane of the molecule. For simplicity, only the framework of the molecule is shown.

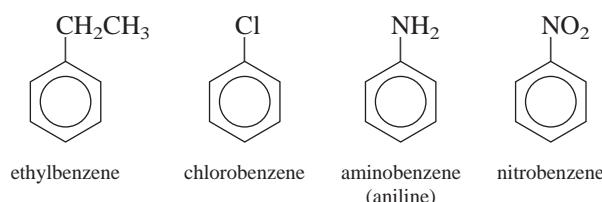


**Figure 11.15**  
(a) The six  $2p_z$  orbitals on the carbon atoms in benzene. (b) The delocalized molecular orbital formed by the overlap of the  $2p_z$  orbitals. The delocalized molecular orbital possesses pi symmetry and lies above and below the plane of the benzene ring. Actually, these  $2p_z$  orbitals can combine in six different ways to yield three bonding molecular orbitals and three antibonding molecular orbitals. The one shown here is the most stable.

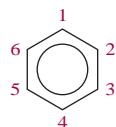
is therefore between 1 and 2. Thus, molecular orbital theory offers an alternative to the resonance approach, which is based on valence bond theory.

## Nomenclature of Aromatic Compounds

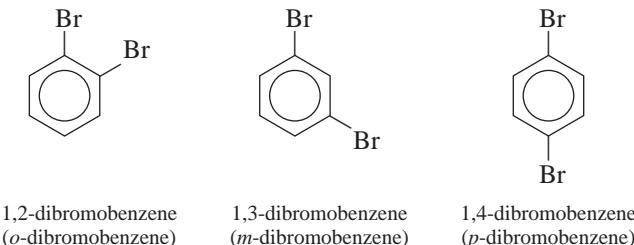
The naming of monosubstituted benzenes, that is, benzenes in which one H atom has been replaced by another atom or a group of atoms, is quite straightforward, as shown next:



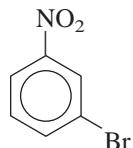
If more than one substituent is present, we must indicate the location of the second group relative to the first. The systematic way to accomplish this is to number the carbon atoms as follows:



Three different dibromobenzenes are possible:

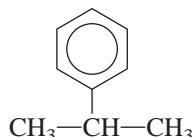


The prefixes *o*- (*ortho*-), *m*- (*meta*-), and *p*- (*para*-) are also used to denote the relative positions of the two substituted groups, as just shown for the dibromobenzenes. Compounds in which the two substituted groups are different are named accordingly. Thus,



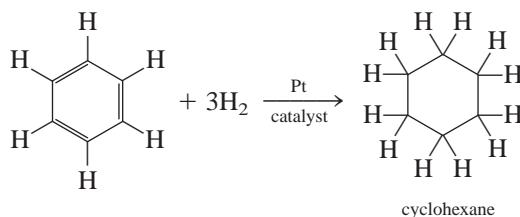
is named 3-bromonitrobenzene, or *m*-bromonitrobenzene.

Finally we note that the group containing benzene minus a hydrogen atom ( $C_6H_5$ ) is called the *phenyl* group. Thus, the following molecule is called 2-phenylpropane:



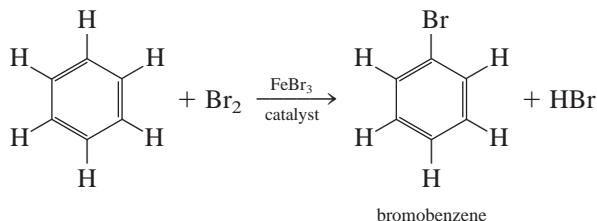
## Properties and Reactions of Aromatic Compounds

Benzene is a colorless, flammable liquid obtained chiefly from petroleum and coal tar. Perhaps the most remarkable chemical property of benzene is its relative inertness. Although it has the same empirical formula as acetylene ( $\text{CH}$ ) and a high degree of unsaturation, it is much less reactive than either ethylene or acetylene. The stability of benzene is the result of electron delocalization. In fact, benzene can be hydrogenated, but only with difficulty. The following reaction is carried out at significantly higher temperatures and pressures than are similar reactions for the alkenes:

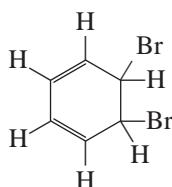


A catalyst is a substance that can speed up the rate of a reaction without itself being used up. More on this topic in Chapter 14.

We saw earlier that alkenes react readily with halogens and hydrogen halides to form addition products, because the pi bond in  $\text{C}=\text{C}$  can be broken more easily. The most common reaction of halogens with benzene is substitution. For example,

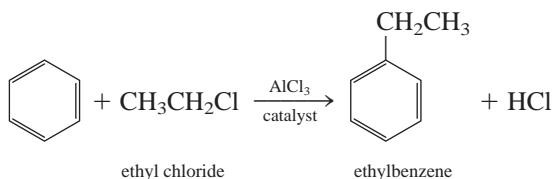


Note that if the reaction were addition, electron delocalization would be destroyed in the product



and the molecule would not have the aromatic characteristic of chemical unreactivity.

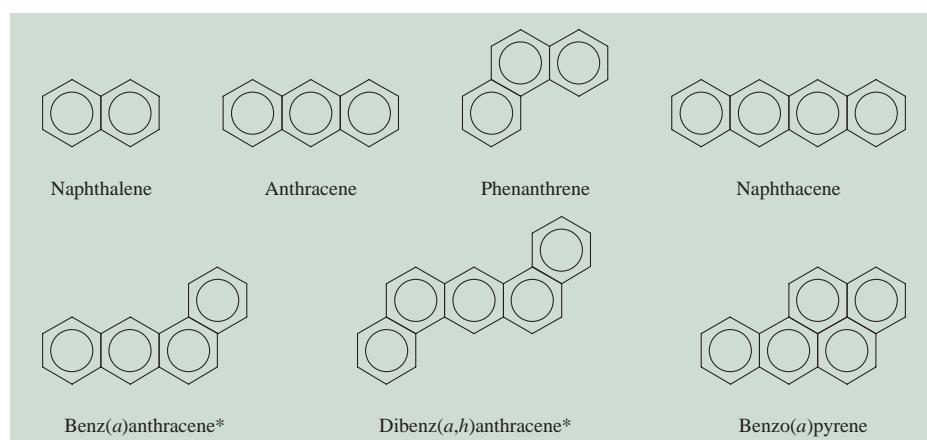
Alkyl groups can be introduced into the ring system by allowing benzene to react with an alkyl halide using  $\text{AlCl}_3$  as the catalyst:



An enormously large number of compounds can be generated from substances in which benzene rings are fused together. Some of these *polycyclic* aromatic hydrocarbons are shown in Figure 11.16. The best known of these compounds is naphthalene,

**Figure 11.16**

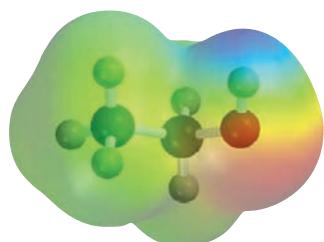
Some polycyclic aromatic hydrocarbons. Compounds denoted by \* are potent carcinogens. An enormous number of such compounds exist in nature.



which is used in mothballs. These and many other similar compounds are present in coal tar. Some of the compounds with several rings are powerful carcinogens—they can cause cancer in humans and other animals.

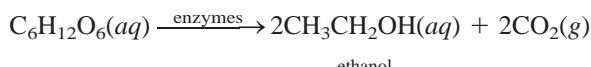
## 11.4 Chemistry of the Functional Groups

We now examine some organic functional groups, groups that are responsible for most of the reactions of the parent compounds. In particular, we focus on oxygen-containing and nitrogen-containing compounds.



