24.6 INTRODUCTION TO BIOCHEMISTRY

We introduce the chemistry of living organisms, known as *biochemistry*, *biological chemistry*, or *chemical biology*. Important classes of compounds that occur in living systems are *proteins*, *carbohydrates*, *lipids*, and *nucleic acids*.

24.7 PROTEINS

We learn that proteins are polymers of *amino acids* linked with *amide* (also called *peptide*) bonds. Proteins are used for structural support and as molecular transporters and enzymes.

24.8 CARBOHYDRATES

We observe that carbohydrates are sugars and polymers of sugars used primarily as fuel by organisms (glucose) or as structural support in plants (cellulose).

24.9 LIPIDS

We recognize that lipids are a large class of molecules used primarily for energy storage in organisms.

24.10 NUCLEIC ACIDS

We learn that nucleic acids are polymers of *nucleotides* that contain an organism's genetic information. *Deoxyribonucleic acid* (DNA) and *ribonucleic acid* (RNA) are polymers composed of nucleotides.

THE CHEMISTRY OF LIFE: ORGANIC AND BIOLOGICAL CHEMISTRY

INSECTS COMMUNICATE BY RELEASING substances called pheromones, which they detect with their antennae. There are sex, alarm, defense, and trail pheromones. For example, isoamyl acetate [3-methylbutyl acetate, $(CH_3)_2CHCH_2COOCH_3$] is an alarm pheromone for bees, attracting other bees and provoking them to sting. Mammals, including humans, may also respond to pheromones, although the identity and function of pheromones in humans are not conclusive. Nevertheless, google "pheromone" and you will find hundreds of sources trying to sell you a pheromone, claiming that it will make you irresistible to the opposite sex.

Although biological systems are almost unimaginably complex, they are nevertheless constructed of molecules of quite modest size, as, for instance, the isoamyl acetate pheromone just described. To understand biology, therefore, we need to understand the chemical behaviors of molecules. This chapter is about the molecules, composed mainly of carbon, hydrogen, oxygen, and nitrogen, that form the basis of organic and biological chemistry.

More than 16 million carbon-containing compounds are known. Chemists make thousands of new compounds every year, about 90% of which contain carbon. The study of compounds whose molecules contain carbon constitutes the branch of chemistry known as **organic chemistry**. This term arose from the eighteenth-century belief that organic compounds could be formed only by living (that is, organic) systems. This idea was disproved in 1828 by the German chemist Friedrich Wöhler when he synthesized urea (H_2NCONH_2), an organic substance found in the urine of mammals, by heating ammonium cyanate (NH_4OCN), an inorganic (“nonliving”) substance.

The study of the chemistry of living species is called *biological chemistry*, *chemical biology*, or **biochemistry**. In this chapter, we present some of the elementary aspects of both organic chemistry and biochemistry.

24.1 GENERAL CHARACTERISTICS OF ORGANIC MOLECULES

What is it about carbon that leads to the tremendous diversity in its compounds and allows it to play such crucial roles in biology and society? Let’s consider some general features of organic molecules and, as we do, review principles we learned in earlier chapters.

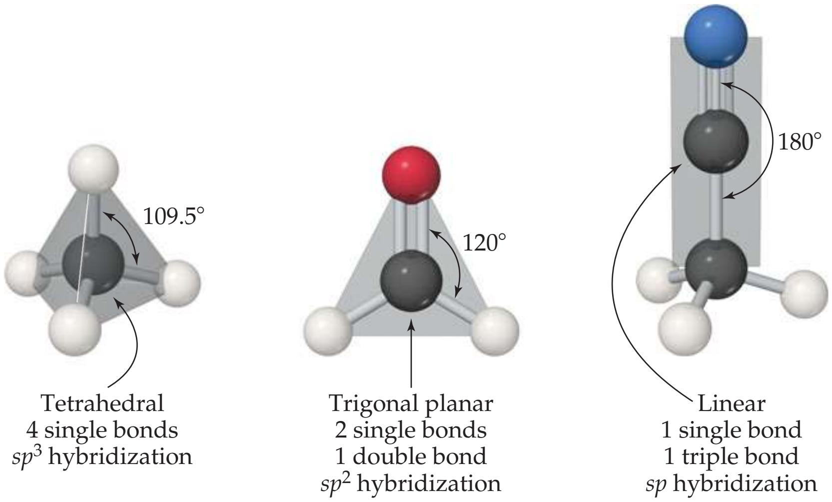
The Structures of Organic Molecules

Because carbon has four valence electrons ($[He]2s^22p^2$), it forms four bonds in virtually all its compounds. When all four bonds are single bonds, the electron pairs are disposed in a tetrahedral arrangement. (Section 9.2) In the hybridization model, the carbon 2*s* and 2*p* orbitals are then sp^3 hybridized. (Section 9.5) When there is one double bond, the arrangement is trigonal planar (sp^2 hybridization). With a triple bond, it is linear (*sp* hybridization). Examples are shown in ▼ **FIGURE 24.1**.

Almost every organic molecule contains C—H bonds. Because the valence shell of H can hold only two electrons, hydrogen forms only one covalent bond. As a result,

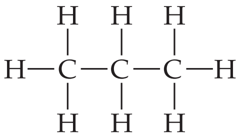
GO FIGURE

What is the geometry around the bottom carbon atom in acetonitrile?



► **FIGURE 24.1 Carbon geometries.** The three common geometries around carbon are tetrahedral as in methane (CH_4), trigonal planar as in formaldehyde (CH_2O), and linear as in acetonitrile (CH_3CN). Notice that in all cases each carbon atom forms four bonds.

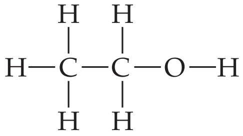
hydrogen atoms are always located on the *surface* of organic molecules whereas the C—C bonds form the *backbone*, or *skeleton*, of the molecule, as in the propane molecule:



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

The Stabilities of Organic Substances

Carbon forms strong bonds with a variety of elements, especially H, O, N, and the halogens. ∞ (Section 8.8) Carbon also has an exceptional ability to bond to itself, forming a variety of molecules made up of chains or rings of carbon atoms. Most reactions with low or moderate activation energy (Section 14.5) begin when a region of high electron density on one molecule encounters a region of low electron density on another molecule. The regions of high electron density may be due to the presence of a multiple bond or to the more electronegative atom in a polar bond. Because of their strength and lack of polarity, both C—C single bonds and C—H bonds are relatively unreactive. To better understand the implications of these facts, consider ethanol:



$$\begin{array}{ccccccccc} & & H & & H & & & & \\ & & | & & | & & & & \\ H & - & C & - & C & - & O & - & H \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array}$$

The differences in the electronegativity values of C (2.5) and O (3.5) and of O and H (2.1) indicate that the C—O and O—H bonds are quite polar. Thus, many reactions of ethanol involve these bonds while the hydrocarbon portion of the molecule remains intact. A group of atoms such as the C—O—H group, which determines how an organic molecule reacts (in other words, how the molecule *functions*), is called a **functional group**. The functional group is the center of reactivity in an organic molecule.

GIVE IT SOME THOUGHT

Which bond is most likely to be the location of a chemical reaction: C═N, C—C, or C—H?

Solubility and Acid–Base Properties of Organic Substances

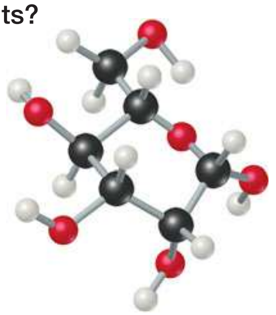
In most organic substances, the most prevalent bonds are carbon–carbon and carbon–hydrogen, which have low polarity. For this reason, the overall polarity of organic molecules is often low, which makes them generally soluble in nonpolar solvents and not very soluble in water. ∞ (Section 13.3) Organic molecules that are soluble in polar solvents are those that have polar groups on the molecule surface, such as glucose and ascorbic acid (▶ **FIGURE 24.2**). Organic molecules that have a long, nonpolar part bonded to a polar, ionic part, such as the stearate ion shown in Figure 24.2, function as *surfactants* and are used in soaps and detergents. ∞ (Section 13.6) The nonpolar part of the molecule extends into a nonpolar medium such as grease or oil, and the polar part extends into a polar medium such as water.

Many organic substances contain acidic or basic groups. The most important acidic organic substances are the carboxylic acids, which bear the functional group —COOH. ∞ (Sections 4.3 and 16.10) The most important basic organic substances are amines, which bear the —NH_2, —NHR, or —NR_2 groups, where R is an organic group made up of carbon and hydrogen atoms. ∞ (Section 16.7)

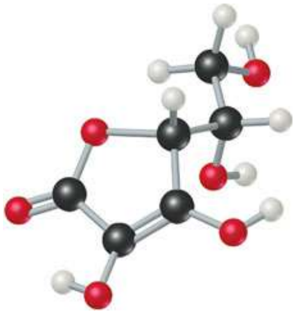
As you read this chapter, you will find many concept links (∞) to related materials in earlier chapters. *We strongly encourage you to follow these links and review the earlier material.* Doing so will enhance your understanding and appreciation of organic chemistry and biochemistry.

GO FIGURE

How would replacing OH groups on ascorbic acid with CH_3 groups affect the substance's solubility in (a) polar solvents and (b) nonpolar solvents?



Glucose ($C_6H_{12}O_6$)



Ascorbic acid ($HC_6H_7O_6$)

Stearate ($C_{17}H_{35}COO^-$)

▲ **FIGURE 24.2 Organic molecules soluble in polar solvents.**

24.2 INTRODUCTION TO HYDROCARBONS

Because carbon compounds are so numerous, it is convenient to organize them into families that have structural similarities. The simplest class of organic compounds is the *hydrocarbons*, compounds composed of only carbon and hydrogen. The key structural feature of hydrocarbons (and of most other organic substances) is the presence of stable carbon–carbon bonds. Carbon is the only element capable of forming stable, extended chains of atoms bonded through single, double, or triple bonds.

Hydrocarbons can be divided into four types, depending on the kinds of carbon–carbon bonds in their molecules. ▼ **TABLE 24.1** shows an example of each type.