### Alcohols

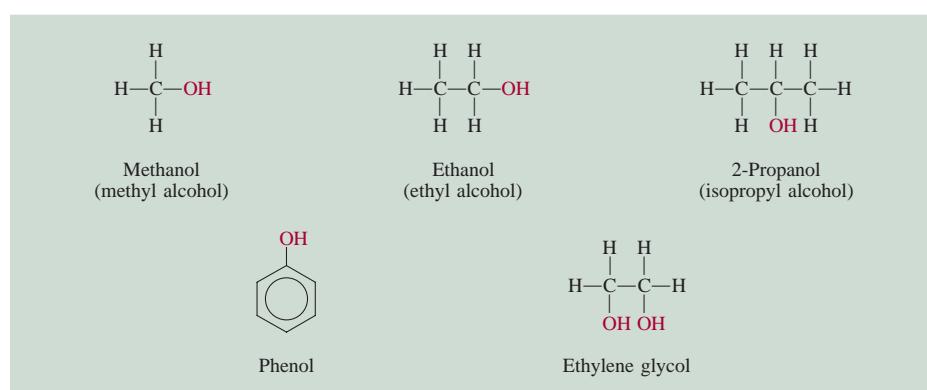
All **alcohols** contain the *hydroxyl functional group*,  $-\text{OH}$ . Some common alcohols are shown in Figure 11.17. Ethyl alcohol, or ethanol, is by far the best known. It is produced biologically by the fermentation of sugar or starch. In the absence of oxygen the enzymes present in bacterial cultures or yeast catalyze the reaction



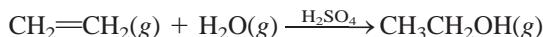
This process gives off energy, which microorganisms, in turn, use for growth and other functions.

**Figure 11.17**

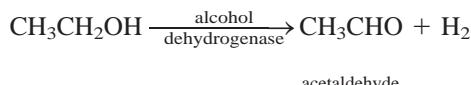
Common alcohols. Note that all the compounds contain the  $\text{OH}$  group. The properties of phenol are quite different from those of the aliphatic alcohols.



Commercially, ethanol is prepared by an addition reaction in which water is combined with ethylene at about 280°C and 300 atm:

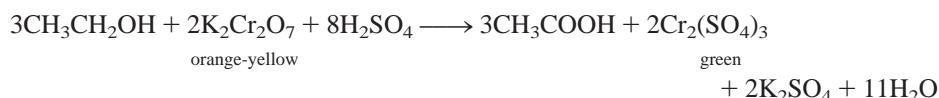


Ethanol has countless applications as a solvent for organic chemicals and as a starting compound for the manufacture of dyes, synthetic drugs, cosmetics, and explosives. It is also a constituent of alcoholic beverages. Ethanol is the only nontoxic (more properly, the least toxic) of the straight-chain alcohols; our bodies produce an enzyme, called *alcohol dehydrogenase*, which helps metabolize ethanol by oxidizing it to acetaldehyde:



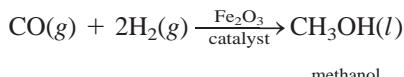
This equation is a simplified version of what actually takes place; the H atoms are taken up by other molecules, so that no H<sub>2</sub> gas is evolved.

Ethanol can also be oxidized by inorganic oxidizing agents, such as acidified potassium dichromate, to acetic acid:



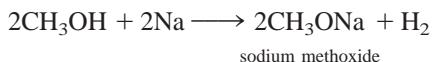
This reaction has been employed by law enforcement agencies to test drivers suspected of being drunk. A sample of the driver's breath is drawn into a device called a breath analyzer, where it is reacted with an acidic potassium dichromate solution. From the color change (orange-yellow to green) it is possible to determine the alcohol content in the driver's blood.

Ethanol is called an aliphatic alcohol because it is derived from an alkane (ethane). The simplest aliphatic alcohol is methanol, CH<sub>3</sub>OH. Called *wood alcohol*, it was prepared at one time by the dry distillation of wood. It is now synthesized industrially by the reaction of carbon monoxide and molecular hydrogen at high temperatures and pressures:



Methanol is highly toxic. Ingestion of only a few milliliters can cause nausea and blindness. Ethanol intended for industrial use is often mixed with methanol to prevent people from drinking it. Ethanol containing methanol or other toxic substances is called *denatured alcohol*.

The alcohols are very weakly acidic; they do not react with strong bases, such as NaOH. The alkali metals react with alcohols to produce hydrogen:



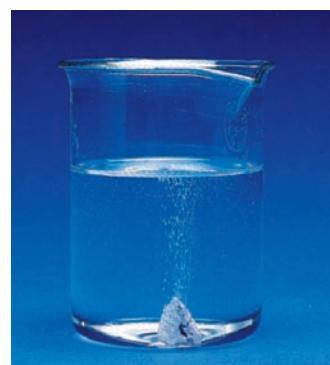
However, the reaction is much less violent than that between Na and water:



Two other familiar aliphatic alcohols are 2-propanol (or isopropyl alcohol), commonly known as rubbing alcohol, and ethylene glycol, which is used as an antifreeze. Most alcohols—especially those with low molar masses—are highly flammable.

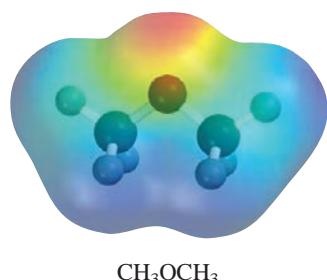


Left: A  $\text{K}_2\text{Cr}_2\text{O}_7$  solution.  
Right: A  $\text{Cr}_2(\text{SO}_4)_3$  solution.

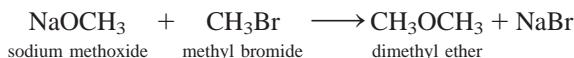


Alcohols react more slowly with sodium metal than water does.

## Ethers



**Ethers** contain the  $R-\text{O}-R'$  linkage, where  $R$  and  $R'$  are a hydrocarbon (aliphatic or aromatic) group. They are formed by the reaction between an alkoxide (containing the  $\text{RO}^-$  ion) and an alkyl halide:

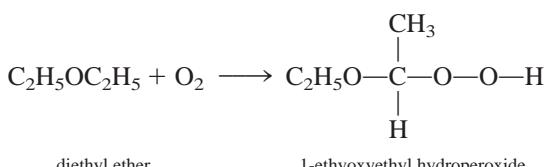


Diethyl ether is prepared on an industrial scale by heating ethanol with sulfuric acid at  $140^\circ\text{C}$



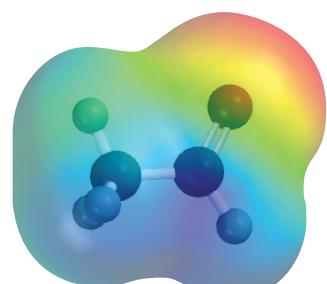
This reaction is an example of a **condensation reaction**, which is characterized by *the joining of two molecules and the elimination of a small molecule, usually water*.

Like alcohols, ethers are extremely flammable. When left standing in air, they have a tendency to slowly form explosive peroxides:



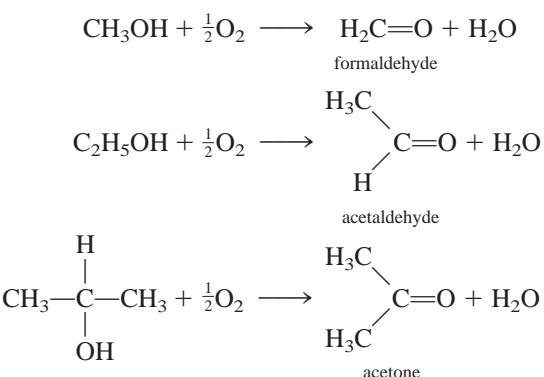
Peroxides contain the  $-\text{O}-\text{O}-$  linkage; the simplest peroxide is hydrogen peroxide,  $\text{H}_2\text{O}_2$ . Diethyl ether, commonly known as “ether,” was used as an anesthetic for many years. It produces unconsciousness by depressing the activity of the central nervous system. The major disadvantages of diethyl ether are its irritating effects on the respiratory system and the occurrence of postanesthetic nausea and vomiting. “Neothyl,” or methyl propyl ether,  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$ , is currently favored as an anesthetic because it is relatively free of side effects.

## Aldehydes and Ketones



$\text{CH}_3\text{CHO}$

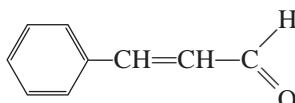
Under mild oxidation conditions, it is possible to convert alcohols to aldehydes and ketones:



The functional group in these compounds is the **carbonyl group**,  $\text{>C=O}$ . In an **aldehyde** at least one hydrogen atom is bonded to the carbon in the carbonyl group.

In a **ketone**, the carbon atom in the carbonyl group is bonded to two hydrocarbon groups.

The simplest aldehyde, formaldehyde ( $\text{H}_2\text{C}=\text{O}$ ) has a tendency to *polymerize*; that is, the individual molecules join together to form a compound of high molar mass. This action gives off much heat and is often explosive, so formaldehyde is usually prepared and stored in aqueous solution (to reduce the concentration). This rather disagreeable-smelling liquid is used as a starting material in the polymer industry and in the laboratory as a preservative for animal specimens. Interestingly, the higher molar mass aldehydes, such as cinnamic aldehyde



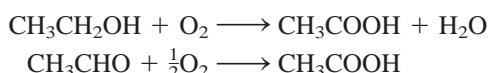
Cinnamic aldehyde gives cinnamon its characteristic aroma.

have a pleasant odor and are used in the manufacture of perfumes.

Ketones generally are less reactive than aldehydes. The simplest ketone is acetone, a pleasant-smelling liquid that is used mainly as a solvent for organic compounds and nail polish remover.

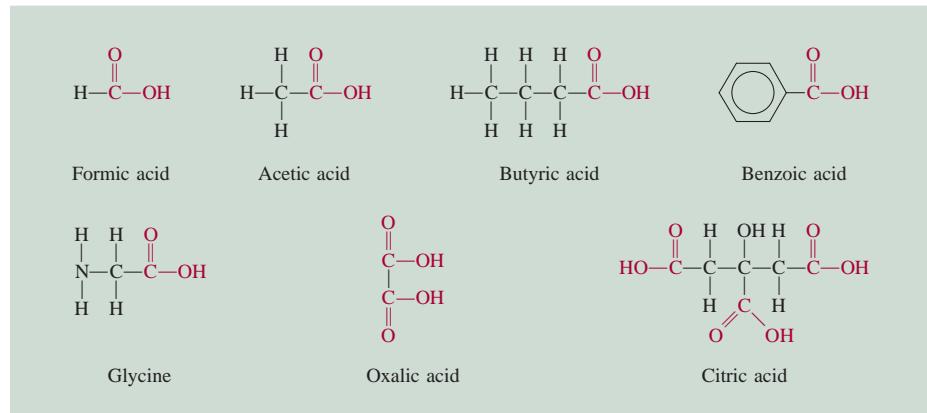
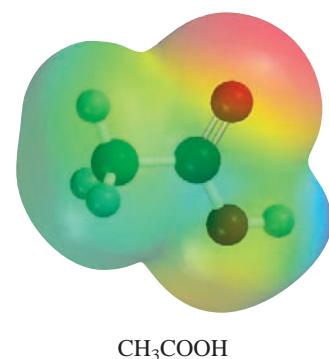
## Carboxylic Acids

Under appropriate conditions both alcohols and aldehydes can be oxidized to **carboxylic acids**, acids that contain the carboxyl group,  $-\text{COOH}$ :



These reactions occur so readily, in fact, that wine must be protected from atmospheric oxygen while in storage. Otherwise, it would soon turn to vinegar due to the formation of acetic acid. Figure 11.18 shows the structure of some of the common carboxylic acids.

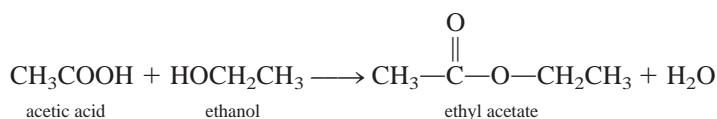
Carboxylic acids are widely distributed in nature; they are found in both the plant and animal kingdoms. All protein molecules are made of amino acids, a special kind of carboxylic acid containing an amino group ( $-\text{NH}_2$ ) and a carboxyl group ( $-\text{COOH}$ ).



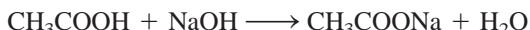
**Figure 11.18**  
Some common carboxylic acids.  
Note that they all contain the  $\text{COOH}$  group. (Glycine is one of the amino acids found in proteins.)

Unlike the inorganic acids HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>, carboxylic acids are usually weak. They react with alcohols to form pleasant-smelling esters:

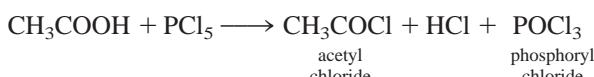
This is a condensation reaction.



Other common reactions of carboxylic acids are neutralization

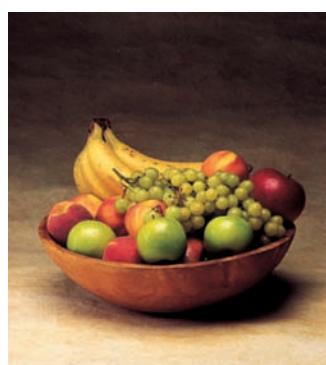


and formation of acid halides, such as acetyl chloride



Acid halides are reactive compounds used as intermediates in the preparation of many other organic compounds.

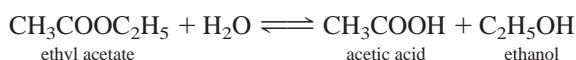
### Esters



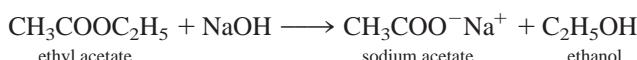
The odor of fruits is mainly due to the ester compounds in them.

**Esters** have the general formula  $R'COOR$ , in which  $R'$  can be H, an alkyl, or an aromatic hydrocarbon group and R is an alkyl or an aromatic hydrocarbon group. Esters are used in the manufacture of perfumes and as flavoring agents in the confectionery and soft-drink industries. Many fruits owe their characteristic smell and flavor to the presence of esters. For example, bananas contain isopentyl acetate [ $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$ ], oranges contain octyl acetate ( $\text{CH}_3\text{COOC}_8\text{H}_{17}$ ), and apples contain methyl butyrate ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_3$ ).

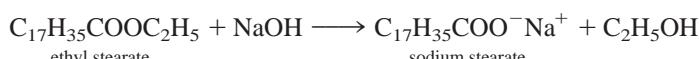
The functional group in esters is  $\text{—COOR}$ . In the presence of an acid catalyst, such as HCl, esters undergo a reaction with water (a *hydrolysis* reaction) to regenerate a carboxylic acid and an alcohol. For example, in acid solution, ethyl acetate is converted to acetic acid:



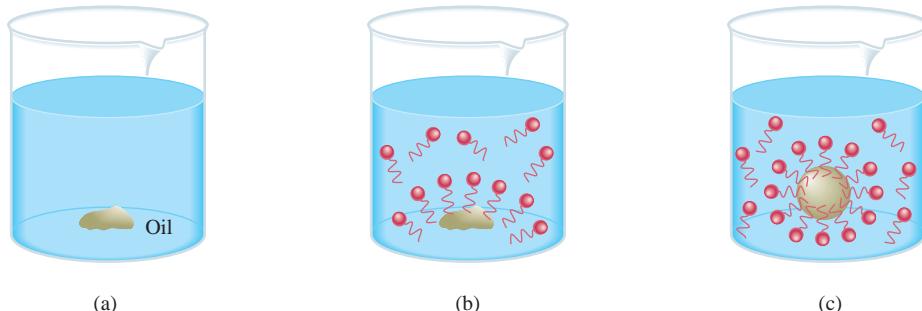
However, this reaction does not go to completion because the reverse reaction, that is, the formation of an ester from an alcohol and an acid, also occurs to an appreciable extent. On the other hand, when the hydrolysis reaction is run in aqueous NaOH solution, ethyl acetate is converted to sodium acetate, which does not react with ethanol, so this reaction goes to completion from left to right:



The term **saponification** (meaning *soapmaking*) was originally used to describe the reaction between an ester and sodium hydroxide to yield soap (sodium stearate):



Saponification is now a general term for alkaline hydrolysis of any type of ester. Soaps are characterized by a long nonpolar hydrocarbon chain and a polar head (the  $\text{—COO}^-$  group). The hydrocarbon chain is readily soluble in oily substances, while the ionic carboxylate group ( $\text{—COO}^-$ ) remains outside the oily nonpolar surface. Figure 11.19 shows the action of soap.