Alkanes contain only single bonds. **Alkenes**, also known as *olefins*, contain at least one $C{=}C$ double bond, and **alkynes** contain at least one $C{\equiv}C$ triple bond. In **aromatic hydrocarbons** the carbon atoms are connected in a planar ring structure, joined by both σ and delocalized π bonds between carbon atoms. Benzene (C_6H_6) is the best-known example of an aromatic hydrocarbon.

Each type of hydrocarbon exhibits different chemical behaviors, as we will see shortly. The physical properties of all four types, however, are similar in many ways. Because hydrocarbon molecules are relatively nonpolar, they are almost completely insoluble in water but dissolve readily in nonpolar solvents. Their melting points and boiling points are determined by dispersion forces. (Section 11.2) As a result, hydrocarbons of very low molecular weight, such as C_2H_6 (bp $= -89$ °C), are gases at room temperature; those of moderate molecular weight, such as C_6H_{14} (bp $= 69$ °C), are liquids; and those of high molecular weight, such as $C_{22}H_{46}$ (mp $= 44$ °C), are solids.

▶ **TABLE 24.2** lists the ten simplest alkanes. Many of these substances are familiar because they are used so widely. Methane is a major component of natural gas and is used for home heating and in gas stoves and water heaters. Propane is the major component of bottled gas used for home heating and cooking in areas where natural gas is not available. Butane is used in disposable lighters and in fuel canisters for gas camping stoves and lanterns. Alkanes with from 5 to 12 carbon atoms per molecule are used to make gasoline. Notice that each succeeding compound in Table 24.2 has an additional CH_2 unit.

TABLE 24.1 • The Four Hydrocarbon Types

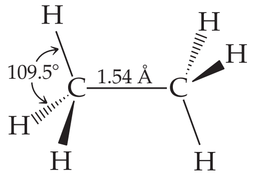
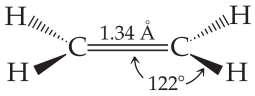
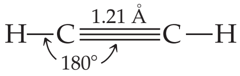
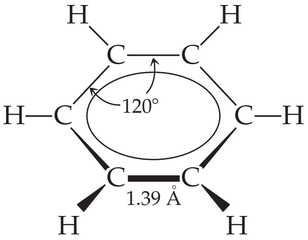
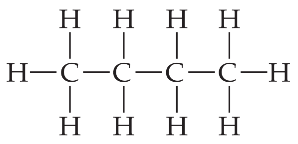
Type	Example			
Alkane	Ethane	CH_3CH_3		
Alkene	Ethylene	$CH_2{=}CH_2$		
Alkyne	Acetylene	$CH{\equiv}CH$		
Aromatic	Benzene	C_6H_6		

TABLE 24.2 • First Ten Members of the Straight-Chain Alkane Series

Molecular Formula	Condensed Structural Formula	Name	Boiling Point (°C)
CH_4	CH_4	Methane	−161
C_2H_6	CH_3CH_3	Ethane	−89
C_3H_8	$CH_3CH_2CH_3$	Propane	−44
C_4H_{10}	$CH_3CH_2CH_2CH_3$	Butane	−0.5
C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	Pentane	36
C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	Hexane	68
C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	Heptane	98
C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	Octane	125
C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	Nonane	151
$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	Decane	174

The formulas for the alkanes given in Table 24.2 are written in a notation called *condensed structural formulas*. This notation reveals the way in which atoms are bonded to one another but does not require drawing in all the bonds. For example, the structural formula and the condensed structural formulas for butane (C_4H_{10}) are



$$\begin{array}{ccccccccc} & & H & & H & & H & & H \\ & & | & & | & & | & & | \\ H & - & C & - & C & - & C & - & C & - H \\ & & | & & | & & | & & | \\ & & H & & H & & H & & H \end{array}$$

$$H_3C{-}CH_2{-}CH_2{-}CH_3$$

or

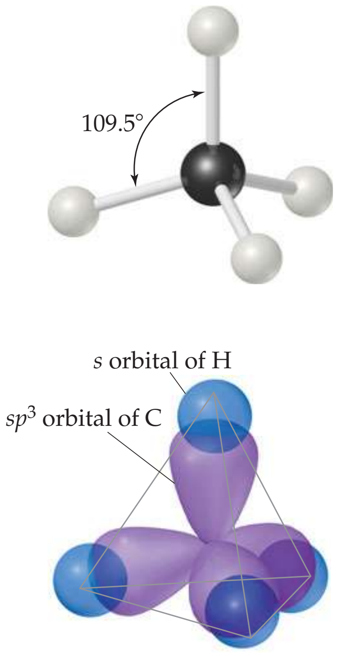
$$CH_3CH_2CH_2CH_3$$

GIVE IT SOME THOUGHT

How many C—H and C—C bonds are formed by the middle carbon atom of propane?

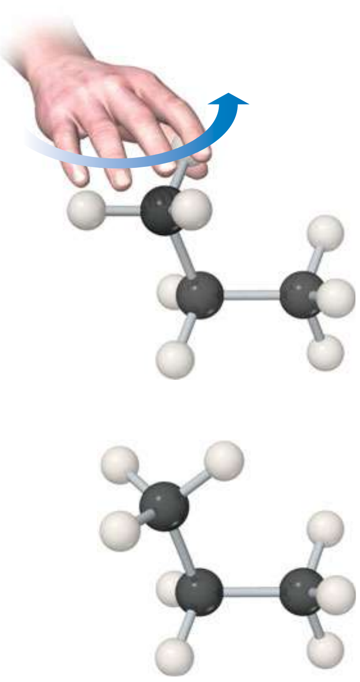
Structures of Alkanes

According to the VSEPR model, the molecular geometry about each carbon atom in an alkane is tetrahedral. (Section 9.2) The bonding may be described as involving sp^3-hybridized orbitals on the carbon, as pictured in ▶ **FIGURE 24.3** for methane. (Section 9.5)



▲ **FIGURE 24.3 Bonds about carbon in methane.** This tetrahedral molecular geometry is found around all carbons in alkanes.

Rotation about a carbon–carbon single bond is relatively easy and occurs rapidly at room temperature. To visualize such rotation, imagine grasping either methyl group of the propane molecule in ▶ **FIGURE 24.4** and rotating the group relative to the rest of the molecule. Because motion of this sort occurs rapidly in alkanes, a long-chain alkane molecule is constantly undergoing motions that cause it to change its shape, something like a length of chain that is being shaken.



▲ **FIGURE 24.4 Rotation about a C—C bond occurs easily and rapidly in all alkanes.**

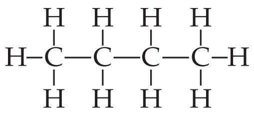
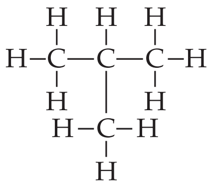
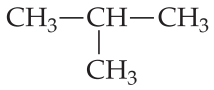
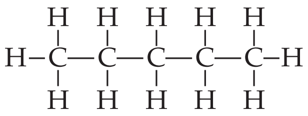
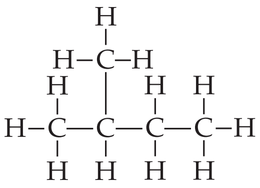
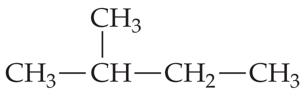
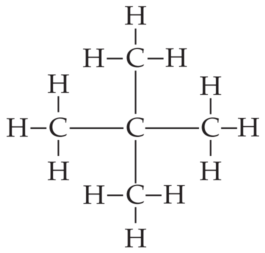
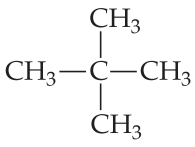
Structural Isomers

The alkanes in Table 24.2 are called *straight-chain hydrocarbons* because all the carbon atoms are joined in a continuous chain. Alkanes consisting of four or more carbon atoms can also form *branched chains*, and when they do, they are called *branched-chain hydrocarbons*. (The branches in organic molecules are often called *side chains*.) ▶ **TABLE 24.3**, for example, shows all the straight-chain and branched-chain alkanes containing four and five carbon atoms.

Compounds that have the same molecular formula but different bonding arrangements (and hence different structures) are called **structural isomers**. Thus, C_4H_{10} has two structural isomers and C_5H_{12} has three. The structural isomers of a given alkane differ slightly from one another in physical properties, as the melting and boiling points in Table 24.3 indicate.

The number of possible structural isomers increases rapidly with the number of carbon atoms in the alkane. There are 18 isomers with the molecular formula C_8H_{18}, for example, and 75 with the molecular formula $C_{10}H_{22}$.

TABLE 24.3 • Isomers of C_4H_{10} and C_5H_{12}

Systematic Name (Common Name)	Structural Formula	Condensed Structural Formula	Space-filling Model	Melting Point (°C)	Boiling Point (°C)
Butane (*n*-butane)		$CH_3CH_2CH_2CH_3$		−138 °C	−0.5 °C
2-Methylpropane (isobutane)		 $CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_3$		−159 °C	−12 °C
Pentane (*n*-pentane)		$CH_3CH_2CH_2CH_2CH_3$		−130 °C	+36 °C
2-Methylbutane (isopentane)		 $CH_3-\overset{\displaystyle CH_3}{\overset{\vert}{CH}}-CH_2-CH_3$		−160 °C	+28 °C
2,2-Dimethylpropane (neopentane)		 $CH_3-\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\displaystyle CH_3}{\underset{\vert}{C}}}}-CH_3$		−16 °C	+9 °C

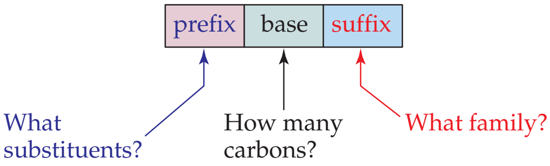
GIVE IT SOME THOUGHT

What evidence can you cite to support the fact that although isomers have the same molecular formula they are in fact different compounds?