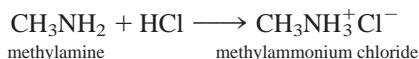
**Figure 11.19**  
*The cleansing action of soap. The soap molecule is represented by a polar head and zigzag hydrocarbon tail. An oily spot (a) can be removed by soap (b) because the nonpolar tail dissolves in the oil, and (c) the entire system becomes soluble in water because the exterior portion is now ionic.*

## Amines

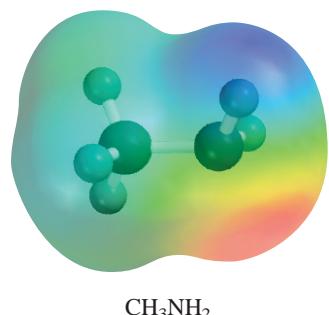
**Amines** are organic bases that have the general formula  $R_3N$ , in which one of the  $R$  groups must be an alkyl group or an aromatic hydrocarbon group. Like ammonia, amines are weak Brønsted bases that react with water as follows:



Like all bases, the amines form salts when allowed to react with acids:



These salts are usually colorless, odorless solids that are soluble in water. Many of the aromatic amines are carcinogenic.

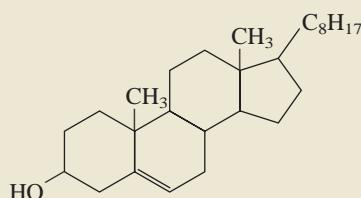


## Summary of Functional Groups

Table 11.4 summarizes the common functional groups, including the C=C and C≡C groups. Organic compounds commonly contain more than one functional group. Generally, the reactivity of a compound is determined by the number and types of functional groups in its makeup.

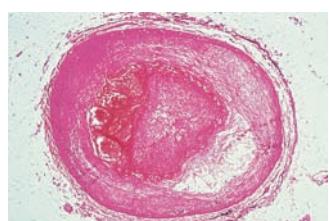
### Example 11.4

Cholesterol is a major component of gallstones, and it is believed that the cholesterol level in the blood is a contributing factor in certain types of heart disease. From the following structure of the compound, predict its reaction with (a)  $\text{Br}_2$ , (b)  $\text{H}_2$  (in the presence of a Pt catalyst), (c)  $\text{CH}_3\text{COOH}$ .



**Strategy** To predict the type of reactions a molecule may undergo, we must first identify the functional groups present (see Table 11.4).

**Solution** There are two functional groups in cholesterol: the hydroxyl group and the carbon-carbon double bond.



An artery becoming blocked by cholesterol.

(Continued)

**TABLE 11.4** Important Functional Groups and Their Reactions

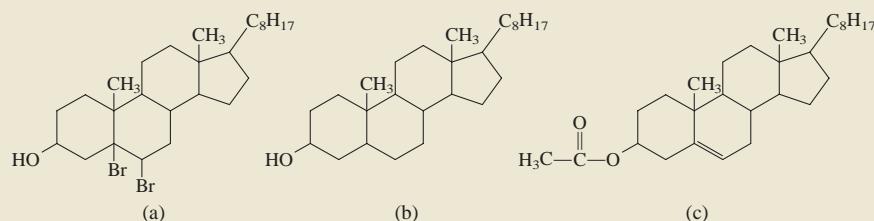
Functional Group	Name	Typical Reactions
	Carbon-carbon double bond	Addition reactions with halogens, hydrogen halides, and water; hydrogenation to yield alkanes
	Carbon-carbon triple bond	Addition reactions with halogens, hydrogen halides; hydrogenation to yield alkenes and alkanes
	Halogen	Exchange reactions: $\text{CH}_3\text{CH}_2\text{Br} + \text{KI} \longrightarrow \text{CH}_3\text{CH}_2\text{I} + \text{KBr}$
	Hydroxyl	Esterification (formation of an ester) with carboxylic acids; oxidation to aldehydes, ketones, and carboxylic acids
	Carbonyl	Reduction to yield alcohols; oxidation of aldehydes to yield carboxylic acids
	Carboxyl	Esterification with alcohols; reaction with phosphorus pentachloride to yield acid chlorides
	Ester	Hydrolysis to yield acids and alcohols
(R = hydrocarbon)		
	Amine	Formation of ammonium salts with acids
(R = H or hydrocarbon)		

- (a) The reaction with bromine results in the addition of bromine to the double-bonded carbons, which become single-bonded.  
 (b) This is a hydrogenation reaction. Again, the carbon-carbon double bond is converted to a carbon-carbon single bond.  
 (c) The acetic acid ( $\text{CH}_3\text{COOH}$ ) reacts with the hydroxyl group to form an ester and water. Figure 11.20 shows the products of these reactions.

**Figure 11.20**

The products formed by the reaction of cholesterol with (a) molecular bromine, (b) molecular hydrogen, and (c) acetic acid.

Similar problem: 11.41.



**Practice Exercise** Predict the products of the following reaction:

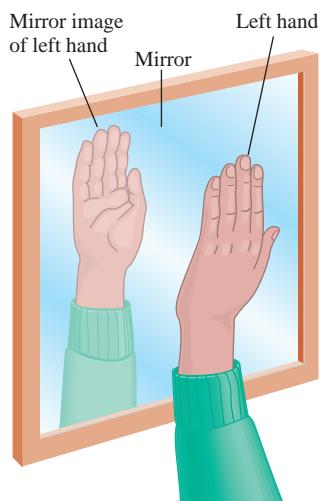


## 11.5 Chirality—The Handedness of Molecules

Many organic compounds can exist as mirror-image twins, in which one partner may cure disease, quell a headache, or smell good, whereas its mirror-reversed counterpart may be poisonous, smell repugnant, or simply be inert. Compounds that come as mirror image pairs are sometimes compared with the left and right hands and are referred to as **chiral**, or *handed*, molecules. Although every molecule can have a mirror image, the difference between chiral and *achiral* (meaning nonchiral) molecules is that only the twins of the former are nonsuperimposable.

Consider the substituted methanes  $\text{CH}_2\text{ClBr}$  and  $\text{CHFClBr}$ . Figure 11.21 shows perspective drawings of these two molecules and their mirror images. The two mirror images of Figure 11.21(a) are superimposable, but those of Figure 11.21(b) are not, no matter how we rotate the molecules. Thus, the  $\text{CHFClBr}$  molecule is chiral. Careful observation shows that most simple chiral molecules contain at least one *asymmetric* carbon atom—that is, a carbon atom bonded to four different atoms or groups of atoms.

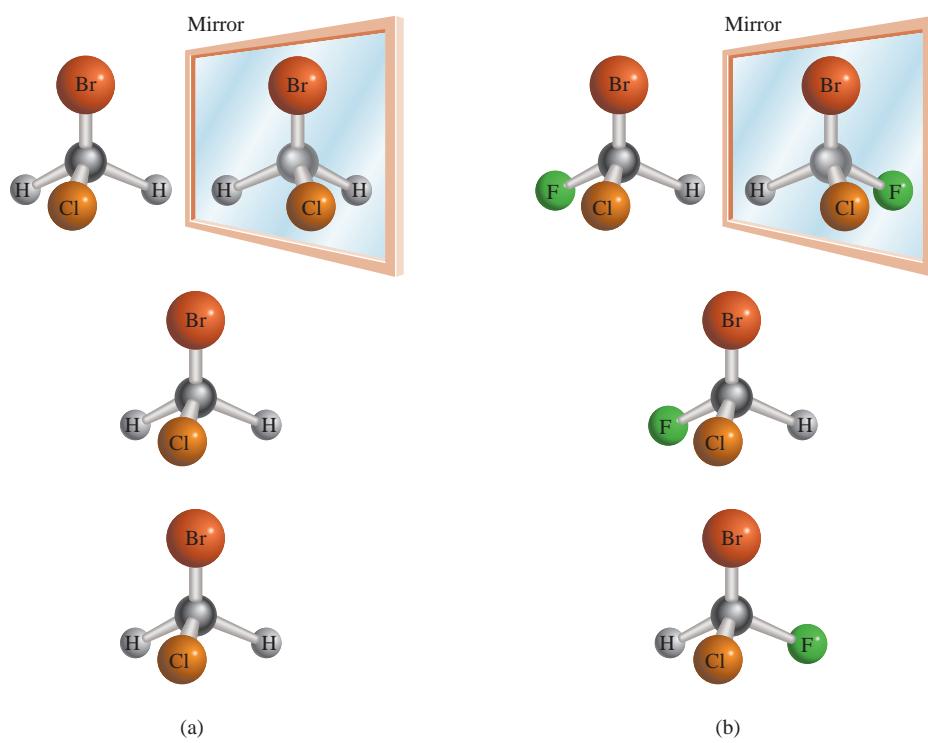
The *nonsuperimposable mirror images of a chiral compound* are called **enantiomers**. Like geometric isomers, enantiomers come in pairs. However, the enantiomers of a compound have identical physical and chemical properties, such as melting point, boiling point, and chemical reactivity toward molecules that are not chiral themselves. Each enantiomer of a chiral molecule is said to be optically active because of its ability to rotate the plane of polarization of polarized light. Unlike ordinary light, which vibrates in all directions, plane-polarized light vibrates only in a single plane. To study the interaction between plane-polarized light and chiral molecules we use a **polarimeter**, shown schematically in Figure 11.22. A



A left hand and its mirror image, which looks the same as the right hand.