Nomenclature of Alkanes

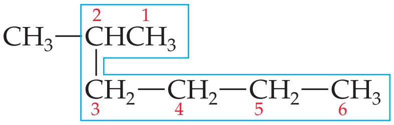
In the first column of Table 24.3, the names in parentheses are called the *common names*. The common name of the isomer with no branches begins with the letter *n* (indicating the “normal” structure). When one CH_3 group branches off the major chain, the common name of the isomer begins with *iso*-, and when two CH_3 groups branch off, the common name begins with *neo*-. As the number of isomers grows, however, it becomes impossible to find a suitable prefix to denote each isomer by a common name. The need for a systematic means of naming organic compounds was recognized as early as 1892, when an organization called the International Union of Chemistry met in Geneva to formulate rules for naming organic substances. Since that time the task of updating the rules for naming compounds has fallen to the International Union of Pure and Applied Chemistry (IUPAC). Chemists everywhere, regardless of their nationality, subscribe to a common system for naming compounds.

The IUPAC names for the isomers of butane and pentane are the ones given first in Table 24.3. These systematic names, as well as those of other organic compounds, have three parts to them:



The following steps summarize the procedures used to name alkanes, which all have names ending with -*ane*. We use a similar approach to write the names of other organic compounds.

1. **Find the longest continuous chain of carbon atoms, and use the name of this chain (given in Table 24.2) as the base name.** Be careful in this step because the longest chain may not be written in a straight line, as in the following structure:



2-Methyl*hexane*

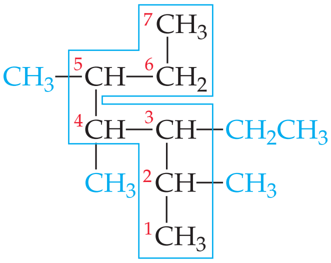
Because the longest continuous chain contains six C atoms, this isomer is named as a substituted hexane. Groups attached to the main chain are called *substituents* because they are substituted in place of an H atom on the main chain. In this molecule the CH_3 group not enclosed by the blue outline is the only substituent in the molecule.

2. **Number the carbon atoms in the longest chain, beginning with the end nearest a substituent.** In our example, we number the C atoms beginning at the upper right because that places the CH_3 substituent on C2 of the chain. (If we had numbered from the lower right, the CH_3 would be on C5.) The chain is numbered from the end that gives the lower number to the substituent position.

3. **Name each substituent.** A substituent formed by removing an H atom from an alkane is called an **alkyl group**. Alkyl groups are named by replacing the -*ane* ending of the alkane name with -*yl*. The methyl group (CH_3), for example, is derived from methane (CH_4) and the ethyl group (C_2H_5) is derived from ethane (C_2H_6). ▶ **TABLE 24.4** lists six common alkyl groups.

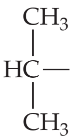
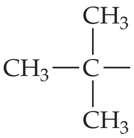
4. **Begin the name with the number or numbers of the carbon or carbons to which each substituent is bonded.** For our compound, the name 2-methylhexane indicates the presence of a methyl group on C2 of a hexane (six-carbon) chain.

5. **When two or more substituents are present, list them in alphabetical order.** The presence of two or more of the same substituent is indicated by the prefixes *di*- (two), *tri*- (three), *tetra*- (four), *penta*- (five), and so forth. The prefixes are ignored in determining the alphabetical order of the substituents:



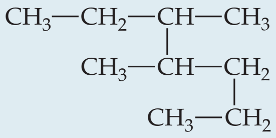
3-Ethyl-2,4,5-trimethylheptane

TABLE 24.4 • Condensed Structural Formulas and Common Names for Several Alkyl Groups

Group	Name
$CH_3—$	Methyl
$CH_3CH_2—$	Ethyl
$CH_3CH_2CH_2—$	Propyl
$CH_3CH_2CH_2CH_2—$	Butyl
	Isopropyl
	*tert*-Butyl

SAMPLE EXERCISE 24.1 Naming Alkanes

Give the systematic name for the following alkane:



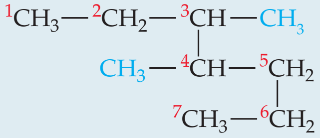
$$\begin{array}{ccccccc}
\mathrm{CH_3} & - & \mathrm{CH_2} & - & \mathrm{CH} & - & \mathrm{CH_3} \\
 & & & & | & & \\
 & & \mathrm{CH_3} & - & \mathrm{CH} & - & \mathrm{CH_2} \\
 & & & & & & | \\
 & & & & \mathrm{CH_3} & - & \mathrm{CH_2}
\end{array}$$

SOLUTION

Analyze We are given the condensed structural formula of an alkane and asked to give its name.

Plan Because the hydrocarbon is an alkane, its name ends in *-ane*. The name of the parent hydrocarbon is based on the longest continuous chain of carbon atoms. Branches are alkyl groups, named after the number of C atoms in the branch and located by counting C atoms along the longest continuous chain.

Solve The longest continuous chain of C atoms extends from the upper left CH_3 group to the lower left CH_3 group and is seven C atoms long:

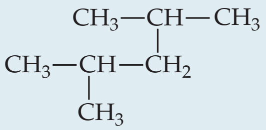


$$\begin{array}{ccccccc}
{}^{1}\mathrm{CH_3} & - & {}^{2}\mathrm{CH_2} & - & {}^{3}\mathrm{CH} & - & \mathrm{CH_3} \\
 & & & & | & & \\
 & & \mathrm{CH_3} & - & {}^{4}\mathrm{CH} & - & {}^{5}\mathrm{CH_2} \\
 & & & & & & | \\
 & & & & {}^{7}\mathrm{CH_3} & - & {}^{6}\mathrm{CH_2}
\end{array}$$

The parent compound is thus heptane. There are two methyl groups branching off the main chain. Hence, this compound is a dimethylheptane. To specify the location of the two methyl groups, we must number the C atoms from the end that gives the lower two numbers to the carbons bearing side chains. This means that we should start numbering at the upper left carbon. There is a methyl group on C3 and one on C4. The compound is thus 3,4-dimethylheptane.

PRACTICE EXERCISE

Name the following alkane:



$$\begin{array}{ccccccc}
 & & \mathrm{CH_3} & - & \mathrm{CH} & - & \mathrm{CH_3} \\
 & & & & | & & \\
\mathrm{CH_3} & - & \mathrm{CH} & - & \mathrm{CH_2} & & \\
 & & | & & & & \\
 & & \mathrm{CH_3} & & & &
\end{array}$$

Answer: 2,4-dimethylpentane

SAMPLE EXERCISE 24.2 Writing Condensed Structural Formulas

Write the condensed structural formula for 3-ethyl-2-methylpentane.

SOLUTION

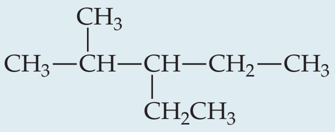
Analyze We are given the systematic name for a hydrocarbon and asked to write its condensed structural formula.

Plan Because the name ends in *-ane*, the compound is an alkane, meaning that all the carbon–carbon bonds are single bonds. The parent hydrocarbon is pentane, indicating five C atoms (Table 24.2). There are two alkyl groups specified, an ethyl group (two carbon atoms, C_2H_5) and a methyl group (one carbon atom, CH_3). Counting from left to right along the five-carbon chain, the name tells us that the ethyl group is attached to C3 and the methyl group is attached to C2.

Solve We begin by writing five C atoms attached by single bonds. These represent the backbone of the parent pentane chain:

$$\mathrm{C{-}C{-}C{-}C{-}C}$$

We next place a methyl group on the second C and an ethyl group on the third C of the chain. We then add hydrogens to all the other C atoms to make four bonds to each carbon:



$$\begin{array}{ccccccccc}
 & & \mathrm{CH_3} & & & & & & \\
 & & | & & & & & & \\
\mathrm{CH_3} & - & \mathrm{CH} & - & \mathrm{CH} & - & \mathrm{CH_2} & - & \mathrm{CH_3} \\
 & & & & | & & & & \\
 & & & & \mathrm{CH_2CH_3} & & & &
\end{array}$$

The formula can be written more concisely as

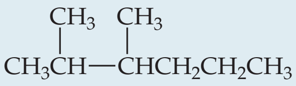
$$CH_3CH(CH_3)CH(C_2H_5)CH_2CH_3$$

where the branching alkyl groups are indicated in parentheses.

PRACTICE EXERCISE

Write the condensed structural formula for 2,3-dimethylhexane.

Answer:



$$\underset{}{CH_3\overset{\overset{CH_3}{|}}{C}H{-}\overset{\overset{CH_3}{|}}{C}HCH_2CH_2CH_3}$$

or $CH_3CH(CH_3)CH(CH_3)CH_2CH_2CH_3$

Cycloalkanes

Alkanes that form rings, or cycles, are called **cycloalkanes**. As ▼ **FIGURE 24.5** illustrates, cycloalkane structures are sometimes drawn as *line structures*, which are polygons in which each corner represents a CH_2 group. This method of representation is similar to that used for benzene rings. (Section 8.6) (Remember from our benzene discussion that in aromatic structures each vertex represents a CH group, not a CH_2 group.)

Carbon rings containing fewer than five carbon atoms are strained because the C—C—C bond angles must be less than the 109.5° tetrahedral angle. The amount of strain increases as the rings get smaller. In cyclopropane, which has the shape of an equilateral triangle, the angle is only 60°; this molecule is therefore much more reactive than propane, its straight-chain analog.

Reactions of Alkanes

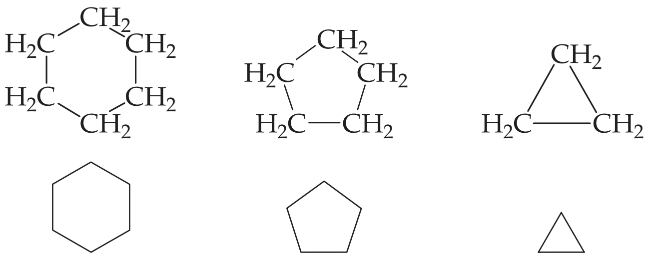
Because they contain only C—C and C—H bonds, most alkanes are relatively unreactive. At room temperature, for example, they do not react with acids, bases, or strong oxidizing agents. Their low chemical reactivity, as noted in Section 24.1, is due primarily to the strength and lack of polarity of C—C and C—H bonds.

Alkanes are not completely inert, however. One of their most commercially important reactions is *combustion* in air, which is the basis of their use as fuels. (Section 3.2) For example, the complete combustion of ethane proceeds as follows:

$$2\,C_2H_6(g) + 7\,O_2(g) \longrightarrow 4\,CO_2(g) + 6\,H_2O(l) \qquad \Delta H^\circ = -2855\text{ kJ}$$

GO FIGURE

The general formula for straight-chain alkanes is C_nH_{2n+2}. What is the general formula for cycloalkanes?