An older term for enantiomers is *optical isomers*.

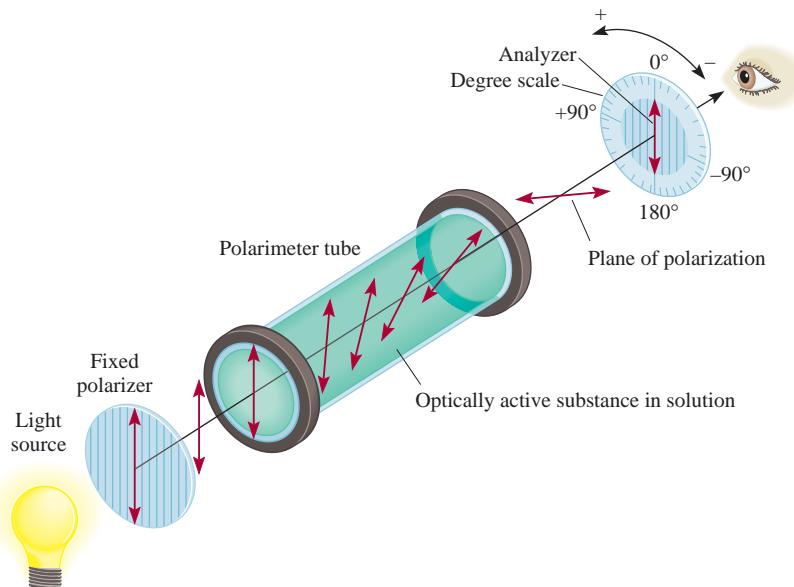


**Figure 11.21**

(a) The  $\text{CH}_2\text{ClBr}$  molecule and its mirror image. Because the molecule and its mirror image are superimposable, the molecule is said to be achiral.  
 (b) The  $\text{CHFClBr}$  molecule and its mirror image. Because the molecule and its mirror image are not superimposable, no matter how we rotate one with respect to the other, the molecule is said to be chiral.

**Figure 11.22**

*Operation of a polarimeter.*  
Initially, the tube is filled with an achiral compound. The analyzer is rotated so that its plane of polarization is perpendicular to that of the polarizer. Under this condition, no light reaches the observer. Next, a chiral compound is placed in the tube as shown. The plane of polarization of the polarized light is rotated as it travels through the tube so that some light reaches the observer. Rotating the analyzer (either to the left or to the right) until no light reaches the observer again allows the angle of optical rotation to be measured.

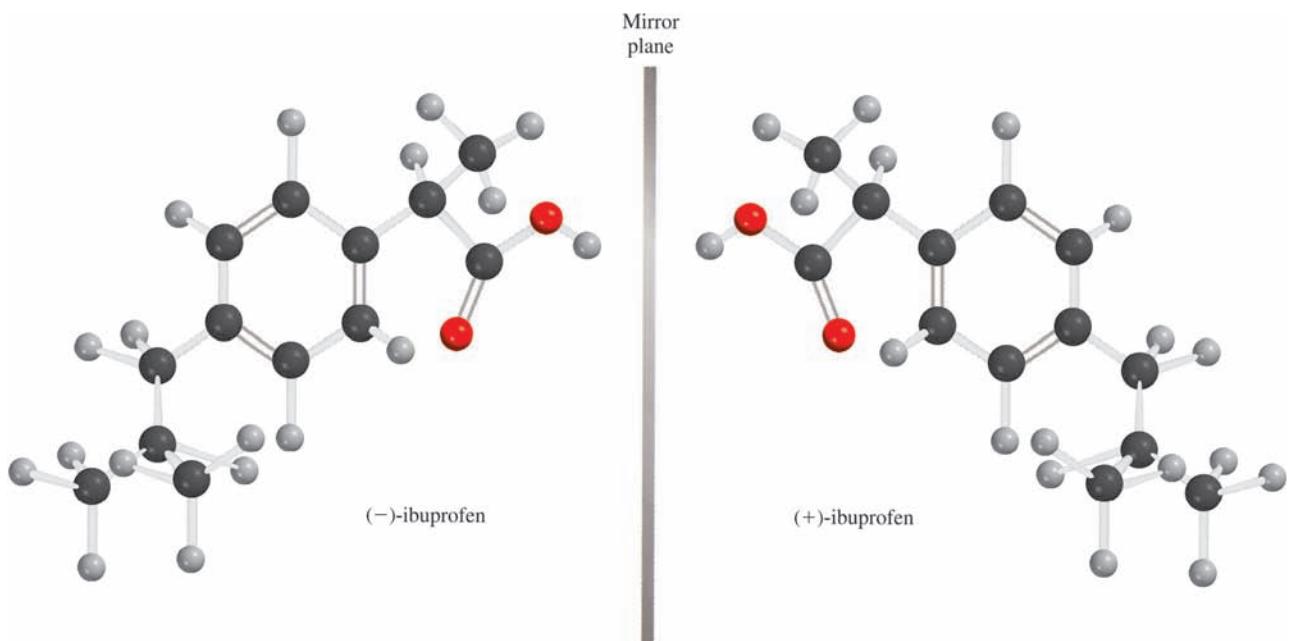


beam of unpolarized light first passes through a polarizer, and then through a sample tube containing a solution of a chiral compound. As the polarized light passes through the sample tube, its plane of polarization is rotated either to the right or to the left. This rotation can be measured directly by turning the analyzer in the appropriate direction until minimal light transmission is achieved (Figure 11.23). If the plane of polarization is rotated to the right, the isomer is said to be dextrorotatory (+); it is levorotatory (−) if the rotation is to the left. Enantiomers of a chiral

**Figure 11.23**

*With one Polaroid sheet over a picture, light passes through. With a second sheet of Polaroid placed over the first so that the axes of polarization of the sheets are perpendicular, little or no light passes through. If the axes of polarization of the two sheets were parallel, light would pass through.*



**Figure 11.24**

The enantiomers of ibuprofen are mirror images of each other. There is only one asymmetric C atom in the molecule. Can you spot it?

substance always rotate the light by the same amount, but in opposite directions. Thus, in an equimolar mixture of two enantiomers, called a **racemic mixture**, the net rotation is zero.

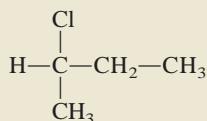
Chirality plays an important role in biological systems. Protein molecules have many asymmetric carbon atoms and their functions are often influenced by their chirality. Because the enantiomers of a chiral compound usually behave very differently from each other in the body, chiral twins are coming under increasing scrutiny among pharmaceutical manufacturers. More than half of the most prescribed drugs in 2006 are chiral. In most of these cases only one enantiomer of the drug works as a medicine, whereas the other form is useless or less effective or may even cause serious side effects. The best-known case in which the use of a racemic mixture of a drug had tragic consequences occurred in Europe in the late 1950s. The drug thalidomide was prescribed for pregnant women there as an antidote to morning sickness. But by 1962, the drug had to be withdrawn from the market after thousands of deformed children had been born to mothers who had taken it. Only later did researchers discover that the sedative properties of thalidomide belong to (+)-thalidomide and that (−)-thalidomide is a potent mutagen. (A *mutagen* is a substance that causes gene mutation, usually leading to deformed offspring.)