Cyclohexane

Each vertex represents one CH_2 group

Cyclopentane

Five vertices = five CH_2 groups

Cyclopropane

Three vertices = three CH_2 groups

▲ **FIGURE 24.5 Condensed structural formulas and line structures for three cycloalkanes.**

CHEMISTRY PUT TO WORK

Gasoline

Petroleum, or crude oil, is a mixture of hydrocarbons plus smaller quantities of other organic compounds containing nitrogen, oxygen, or sulfur. The tremendous demand for petroleum to meet the world's energy needs has led to the tapping of oil wells in such forbidding places as the North Sea and northern Alaska.

The usual first step in the *refining*, or processing, of petroleum is to separate it into fractions on the basis of boiling point (▼ **TABLE 24.5**). Because gasoline is the most commercially important of these fractions, various processes are used to maximize its yield.

Gasoline is a mixture of volatile alkanes and aromatic hydrocarbons. In a traditional automobile engine, a mixture of air and gasoline vapor is compressed by a piston and then ignited by a spark plug. The burning of the gasoline should create a strong, smooth expansion of gas, forcing the piston outward and imparting force along the driveshaft of the engine. If the gas burns too rapidly, the piston receives a single hard slam rather than a strong, smooth push. The result is a "knocking" or "pinging" sound and a reduction in the efficiency with which energy produced by the combustion is converted to work.

The *octane number* of a gasoline is a measure of its resistance to knocking. Gasolines with high octane numbers burn more smoothly and are thus more effective fuels (▶ **FIGURE 24.6**). Branched alkanes and aromatic hydrocarbons have higher octane numbers than straight-chain alkanes. The octane number of gasoline is obtained by comparing its knocking characteristics with those of isooctane (2,2,4-trimethylpentane) and heptane. Isooctane is assigned an octane number of 100, and heptane is assigned 0. Gasoline with the same knocking characteristics as a mixture of 91% isooctane and 9% heptane, for instance, is rated as 91 octane.

TABLE 24.5 • Hydrocarbon Fractions from Petroleum

Fraction	Size Range of Molecules	Boiling-Point Range (°C)	Uses
Gas	C_1 to C_5	−160 to 30	Gaseous fuel, production of H_2
Straight-run gasoline	C_5 to C_{12}	30 to 200	Motor fuel
Kerosene, fuel oil	C_{12} to C_{18}	180 to 400	Diesel fuel, furnace fuel, cracking
Lubricants	C_{16} and up	350 and up	Lubricants
Paraffins	C_{20} and up	Low-melting solids	Candles, matches
Asphalt	C_{36} and up	Gummy residues	Surfacing roads

▲ **FIGURE 24.6 Octane rating.** The octane rating of gasoline measures its resistance to knocking when burned in an engine. The octane rating of the gasoline in the foreground is 89.

The gasoline obtained by fractionating petroleum (called *straight-run* gasoline) contains mainly straight-chain hydrocarbons and has an octane number around 50. To increase its octane rating, it is subjected to a process called *reforming*, which converts the straight-chain alkanes into branched-chain ones.

Cracking is used to produce aromatic hydrocarbons and to convert some of the less-volatile fractions of petroleum into compounds suitable for use as automobile fuel. In cracking, the hydrocarbons are mixed with a catalyst and heated to 400 °C to 500 °C. The catalysts used are either clay minerals or synthetic Al_2O_3–SiO_2 mixtures. In addition to forming molecules more suitable for gasoline, cracking results in the formation of such low-molecular-weight hydrocarbons as ethylene and propene. These substances are used in a variety of reactions to form plastics and other chemicals.

Adding compounds called either *antiknock agents* or octane enhancers increases the octane rating of gasoline. Until the mid-1970s the principal antiknock agent was tetraethyl lead, $(C_2H_5)_4Pb$. It is no longer used, however, because of the environmental hazards of lead and because it poisons catalytic converters. ∞∞ (Section 14.7 "Chemistry Put to Work: Catalytic Converters") Aromatic compounds such as toluene ($C_6H_5CH_3$) and oxygenated hydrocarbons such as ethanol (CH_3CH_2OH) are now generally used as antiknock agents.

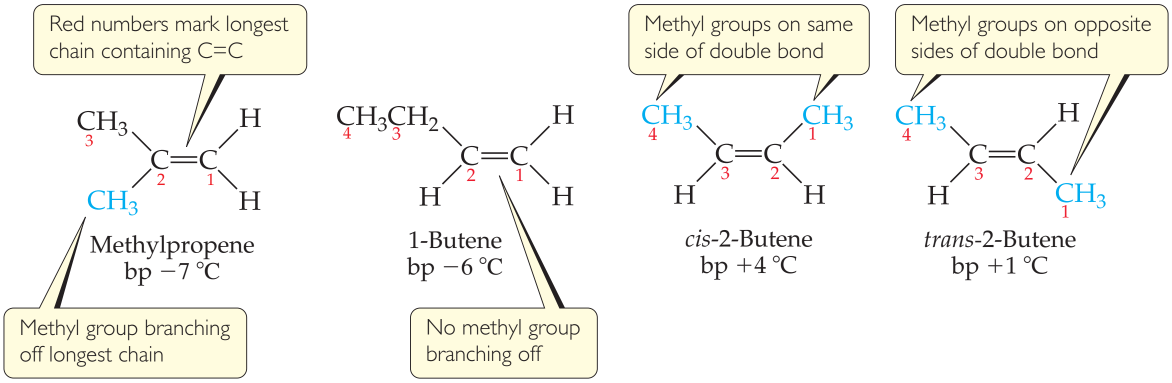
RELATED EXERCISES: 24.19 and 24.20

24.3 ALKENES, ALKYNES, AND AROMATIC HYDROCARBONS

Because alkanes have only single bonds, they contain the largest possible number of hydrogen atoms per carbon atom. As a result, they are called *saturated hydrocarbons*. Alkenes, alkynes, and aromatic hydrocarbons contain multiple bonds (double, triple, or delocalized π bonds). As a result, they contain less hydrogen than an alkane with the

GO FIGURE

How many isomers are there for propene, C_3H_6?



Red numbers mark longest chain containing C=C

Methyl group branching off longest chain

No methyl group branching off

Methyl groups on same side of double bond

Methyl groups on opposite sides of double bond

▲ **FIGURE 24.7** **The alkene C_4H_8 has four structural isomers.**

same number of carbon atoms. Collectively, they are called *unsaturated hydrocarbons*. On the whole, unsaturated molecules are more reactive than saturated ones.

Alkenes

Alkenes are unsaturated hydrocarbons that contain at least one $C{=}C$ bond. The simplest alkene is $CH_2{=}CH_2$, called ethene (IUPAC) or ethylene, which plays important roles as a plant hormone in seed germination and fruit ripening. The next member of the series is $CH_3{-}CH{=}CH_2$, called propene or propylene. Alkenes with four or more carbon atoms have several isomers. For example, the alkene C_4H_8 has the four structural isomers shown in ▲ **FIGURE 24.7**. Notice both their structures and their names.

The names of alkenes are based on the longest continuous chain of carbon atoms that contains the double bond. The chain is named by changing the ending of the name of the corresponding alkane from -*ane* to -*ene*. The compound on the left in Figure 24.7, for example, has a double bond as part of a three-carbon chain; thus, the parent alkene is propene.

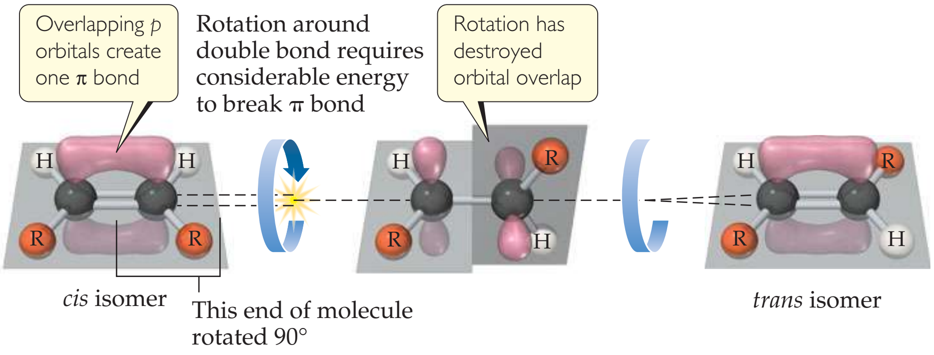
The location of the double bond along an alkene chain is indicated by a prefix number that designates the double-bond carbon atom that is nearest an end of the chain. The chain is always numbered from the end that brings us to the double bond sooner and hence gives the smallest-numbered prefix. In propene the only possible location for the double bond is between the first and second carbons; thus, a prefix indicating its location is unnecessary. For butene (Figure 24.7) there are two possible positions for the double bond, either after the first carbon (1-butene) or after the second carbon (2-butene).

GIVE IT SOME THOUGHT

How many distinct locations are there for a double bond in a five-carbon linear chain?

If a substance contains two or more double bonds, the location of each is indicated by a numerical prefix, and the ending of the name is altered to identify the number of double bonds: diene (two), triene (three), and so forth. For example, $CH_2{=}CH{-}CH_2{-}CH{=}CH_2$ is 1,4-pentadiene.

The two isomers on the right in Figure 24.7 differ in the relative locations of their methyl groups. These two compounds are **geometric isomers**, compounds that have the same molecular formula and the same groups bonded to one another but differ in the spatial arrangement of these groups. ∞∞ (Section 23.4) In the cis isomer the two methyl groups are on the same side of the double bond, whereas in the trans isomer they are on opposite sides. Geometric isomers possess distinct physical properties and can differ significantly from each other in their chemical behavior.



▶ FIGURE 24.8 Geometric isomers exist because rotation about a carbon–carbon double bond requires too much energy to occur at ordinary temperatures.

Geometric isomerism in alkenes arises because, unlike the C—C bond, the C═C bond resists twisting. Recall from Section 9.6 that the double bond between two carbon atoms consists of a σ and a π bond. ▲ **FIGURE 24.8** shows a cis alkene. The carbon–carbon bond axis and the bonds to the hydrogen atoms and to the alkyl groups (designated R) are all in a plane, and the p orbitals that form the π bond are perpendicular to that plane. As Figure 24.8 shows, rotation around the carbon–carbon double bond requires the π bond to be broken, a process that requires considerable energy (about 250 kJ/mol). Because rotation doesn't occur easily around the carbon–carbon bond, the cis and trans isomers of an alkene cannot readily interconvert and, therefore, exist as distinct compounds.

SAMPLE EXERCISE 24.3 Drawing Isomers

Draw all the structural and geometric isomers of pentene, C_5H_{10}, that have an unbranched hydrocarbon chain.

SOLUTION

Analyze We are asked to draw all the isomers (both structural and geometric) for an alkene with a five-carbon chain.

Plan Because the compound is named pentene and not pentadiene or pentatriene, we know that the five-carbon chain contains only one carbon–carbon double bond. Thus, we begin by placing the double bond in various locations along the chain, remembering that the chain can be numbered from either end. After finding the different unique locations for the double bond, we consider whether the molecule can have cis and trans isomers.

Solve There can be a double bond after either the first carbon (1-pentene) or second carbon (2-pentene). These are the only two possibilities because the chain can be numbered from either end. Thus, what we might erroneously call 3-pentene is actually 2-pentene, as seen by numbering the carbon chain from the other end:

$$\overset{1}{C}{=}\overset{2}{C}{-}\overset{3}{C}{-}\overset{4}{C}{-}\overset{5}{C}$$

$$\overset{1}{C}{-}\overset{2}{C}{=}\overset{3}{C}{-}\overset{4}{C}{-}\overset{5}{C}$$

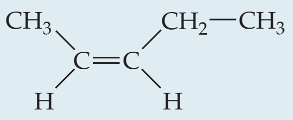
$$\overset{1}{C}{-}\overset{2}{C}{-}\overset{3}{C}{=}\overset{4}{C}{-}\overset{5}{C} \quad \text{renumbered as} \quad \overset{5}{C}{-}\overset{4}{C}{-}\overset{3}{C}{=}\overset{2}{C}{-}\overset{1}{C}$$

$$\overset{1}{C}{-}\overset{2}{C}{-}\overset{3}{C}{-}\overset{4}{C}{=}\overset{5}{C} \quad \text{renumbered as} \quad \overset{5}{C}{-}\overset{4}{C}{-}\overset{3}{C}{-}\overset{2}{C}{=}\overset{1}{C}$$

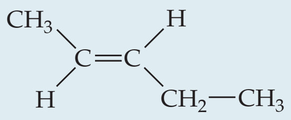
Because the first C atom in 1-pentene is bonded to two H atoms, there are no cis-trans isomers. There are cis and trans isomers for 2-pentene, however. Thus, the three isomers for pentene are

$$CH_2{=}CH{-}CH_2{-}CH_2{-}CH_3$$

1-Pentene



cis-2-Pentene



trans-2-Pentene

(You should convince yourself that *cis*-3-pentene is identical to *cis*-2-pentene and *trans*-3-pentene is identical to *trans*-2-pentene. However, *cis*-2-pentene and *trans*-2-pentene are the correct names because they have smaller numbered prefixes.)

PRACTICE EXERCISE

How many straight-chain isomers are there of hexene, C_6H_{12}?

Answer: five (1-hexene, *cis*-2-hexene, *trans*-2-hexene, *cis*-3-hexene, *trans*-3-hexene)

Alkynes

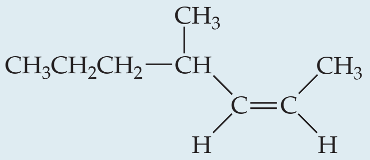
Alkynes are unsaturated hydrocarbons containing one or more $C{\equiv}C$ bonds. The simplest alkyne is acetylene (C_2H_2), a highly reactive molecule. When acetylene is burned in a stream of oxygen in an oxyacetylene torch, the flame reaches about 3200 K. Because alkynes in general are highly reactive, they are not as widely distributed in nature as alkenes; alkynes, however, are important intermediates in many industrial processes.

Alkynes are named by identifying the longest continuous chain containing the triple bond and modifying the ending of the name of the corresponding alkane from *-ane* to *-yne*, as shown in Sample Exercise 24.4.

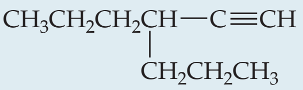
SAMPLE EXERCISE 24.4 Naming Unsaturated Hydrocarbons

Name the following compounds:

(a)



(b)



$$CH_3CH_2CH_2\underset{\displaystyle CH_2CH_2CH_3}{\underset{|}{CH}}{-}C{\equiv}CH$$

SOLUTION

Analyze We are given the condensed structural formulas for an alkene and an alkyne and asked to name the compounds.

Plan In each case the name is based on the number of carbon atoms in the longest continuous carbon chain that contains the multiple bond. In the alkene, care must be taken to indicate whether cis-trans isomerism is possible and, if so, which isomer is given.

Solve

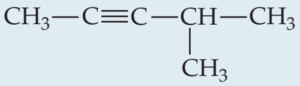
(a) The longest continuous chain of carbons that contains the double bond is seven carbons long, so the parent hydrocarbon is heptene. Because the double bond begins at carbon 2 (numbering from the end closer to the double bond), we have 2-heptene. With a methyl group at carbon atom 4, we have 4-methyl-2-heptene. The geometrical configuration at the double bond is cis (that is, the alkyl groups are bonded to the double bond on the same side). Thus, the full name is 4-methyl-*cis*-2-heptene.

(b) The longest continuous chain containing the triple bond has six carbons, so this compound is a derivative of hexyne. The triple bond comes after the first carbon (numbering from the right), making it 1-hexyne. The branch from the hexyne chain contains three carbon atoms, making it a propyl group. Because this substituent is located on C3 of the hexyne chain, the molecule is 3-propyl-1-hexyne.

PRACTICE EXERCISE

Draw the condensed structural formula for 4-methyl-2-pentyne.

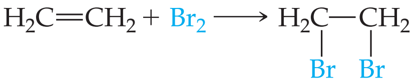
Answer:



$$CH_3{-}C{\equiv}C{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_3$$

Addition Reactions of Alkenes and Alkynes

The presence of carbon–carbon double or triple bonds in hydrocarbons markedly increases their chemical reactivity. The most characteristic reactions of alkenes and alkynes are **addition reactions**, in which a reactant is added to the two atoms that form the multiple bond. A simple example is the addition of a halogen to ethylene:



$$H_2C{=}CH_2 + Br_2 \longrightarrow \underset{\displaystyle Br}{\underset{|}{H_2C}}{-}\underset{\displaystyle Br}{\underset{|}{CH_2}} \qquad [24.1]$$

The pair of electrons that forms the π bond in ethylene is uncoupled and is used to form two σ bonds to the two bromine atoms. The σ bond between the carbon atoms is retained.

Addition of H_2 to an alkene converts it to an alkane:

$$CH_3CH{=}CHCH_3 + H_2 \xrightarrow{\text{Ni, 500 °C}} CH_3CH_2CH_2CH_3 \qquad [24.2]$$

The reaction between an alkene and H_2, referred to as *hydrogenation*, does not occur readily at ordinary temperatures and pressures. One reason for the lack of reactivity of H_2 toward alkenes is the stability of the H_2 bond. To promote the reaction, a catalyst is used to assist in rupturing the H—H bond. The most widely used catalysts are finely divided metals on which H_2 is adsorbed. (Section 14.7)

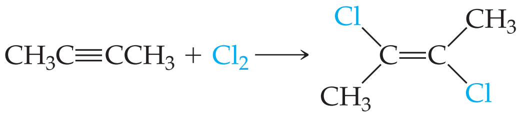
Hydrogen halides and water can also add to the double bond of alkenes, as in these reactions of ethylene:

$$CH_2{=}CH_2 + HBr \longrightarrow CH_3CH_2Br \qquad [24.3]$$

$$CH_2{=}CH_2 + H_2O \xrightarrow{H_2SO_4} CH_3CH_2OH \qquad [24.4]$$

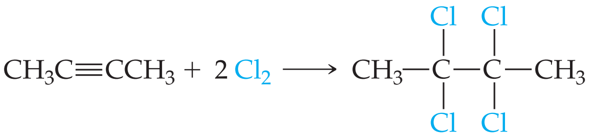
The addition of water is catalyzed by a strong acid, such as H_2SO_4.

The addition reactions of alkynes resemble those of alkenes, as shown in these examples:



[24.5]

2-Butyne *trans*-2,3-Dichloro-2-butene



$$CH_3C{\equiv}CCH_3 + 2\,Cl_2 \longrightarrow CH_3{-}\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}}{-}\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}}{-}CH_3$$

[24.6]

2-Butyne 2,2,3,3-Tetrachlorobutane

SAMPLE EXERCISE 24.5 Identifying the Product of a Hydrogenation Reaction

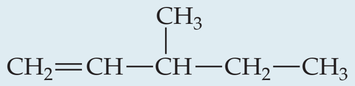
Write the condensed structural formula for the product of the hydrogenation of 3-methyl-1-pentene.

SOLUTION

Analyze We are asked to predict the compound formed when a particular alkene undergoes hydrogenation (reaction with H_2) and to write the condensed structural formula of the product.

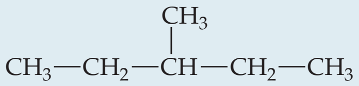
Plan To determine the condensed structural formula of the product, we must first write the condensed structural formula or Lewis structure of the reactant. In the hydrogenation of the alkene, H_2 adds to the double bond, producing an alkane.

Solve The name of the starting compound tells us that we have a chain of five C atoms with a double bond at one end (position 1) and a methyl group on C3:



$$CH_2{=}CH{-}\overset{\overset{CH_3}{|}}{CH}{-}CH_2{-}CH_3$$

Hydrogenation—the addition of two H atoms to the carbons of the double bond—leads to the following alkane:



$$CH_3{-}CH_2{-}\overset{\overset{CH_3}{|}}{CH}{-}CH_2{-}CH_3$$

Comment The longest chain in this alkane has five carbon atoms; the product is therefore 3-methylpentane.