Figure 11.24 shows the two enantiomeric forms of another drug, ibuprofen. This popular pain reliever is sold as a racemic mixture, but only the one on the left is potent. The other form is ineffective but also harmless. Organic chemists today are actively researching ways to synthesize enantiomerically pure drugs, or “chiral drugs.” Chiral drugs contain only one enantiomeric form both for efficiency and for protection against possible side effects from its mirror-image twin.

**As of 2006, one of the best-selling chiral drugs, Lipitor, which controls cholesterol level, is sold as a pure enantiomer.**

### Example 11.5

Is the following molecule chiral?

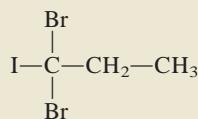


**Strategy** Recall the condition for chirality. Is the central C atom asymmetric; that is, does it have four different atoms or different groups attached to it?

**Solution** We note that the central carbon atom is bonded to a hydrogen atom, a chlorine atom, a  $-\text{CH}_3$  group, and a  $-\text{CH}_2-\text{CH}_3$  group. Therefore, the central carbon atom is asymmetric and the molecule is chiral.

Similar problems: 11.45, 11.46.

**Practice Exercise** Is the following molecule chiral?



## SUMMARY OF FACTS AND CONCEPTS

- Because carbon atoms can link up with other carbon atoms in straight and branched chains, carbon can form more compounds than most other elements.
- Alkanes and cycloalkanes are saturated hydrocarbons. Methane,  $\text{CH}_4$ , is the simplest of the alkanes, a family of hydrocarbons with the general formula  $\text{C}_n\text{H}_{2n+2}$ . The cycloalkanes are a subfamily of alkanes whose carbon atoms are joined in a ring. Ethylene,  $\text{CH}_2=\text{CH}_2$ , is the simplest of alkenes, a class of hydrocarbons containing carbon-carbon double bonds and having the general formula  $\text{C}_n\text{H}_{2n}$ . Unsymmetrical alkenes can exist as *cis* and *trans* isomers. Acetylene,  $\text{CH}\equiv\text{CH}$ , is the simplest of the alkynes, which are compounds that have the general formula  $\text{C}_n\text{H}_{2n-2}$  and contain carbon-carbon triple bonds. Compounds that contain one or more benzene rings are called aromatic hydrocarbons. The stability of the benzene molecule is the result of electron delocalization.
- Functional groups determine the chemical reactivity of molecules in which they are found. Classes of compounds characterized by their functional groups include alcohols, ethers, aldehydes and ketones, carboxylic acids and esters, and amines.
- Chirality refers to molecules that have nonsuperimposable mirror images. Most chiral molecules contain one or more asymmetric carbon atoms. Chiral molecules are widespread in biological systems and are important in drug design.

## KEY WORDS

Addition reaction, p. 367	Aromatic hydrocarbon, p. 356	Enantiomer, p. 381	Organic chemistry, p. 356
Alcohol, p. 374	Carboxylic acid, p. 377	Ester, p. 378	Polarimeter, p. 381
Aldehyde, p. 376	Chiral, p. 381	Ether, p. 376	Racemic mixture, p. 383
Aliphatic hydrocarbon, p. 356	Condensation reaction, 376	Functional group, p. 356	Radical, p. 363
Alkane, p. 356	Conformations, p. 359	Geometric isomers, p. 365	Saponification, p. 378
Alkene, p. 364	Cycloalkane, p. 364	Hydrocarbon, p. 356	Saturated hydrocarbon, p. 356
Alkyne, p. 369	Delocalized molecular orbitals, p. 371	Hydrogenation, p. 367	Structural isomer, p. 357
Amine, p. 379		Ketone, p. 377	Unsaturated hydrocarbon, p. 367

## QUESTIONS AND PROBLEMS

### Aliphatic Hydrocarbons

#### Review Questions

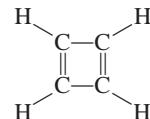
- 11.1 Explain why carbon is able to form so many more compounds than most other elements.
- 11.2 What is the difference between aliphatic and aromatic hydrocarbons?
- 11.3 What do “saturated” and “unsaturated” mean when applied to hydrocarbons? Give examples of a saturated hydrocarbon and an unsaturated hydrocarbon.
- 11.4 What are structural isomers?
- 11.5 Use ethane as an example to explain the meaning of conformations. What are Newman projections? How do the conformations of a molecule differ from structural isomers?
- 11.6 Draw skeletal structures of the boat and chair forms of cyclohexane.
- 11.7 Alkenes exhibit geometric isomerism because rotation about the C=C bond is restricted. Explain.
- 11.8 Why is it that alkanes and alkynes, unlike alkenes, have no geometric isomers?
- 11.9 What is Markovnikov’s rule?
- 11.10 Describe reactions that are characteristic of alkanes, alkenes, and alkynes.

#### Problems

- 11.11 Draw all possible structural isomers for this alkane:  $C_7H_{16}$ .
- 11.12 How many distinct chloropentanes,  $C_5H_{11}Cl$ , could be produced in the direct chlorination of *n*-pentane,  $CH_3(CH_2)_3CH_3$ ? Draw the structure of each molecule.
- 11.13 Draw all possible isomers for the molecule  $C_4H_8$ .
- 11.14 Draw all possible isomers for the molecule  $C_3H_5Br$ .
- 11.15 The structural isomers of pentane,  $C_5H_{12}$ , have quite different boiling points (see Example 11.1). Explain the observed variation in boiling point, in terms of structure.
- 11.16 Discuss how you can determine which of these compounds might be alkanes, cycloalkanes, alkenes, or alkynes, without drawing their formulas: (a)  $C_6H_{12}$ , (b)  $C_4H_6$ , (c)  $C_5H_{12}$ , (d)  $C_7H_{14}$ , (e)  $C_3H_4$ .
- 11.17 Draw Newman projections of the staggered and eclipsed conformations of propane. Rank them in stability.
- 11.18 Draw Newman projections of four different conformations of butane. Rank them in stability. (*Hint:* Two of the conformations represent the most stable forms and the other two the least stable forms.)

- 11.19 Draw the structures of *cis*-2-butene and *trans*-2-butene. Which of the two compounds would give off more heat on hydrogenation to butane? Explain.

- 11.20 Would you expect cyclobutadiene to be a stable molecule? Explain.



- 11.21 How many different isomers can be derived from ethylene if two hydrogen atoms are replaced by a fluorine atom and a chlorine atom? Draw their structures and name them. Indicate which are structural isomers and which are geometric isomers.

- 11.22 Suggest two chemical tests that would help you distinguish between these two compounds:

- (a)  $CH_3CH_2CH_2CH_2CH_3$
- (b)  $CH_3CH_2CH_2CH=CH_2$

- 11.23 Sulfuric acid ( $H_2SO_4$ ) adds to the double bond of alkenes as  $H^+$  and  $\overset{-}{OSO}_3H$ . Predict the products when sulfuric acid reacts with (a) ethylene and (b) propene.

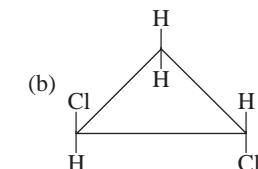
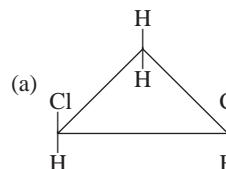
- 11.24 Acetylene is an unstable compound. It has a tendency to form benzene as follows:



Calculate the standard enthalpy change in kJ/mol for this reaction at 25°C.

- 11.25 Predict products when HBr is added to (a) 1-butene and (b) 2-butene.

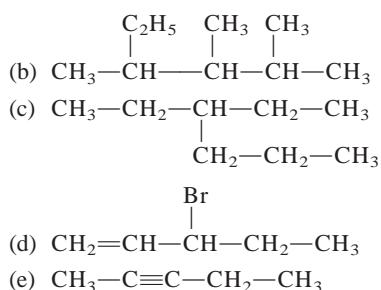
- 11.26 Geometric isomers are not restricted to compounds containing the C=C bond. For example, certain disubstituted cycloalkanes can exist in the *cis* and the *trans* forms. Label the following molecules as the *cis* and *trans* isomer, of the same compound:



- 11.27 Write the structural formulas for these organic compounds: (a) 3-methylhexane, (b) 1,3,5-trichlorocyclohexane, (c) 2,3-dimethylpentane, (d) 2-bromo-4-phenylpentane, (e) 3,4,5-trimethyloctane.