PRACTICE EXERCISE

Addition of HCl to an alkene forms 2-chloropropane. What is the alkene?

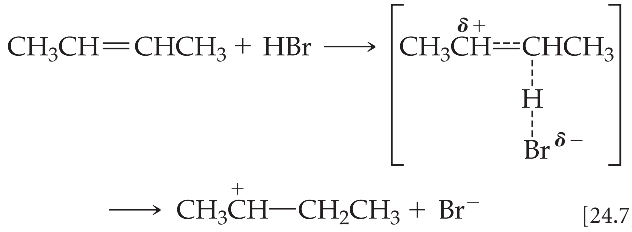
Answer: propene

A CLOSER LOOK

MECHANISM OF ADDITION REACTIONS

As the understanding of chemistry has grown, chemists have advanced from simply cataloging reactions known to occur to explaining *how* they occur. An explanation of how a reaction occurs is called a *mechanism.* (Section 14.6)

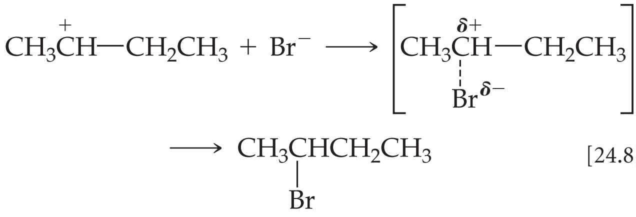
The addition reaction between HBr and an alkene, for instance, is thought to proceed in two steps. In the first step, which is rate determining (Section 14.6), the HBr attacks the electron-rich double bond, transferring a proton to one of the double-bond carbons. In the reaction of 2-butene with HBr, for example, the first step is



$$\mathrm{CH_3CH{=}CHCH_3 + HBr \longrightarrow \left[\begin{array}{c}\mathrm{CH_3\overset{\delta+}{C}H{\cdots}CHCH_3}\\ \vdots\\ \mathrm{H}\\ \vdots\\ \mathrm{Br^{\delta-}}\end{array}\right] \longrightarrow CH_3\overset{+}{C}H{-}CH_2CH_3 + Br^-} \quad [24.7]$$

The electron pair that formed the π bond is used to form the new C—H bond.

The second, faster step is addition of Br^- to the positively charged carbon. The bromide ion donates a pair of electrons to the carbon, forming the C—Br bond:



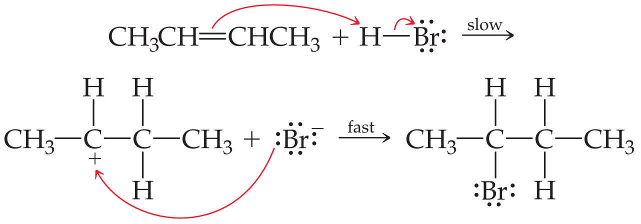
$$\mathrm{CH_3\overset{+}{C}H{-}CH_2CH_3 + Br^- \longrightarrow \left[\begin{array}{c}\mathrm{CH_3\overset{\delta+}{C}H{-}CH_2CH_3}\\ \vdots\\ \mathrm{Br^{\delta-}}\end{array}\right] \longrightarrow CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_2CH_3} \quad [24.8]$$

Because the rate-determining step involves both the alkene and the acid, the rate law for the reaction is second order, first order in the alkene and first order in HBr:

$$\text{Rate} = -\frac{\Delta[\mathrm{CH_3CH{=}CHCH_3}]}{\Delta t} = k[\mathrm{CH_3CH{=}CHCH_3}][\mathrm{HBr}] \quad [24.9]$$

The energy profile for the reaction is shown in ▼ **FIGURE 24.9**. The first energy maximum represents the transition state in the first step, and the second maximum represents the transition state in the second step. The energy minimum represents the energies of the intermediate species, $\mathrm{CH_3\overset{+}{C}H{-}CH_2CH_3}$ and $\mathrm{Br^-}$.

To show electron movement in reactions like these, chemists often use curved arrows pointing in the direction of electron flow. For the addition of HBr to 2-butene, for example, the shifts in electron positions are shown as

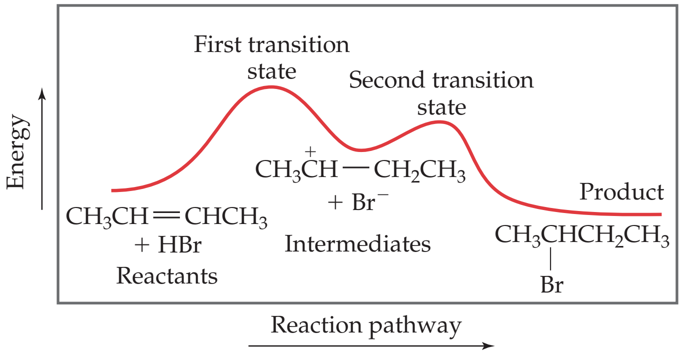


$$\mathrm{CH_3CH{=}CHCH_3 + H{-}\ddot{\underset{..}{Br}}{:} \xrightarrow{slow}}$$

$$\mathrm{CH_3{-}\underset{+}{\overset{\displaystyle H}{\overset{|}{C}}}{-}\underset{\underset{\displaystyle H}{|}}{\overset{\displaystyle H}{\overset{|}{C}}}{-}CH_3 + {:}\ddot{\underset{..}{Br}}{:}^- \xrightarrow{fast} CH_3{-}\underset{\underset{\displaystyle :\ddot{Br}:}{|}}{\overset{\displaystyle H}{\overset{|}{C}}}{-}\underset{\underset{\displaystyle H}{|}}{\overset{\displaystyle H}{\overset{|}{C}}}{-}CH_3}$$

GO FIGURE

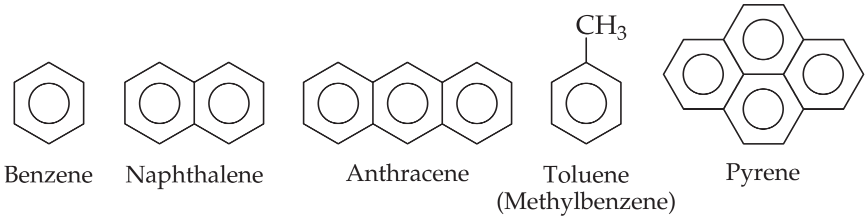
What features of an energy profile allow you to distinguish between an intermediate and a transition state?



▲ **FIGURE 24.9 Energy profile for addition of HBr to 2-butene.** The two maxima tell you that this is a two-step mechanism.

Aromatic Hydrocarbons

The simplest aromatic hydrocarbon, benzene (C_6H_6), is shown in ▼ **FIGURE 24.10** along with some other aromatic hydrocarbons. Benzene is the most important aromatic hydrocarbon, and most of our discussion focuses on it.



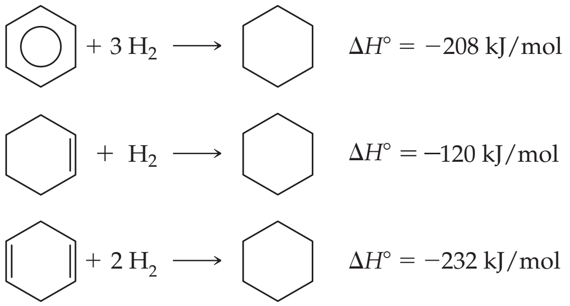
Benzene Naphthalene Anthracene Toluene (Methylbenzene) Pyrene

◀ **FIGURE 24.10 Line formulas and common names of several aromatic compounds.** The aromatic rings are represented by hexagons with a circle inscribed inside to denote delocalized π bonds. Each corner represents a carbon atom. Each carbon is bound to three other atoms—either three carbons or two carbons and a hydrogen—so that each carbon has the requisite four bonds.

Stabilization of π Electrons by Delocalization

The planar structure of benzene, with its 120° bond angles, suggests a high degree of unsaturation. You might therefore expect benzene to resemble the alkenes and to be highly reactive. Benzene and the other aromatic hydrocarbons, however, are much more stable than alkenes because the π electrons are delocalized in the π orbitals. ∞ (Section 9.6)

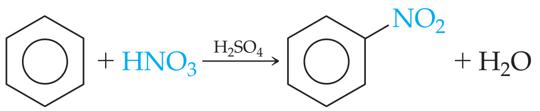
We can estimate the stabilization of the π electrons in benzene by comparing the energy required to form cyclohexane by adding hydrogen to benzene, to cyclohexene (one double bond) and to 1,4-cyclohexadiene (two double bonds):



From the second and third reactions, it appears that the energy required to hydrogenate each double bond is roughly 118 kJ/mol for each bond. Benzene contains the equivalent of three double bonds. We might expect, therefore, the energy required to hydrogenate benzene to be about 3 times −118, or −354 kJ/mol, if benzene behaved as though it were "cyclohexatriene," that is, if it behaved as though it had three isolated double bonds in a ring. Instead, the energy released is 146 kJ less than this, indicating that benzene is more stable than would be expected for three double bonds. The difference of 146 kJ/mol between the "expected" heat (that is, enthalpy) of hydrogenation, −354 kJ/mol, and the observed heat of hydrogenation, −208 kJ/mol, is due to stabilization of the π electrons through delocalization in the π orbitals that extend around the ring.

Substitution Reactions

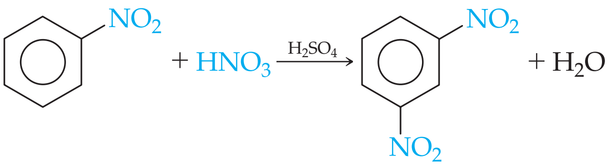
Although aromatic hydrocarbons are unsaturated, *they do not readily undergo addition reactions*. The delocalized π bonding causes aromatic compounds to behave quite differently from alkenes and alkynes. Benzene, for example, does not add Cl_2 or Br_2 to its double bonds under ordinary conditions. In contrast, aromatic hydrocarbons undergo **substitution reactions** relatively easily. In a substitution reaction one hydrogen atom of a molecule is removed and replaced (substituted) by another atom or group of atoms. When benzene is warmed in a mixture of nitric and sulfuric acids, for example, one of the benzene hydrogens is replaced by the nitro group, NO_2:



[24.10]

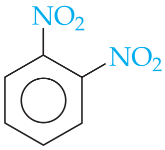
Benzene Nitrobenzene

More vigorous treatment results in substitution of a second nitro group into the molecule:

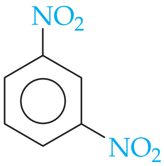


[24.11]

There are three isomers of benzene that contain two nitro groups—*ortho*-, *meta*-, and *para*-dinitrobenzene:



ortho-Dinitrobenzene
mp 118 °C

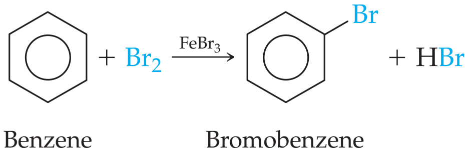


meta-Dinitrobenzene
mp 90 °C

para-Dinitrobenzene
mp 174 °C

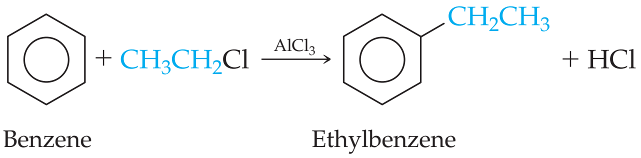
In the reaction of Equation 24.11, the principal product is the *meta* isomer.

Bromination of benzene, carried out with $FeBr_3$ as a catalyst, is another substitution reaction:



[24.12]

In a similar reaction, called the *Friedel-Crafts reaction*, alkyl groups can be substituted onto an aromatic ring by reacting an alkyl halide with an aromatic compound in the presence of $AlCl_3$ as a catalyst:



[24.13]

GIVE IT SOME THOUGHT

When the aromatic hydrocarbon naphthalene, shown in Figure 24.10, reacts with nitric and sulfuric acids, two compounds containing one nitro group are formed. Draw the structures of these two compounds.

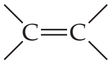
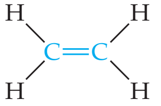
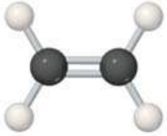
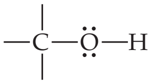
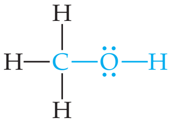
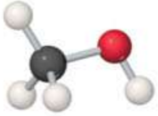
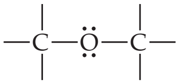
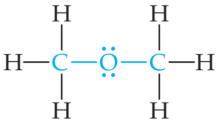
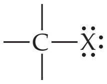
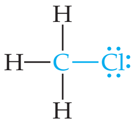
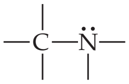
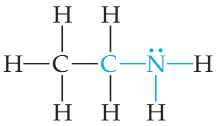
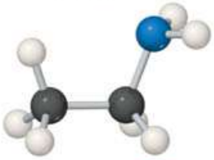
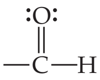
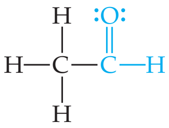
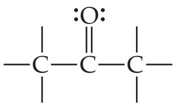
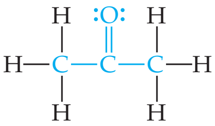
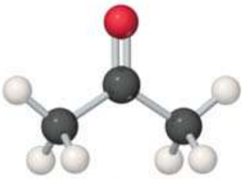
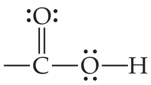
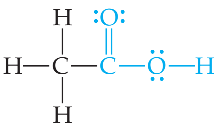
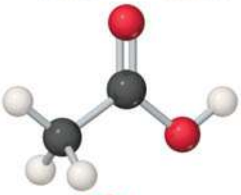
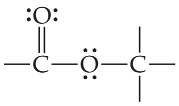
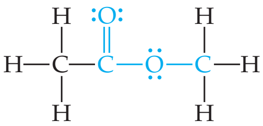
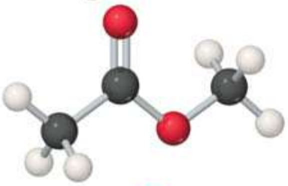
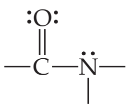
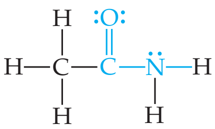
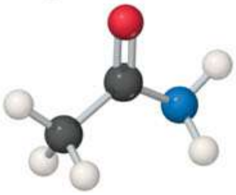
24.4 | ORGANIC FUNCTIONAL GROUPS

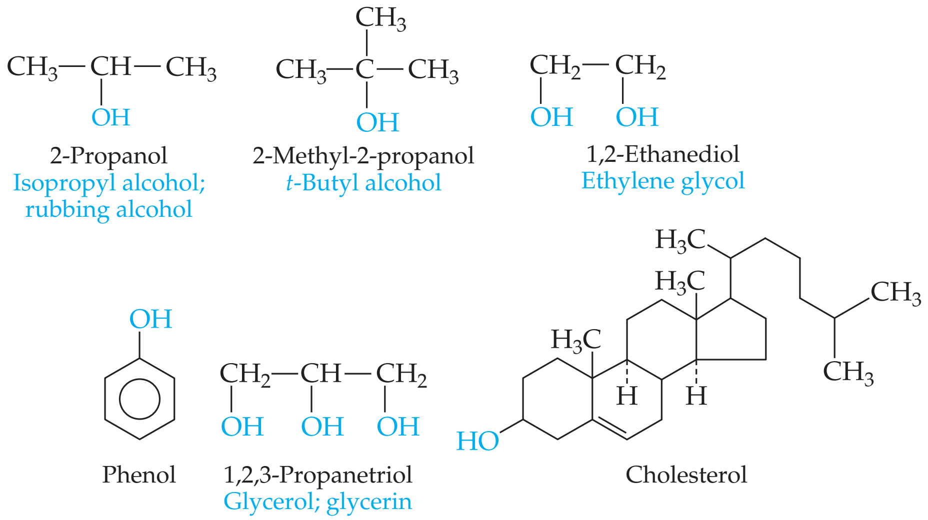
The $C{=}C$ double bonds of alkenes and $C{\equiv}C$ triple bonds of alkynes are just two of many functional groups in organic molecules. As noted earlier, these functional groups each undergo characteristic reactions, and the same is true of all other functional groups. Each kind of functional group often undergoes the same kinds of reactions in every molecule, regardless of the size and complexity of the molecule. Thus, the chemistry of an organic molecule is largely determined by the functional groups it contains.

▶ **TABLE 24.6** lists the most common functional groups. Notice that, except for $C{=}C$ and $C{\equiv}C$, they all contain either O, N, or a halogen atom, X.

We can think of organic molecules as being composed of functional groups bonded to one or more alkyl groups. The alkyl groups, which are made of $C{-}C$ and $C{-}H$ single bonds, are the less reactive portions of the molecules. In describing general features of organic compounds, chemists often use the designation R to represent any alkyl group: methyl, ethyl, propyl, and so on. Alkanes, for example, which contain no functional group, are represented as $R{-}H$. Alcohols, which contain the group $-OH$, are represented as $R{-}OH$. If two or more different alkyl groups are present in a molecule, we designate them R, R′, R″, and so forth.

TABLE 24.6 • Common Functional Groups

			Example		
Functional Group	**Compound Type**	**Suffix or Prefix**	**Structural Formula**	**Ball-and-stick Model**	**Systematic Name** (common name)
	Alkene	*-ene*			Ethene (Ethylene)
—C≡C—	Alkyne	*-yne*	H—C≡C—H		Ethyne (Acetylene)
	Alcohol	*-ol*			Methanol (Methyl alcohol)
	Ether	*ether*			Dimethyl ether
 (X = halogen)	Haloalkane	*halo-*			Chloromethane (Methyl chloride)
	Amine	*-amine*			Ethylamine
	Aldehyde	*-al*			Ethanal (Acetaldehyde)
	Ketone	*-one*			Propanone (Acetone)
	Carboxylic acid	*-oic acid*			Ethanoic acid (Acetic acid)
	Ester	*-oate*			Methyl ethanoate (Methyl acetate)
	Amide	*-amide*			Ethanamide (Acetamide)



◀ **FIGURE 24.11 Condensed structural formulas of six important alcohols.** Common names are given in blue.

Alcohols

Alcohols are hydrocarbon derivatives in which one or more hydrogens of a parent hydrocarbon have been replaced by the functional group —OH, called either the *hydroxyl group* or the *alcohol group*. Note in ▲ **FIGURE 24.11** that the name for an alcohol ends in *-ol*. The simple alcohols are named by changing the last letter in the name of the corresponding alkane to *-ol*—for example, ethan*e* becomes ethan*ol*. Where necessary, the location of the OH group is designated by a numeric prefix that indicates the number of the carbon atom bearing the OH group.

The O—H bond is polar, so alcohols are much more soluble in polar solvents than are hydrocarbons. The —OH functional group can also participate in hydrogen bonding. As a result, the boiling points of alcohols are much higher than those of their parent alkanes.

▶ **FIGURE 24.12** shows several commercial products that consist entirely or in large part of an organic alcohol.

▲ **FIGURE 24.12 Everyday alcohols.** Many of the products we use every day—from rubbing alcohol to hair spray and antifreeze—are composed either entirely or mainly of alcohols.

The simplest alcohol, methanol (methyl alcohol), has many industrial uses and is produced on a large scale by heating carbon monoxide and hydrogen under pressure in the presence of a metal oxide catalyst:

$$\mathrm{CO}(g) + 2\,\mathrm{H_2}(g) \xrightarrow[400\ ^\circ\mathrm{C}]{200-300\ \mathrm{atm}} \mathrm{CH_3OH}(g) \qquad [24.14]$$

Because methanol has a very high octane rating as an automobile fuel, it is used as a gasoline additive and as a fuel in its own right.

Ethanol (ethyl alcohol, C_2H_5OH) is a product of the fermentation of carbohydrates such as sugars and starches. In the absence of air, yeast cells convert these carbohydrates into ethanol and CO_2:

$$\mathrm{C_6H_{12}O_6}(aq) \xrightarrow{\text{yeast}} 2\,\mathrm{C_2H_5OH}(aq) + 2\,\mathrm{CO_2}(g) \qquad [24.15]$$

In the process, the yeast cells derive energy necessary for growth. This reaction is carried out under carefully controlled conditions to produce beer, wine, and other beverages in which ethanol is the active ingredient.