- 11.28 Name these compounds:

- (a)  $CH_3—\overset{CH_3}{|}—CH—CH_2—CH_2—CH_3$



## Aromatic Hydrocarbons

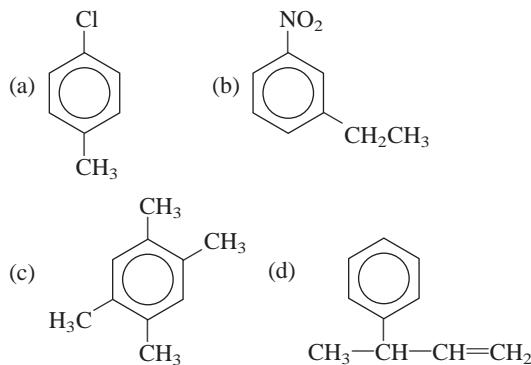
### Review Questions

- 11.29 Comment on the extra stability of benzene compared to ethylene. Why does ethylene undergo addition reactions while benzene usually undergoes substitution reactions?
- 11.30 Benzene and cyclohexane both contain six-membered rings. Benzene is planar and cyclohexane is nonplanar. Explain.

### Problems

- 11.31 Write structures for the compounds shown below:  
 (a) 1-bromo-3-methylbenzene, (b) 1-chloro-2-propylbenzene, (c) 1,2,4,5-tetramethylbenzene.

- 11.32 Name these compounds:



## Chemistry of the Functional Groups

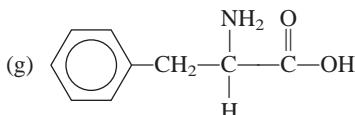
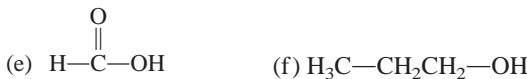
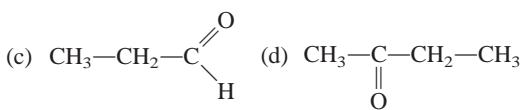
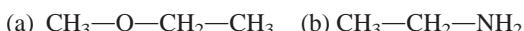
### Review Questions

- 11.33 What are functional groups? Why is it logical and useful to classify organic compounds according to their functional groups?
- 11.34 Draw the Lewis structure for each of these functional groups: alcohol, ether, aldehyde, ketone, carboxylic acid, ester, amine.

### Problems

- 11.35 Draw one possible structure for molecules with these formulas: (a)  $\text{CH}_4\text{O}$ , (b)  $\text{C}_2\text{H}_6\text{O}$ , (c)  $\text{C}_3\text{H}_6\text{O}_2$ , (d)  $\text{C}_3\text{H}_8\text{O}$ .

- 11.36 Classify each of these molecules as alcohol, aldehyde, ketone, carboxylic acid, amine, or ether:



- 11.37 Generally aldehydes are more susceptible to oxidation in air than are ketones. Use acetaldehyde and acetone as examples and show why ketones such as acetone are more stable than aldehydes in this respect.

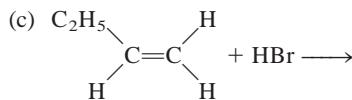
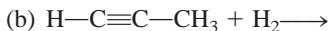
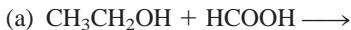
- 11.38 Complete this equation and identify the products:



- 11.39 A compound has the empirical formula  $\text{C}_5\text{H}_{12}\text{O}$ . Upon controlled oxidation, it is converted into a compound of empirical formula  $\text{C}_5\text{H}_{10}\text{O}$ , which behaves as a ketone. Draw possible structures for the original compound and the final compound.

- 11.40 A compound having the molecular formula  $\text{C}_4\text{H}_{10}\text{O}$  does not react with sodium metal. In the presence of light, the compound reacts with  $\text{Cl}_2$  to form three compounds having the formula  $\text{C}_4\text{H}_9\text{OCl}$ . Draw a structure for the original compound that is consistent with this information.

- 11.41 Predict the product or products of each of these reactions:



- 11.42 Identify the functional groups in each of these molecules:



## Chirality

### Review Questions

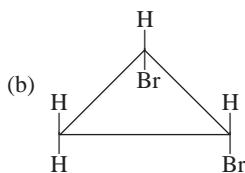
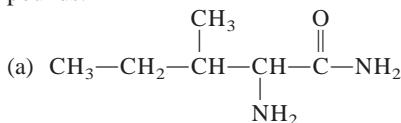
- 11.43 What factor determines whether a carbon atom in a compound is asymmetric?
- 11.44 Give examples of a chiral substituted alkane and an achiral substituted alkane.

### Problems

11.45 Which of these amino acids are chiral:

- $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$ ,
- $\text{CH}_2(\text{NH}_2)\text{COOH}$ ,
- $\text{CH}_2(\text{OH})\text{CH}(\text{NH}_2)\text{COOH}$ ?

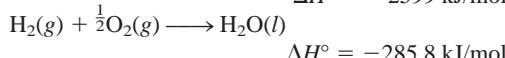
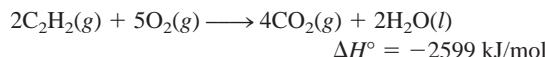
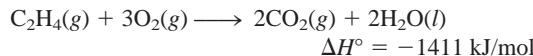
11.46 Indicate the asymmetric carbon atoms in these compounds:



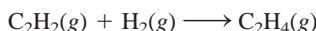
### Additional Problems

11.47 Draw all the possible structural isomers for the molecule having the formula  $\text{C}_7\text{H}_7\text{Cl}$ . The molecule contains one benzene ring.

11.48 Given these data



calculate the heat of hydrogenation for acetylene:



11.49 State which member of each of these pairs of compounds is the more reactive and explain why:  
(a) propane and cyclopropane, (b) ethylene and methane, (c) acetaldehyde and acetone.

11.50 Like ethylene, tetrafluoroethylene ( $\text{C}_2\text{F}_4$ ) undergoes polymerization reaction to form polytetrafluoroethylene (Teflon). Draw a repeating unit of the polymer.

11.51 An organic compound is found to contain 37.5 percent carbon, 3.2 percent hydrogen, and 59.3 percent fluorine by mass. These pressure and volume data were obtained for 1.00 g of this substance at  $90^\circ\text{C}$ :

P (atm)	V (L)
2.00	0.332
1.50	0.409
1.00	0.564
0.50	1.028

The molecule is known to have no dipole moment.  
(a) What is the empirical formula of this substance? (b) Does this substance behave as an ideal gas? (c) What is its molecular formula? (d) Draw the Lewis structure of this molecule and describe its geometry. (e) What is the systematic name of this compound?

11.52 State at least one commercial use for each of the following compounds: (a) 2-propanol, (b) acetic acid, (c) naphthalene, (d) methanol, (e) ethanol, (f) ethylene glycol, (g) methane, (h) ethylene.

11.53 How many liters of air (78 percent  $\text{N}_2$ , 22 percent  $\text{O}_2$  by volume) at  $20^\circ\text{C}$  and 1.00 atm are needed for the complete combustion of 1.0 L of octane,  $\text{C}_8\text{H}_{18}$ , a typical gasoline component that has a density of 0.70 g/mL?

11.54 How many carbon-carbon sigma bonds are present in each of these molecules? (a) 2-butyne, (b) anthracene (see Figure 11.16), (c) 2,3-dimethylpentane.

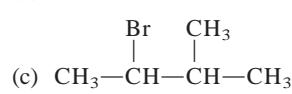
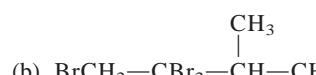
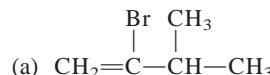
11.55 How many carbon-carbon sigma bonds are present in each of these molecules? (a) benzene, (b) cyclobutane, (c) 3-ethyl-2-methylpentane.

11.56 The combustion of 20.63 mg of compound Y, which contains only C, H, and O, with excess oxygen gave 57.94 mg of  $\text{CO}_2$  and 11.85 mg of  $\text{H}_2\text{O}$ . (a) Calculate how many milligrams of C, H, and O were present in the original sample of Y. (b) Derive the empirical formula of Y. (c) Suggest a plausible structure for Y if the empirical formula is the same as the molecular formula.

11.57 Draw all the structural isomers of compounds with the formula  $\text{C}_4\text{H}_8\text{Cl}_2$ . Indicate which isomers are chiral and give them systematic names.

11.58 The combustion of 3.795 mg of liquid B, which contains only C, H, and O, with excess oxygen gave 9.708 mg of  $\text{CO}_2$  and 3.969 mg of  $\text{H}_2\text{O}$ . In a molar mass determination, 0.205 g of B vaporized at 1.00 atm and  $200.0^\circ\text{C}$  and occupied a volume of 89.8 mL. Derive the empirical formula, molar mass, and molecular formula of B and draw three plausible structures.

11.59 Beginning with 3-methyl-1-butyne, show how you would prepare these compounds:



11.60 Write structural formulas for these compounds:  
(a) *trans*-2-pentene, (b) 2-ethyl-1-butene, (c) 4-ethyl-*trans*-2-heptene, (d) 3-phenyl-1-butyne.

**11.61** Suppose benzene contained three distinct single bonds and three distinct double bonds. How many different structural isomers would there be for dichlorobenzene ( $C_6H_4Cl_2$ )? Draw all your proposed structures.

**11.62** Write the structural formula of an aldehyde that is an isomer of acetone.

**11.63** Draw structures for these compounds: (a) cyclopentane, (b) *cis*-2-butene, (c) 2-hexanol, (d) 1,4-dibromobenzene, (e) 2-butyne.

**11.64** Name the classes to which these compounds belong:

- |                 |                   |
|-----------------|-------------------|
| (a) $C_4H_9OH$  | (b) $CH_3OC_2H_5$ |
| (c) $C_2H_5CHO$ | (d) $C_6H_5COOH$  |
| (e) $CH_3NH_2$  |                   |

**11.65** Ethanol,  $C_2H_5OH$ , and dimethyl ether,  $CH_3OCH_3$ , are structural isomers. Compare their melting points, boiling points, and solubilities in water.

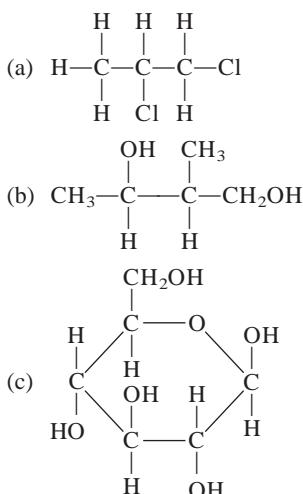
**11.66** Amines are Brønsted bases. The unpleasant smell of fish is due to the presence of certain amines. Explain why cooks often add lemon juice to suppress the odor of fish (in addition to enhancing the flavor).

**11.67** You are given two bottles, each containing a colorless liquid. You are told that one liquid is cyclohexane and the other is benzene. Suggest one chemical test that would enable you to distinguish between these two liquids.

**11.68** Give the chemical names of these organic compounds and write their formulas: marsh gas, grain alcohol, wood alcohol, rubbing alcohol, antifreeze, mothballs, chief ingredient of vinegar.

**11.69** The compound  $CH_3-C\equiv C-CH_3$  is hydrogenated to an alkene using platinum as the catalyst. If the product is the pure *cis* isomer, what can you deduce about the mechanism?

**11.70** How many asymmetric carbon atoms are present in each of these compounds?



**11.71** Isopropyl alcohol is prepared by reacting propene ( $CH_3CHCH_2$ ) with sulfuric acid, followed by treatment with water. (a) Show the sequence of steps leading to the product. What is the role of sulfuric acid? (b) Draw the structure of an alcohol that is an isomer of isopropyl alcohol. (c) Is isopropyl alcohol a chiral molecule? (d) What property of isopropyl alcohol makes it useful as a rubbing alcohol?

**11.72** When a mixture of methane and bromine vapor is exposed to light, this reaction occurs slowly:



Suggest a mechanism for this reaction. (Hint: Bromine vapor is deep red; methane is colorless.)

## SPECIAL PROBLEMS

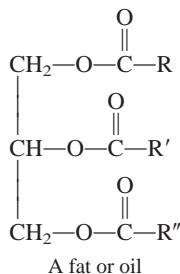
**11.73** Octane number is assigned to gasoline to indicate the tendency of “knocking” in the automobile’s engine. The higher the octane number, the more smoothly the fuel will burn without knocking. Branched-chain aliphatic hydrocarbons have higher octane numbers than straight-chain aliphatic hydrocarbons, and aromatic hydrocarbons have the highest octane numbers.

- (a) Arrange these compounds in the order of decreasing octane numbers: 2,2,4-trimethylpentane, toluene (methylbenzene), *n*-heptane, and 2-methylhexane.

(b) Oil refineries carry out *catalytic reforming* in which a straight-chain hydrocarbon, in the presence of a catalyst, is converted to an aromatic molecule and a useful by-product. Write an equation for the conversion from *n*-heptane to toluene.

(c) Until 2000, *tert*-butylmethyl ether had been widely used as an antiknocking agent to enhance the octane number of gasoline. Write the structural formula of the compound.

- 11.74** Fats and oils are names for the same class of compounds, called triglycerides, which contain three ester groups

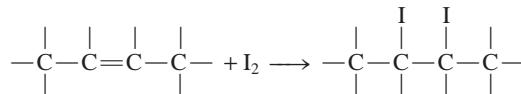


in which R, R', and R" represent long hydrocarbon chains.

- (a) Suggest a reaction that leads to the formation of a triglyceride molecule, starting with glycerol and carboxylic acids (see p. 398 for structure of glycerol).
- (b) In the old days, soaps were made by hydrolyzing animal fat with lye (a sodium hydroxide solution). Write an equation for this reaction.
- (c) The difference between fats and oils is that at room temperature, the former are solid and the latter are liquids. Fats are usually produced by animals, whereas oils are commonly found in plants. The melting points of these substances are determined by the number of C=C bonds (or the extent of unsaturation) present—the larger the number of C=C bonds, the lower the melting point and the more likely the substance is a liquid. Explain.
- (d) One way to convert liquid oil to solid fat is to hydrogenate the oil, a process by which some or all of the C=C bonds are converted to C—C bonds. This procedure prolongs shelf life of the oil by removing the more reactive C=C group and facilitates packaging. How

would you carry out such a process (that is, what reagents and catalyst would you employ)?

- (e) The degree of unsaturation of oil can be determined by reacting the oil with iodine, which reacts with the C=C as follows:



The procedure is to add a known amount of iodine to the oil and allow the reaction to go to completion. The amount of excess (unreacted) iodine is determined by titrating the remaining iodine with a standard sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) solution:



The number of grams of iodine that reacts with 100 g of oil is called the *iodine number*. In one case, 43.8 g of  $\text{I}_2$  were treated with 35.3 g of corn oil. The excess iodine required 20.6 mL of 0.142 M  $\text{Na}_2\text{S}_2\text{O}_3$  for neutralization. Calculate the iodine number of the corn oil.

- 11.75** 2-Butanone can be reduced to 2-butanol by reagents such as lithium aluminum hydride ( $\text{LiAlH}_4$ ). (a) Write the formula of the product. Is it chiral? (b) In reality, the product does not exhibit optical activity. Explain.
- 11.76** Write the structures of three alkenes that yield 2-methylbutane on hydrogenation.
- 11.77** Write the structural formulas of the alcohols with the formula  $\text{C}_6\text{H}_{13}\text{O}$  and indicate those that are chiral. Show only the C atoms and the —OH groups.
- 11.78** An alcohol was converted to a carboxylic acid with acidic potassium dichromate. A 4.46-g sample of the acid was added to 50.0 mL of 2.27 M NaOH and the excess NaOH required 28.7 mL of 1.86 M HCl for neutralization. What is the molecular formula of the alcohol?

## ANSWERS TO PRACTICE EXERCISES

**11.1 5.** **11.2** 4,6-diethyl-2-methyloctane



**11.3**  $\text{CH}_3-\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$

**11.4**  $\text{CH}_3\text{CH}_2\text{COOCH}_3$  and  $\text{H}_2\text{O}$ . **11.5** No.