The simplest polyhydroxyl alcohol (an alcohol containing more than one OH group) is 1,2-ethanediol (ethylene glycol, $HOCH_2CH_2OH$), the major ingredient in automobile antifreeze. Another common polyhydroxyl alcohol is 1,2,3-propanetriol [glycerol, $HOCH_2CH(OH)CH_2OH$], a viscous liquid that dissolves readily in water and is used in cosmetics as a skin softener and in foods and candies to keep them moist.

Phenol is the simplest compound with an OH group attached to an aromatic ring. One of the most striking effects of the aromatic group is the greatly increased acidity of the OH group. Phenol is about 1 million times more acidic in water than a nonaromatic alcohol. Even so, it is not a very strong acid ($K_a = 1.3 \times 10^{-10}$). Phenol is used industrially to make plastics and dyes, and as a topical anesthetic in throat sprays.

Cholesterol, shown in Figure 24.11, is a biochemically important alcohol. The OH group forms only a small component of this molecule, so cholesterol is only slightly soluble in water (0.26 g per 100 mL of H_2O). Cholesterol is a normal component of our bodies; when present in excessive amounts, however, it may precipitate from solution. It precipitates in the gallbladder to form crystalline lumps called *gallstones*. It may also precipitate against the walls of veins and arteries and thus contribute to high blood pressure and other cardiovascular problems.

Ethers

Compounds in which two hydrocarbon groups are bonded to one oxygen are called **ethers**. Ethers can be formed from two molecules of alcohol by splitting out a molecule of water. The reaction is catalyzed by sulfuric acid, which takes up water to remove it from the system:

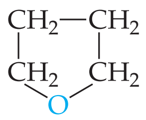
$$CH_3CH_2{-}OH + H{-}OCH_2CH_3 \xrightarrow{H_2SO_4} CH_3CH_2{-}O{-}CH_2CH_3 + H_2O \qquad [24.16]$$

A reaction in which water is split out from two substances is called a *condensation reaction*. (Sections 12.8 and 22.8)

Both diethyl ether and the cyclic ether tetrahydrofuran are common solvents for organic reactions:

$$CH_3CH_2{-}O{-}CH_2CH_3$$

Diethyl ether

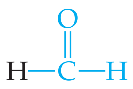


Tetrahydrofuran (THF)

Aldehydes and Ketones

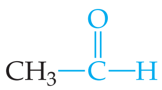
Several of the functional groups listed in Table 24.6 contain the **carbonyl group**, C=O. This group, together with the atoms attached to its carbon, defines several important functional groups that we consider in this section.

In **aldehydes** the carbonyl group has at least one hydrogen atom attached:



$$H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H$$

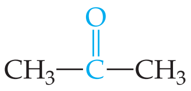
Methanal
Formaldehyde



$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H$$

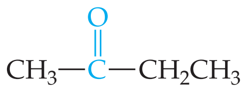
Ethanal
Acetaldehyde

In **ketones** the carbonyl group occurs at the interior of a carbon chain and is therefore flanked by carbon atoms:



$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$$

Propanone
Acetone



$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2CH_3$$

2-Butanone
Methyl ethyl ketone

Notice that the systematic names of aldehydes contain *-al* and that ketone names contain *-one*.

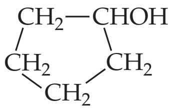
Aldehydes and ketones can be prepared by controlled oxidation of alcohols. Complete oxidation results in formation of CO_2 and H_2O, as in the burning of methanol:

$$CH_3OH(g) + \tfrac{3}{2}\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g)$$

Controlled partial oxidation to form other organic substances, such as aldehydes and ketones, is carried out by using various oxidizing agents, such as air, hydrogen peroxide (H_2O_2), ozone (O_3), and potassium dichromate ($K_2Cr_2O_7$).

GIVE IT SOME THOUGHT

Write the condensed structural formula for the ketone that would result from partial oxidation of the alcohol



Many compounds found in nature contain an aldehyde or ketone functional group. Vanilla and cinnamon flavorings are naturally occurring aldehydes. Two isomers of the ketone carvone impart the characteristic flavors of spearmint leaves and caraway seeds.

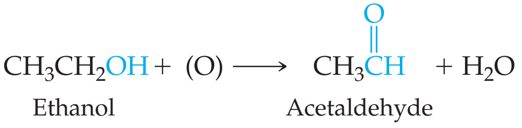
Ketones are less reactive than aldehydes and are used extensively as solvents. Acetone, the most widely used ketone, is completely miscible with water, yet it dissolves a wide range of organic substances.

Carboxylic Acids and Esters

Carboxylic acids contain the *carboxyl* functional group, often written COOH. ∞ (Section 16.10) These weak acids are widely distributed in nature and are common in consumer products [▶ **FIGURE 24.13**(a)]. They are also important in the manufacture of polymers used to make fibers, films, and paints. ▼ **FIGURE 24.14** shows the formulas of several carboxylic acids.

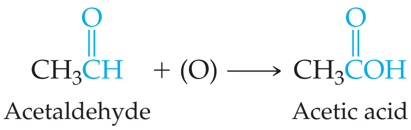
The common names of many carboxylic acids are based on their historical origins. Formic acid, for example, was first prepared by extraction from ants; its name is derived from the Latin word *formica*, "ant."

Carboxylic acids can be produced by oxidation of alcohols in which the OH group is attached to a CH_2 group. Under appropriate conditions, the aldehyde may be isolated as the first product of oxidation, as in the sequence



$$\underset{\text{Ethanol}}{\mathrm{CH_3CH_2OH}} + (\mathrm{O}) \longrightarrow \underset{\text{Acetaldehyde}}{\mathrm{CH_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{H}} + \mathrm{H_2O}$$

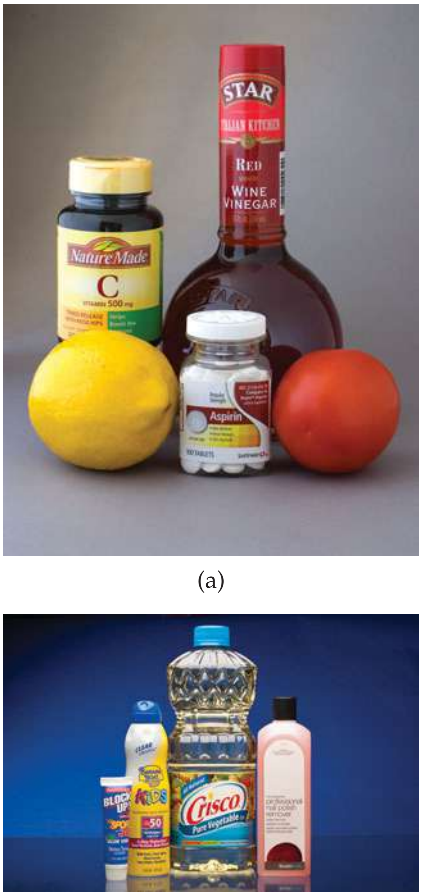
[24.17]



$$\underset{\text{Acetaldehyde}}{\mathrm{CH_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{H}} + (\mathrm{O}) \longrightarrow \underset{\text{Acetic acid}}{\mathrm{CH_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OH}}$$

[24.18]

where (O) represents any oxidant that can provide oxygen atoms. The air oxidation of ethanol to acetic acid is responsible for causing wines to turn sour, producing vinegar.



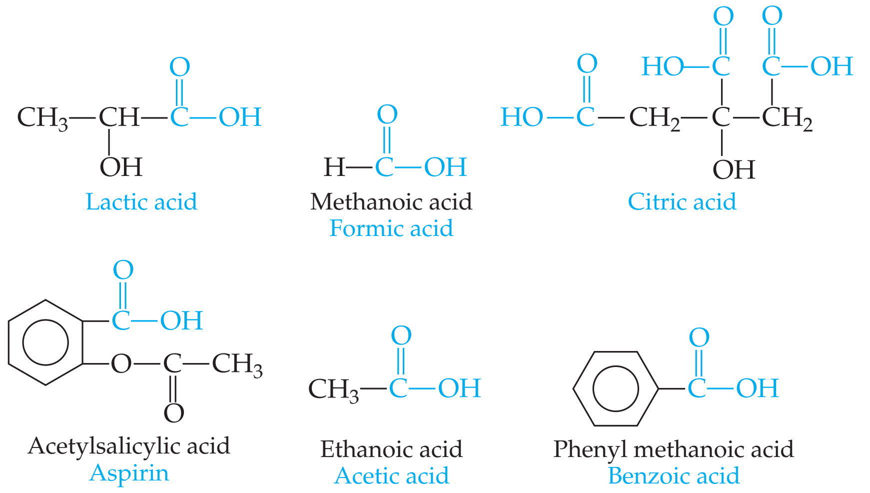
(a)

(b)

▲ **FIGURE 24.13 Everyday carboxylic acids and esters.** (a) Vinegar contains acetic acid; vitamin C is ascorbic acid; citrus fruits and tomatoes contain citric acid; and aspirin is acetylsalicylic acid (which is both an acid and an ester). (b) Many sunburn lotions contain the ester benzocaine; some nail polish removers contain ethyl acetate; vegetable oils are also esters.

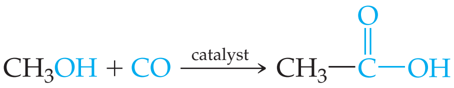
GO FIGURE

Which of these substances have both a carboxylic acid functional group and an alcohol functional group?



◀ **FIGURE 24.14 Structural formulas of common carboxylic acids.** The monocarboxylic acids are generally referred to by their common names, given in blue type.

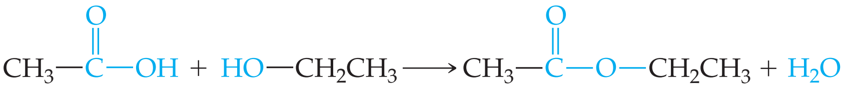
Acetic acid can also be produced by the reaction of methanol with carbon monoxide in the presence of a rhodium catalyst:



$$CH_3OH + CO \xrightarrow{\text{catalyst}} CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH \qquad [24.19]$$

This reaction involves, in effect, the insertion of a carbon monoxide molecule between the CH_3 and OH groups. A reaction of this kind is called *carbonylation*.

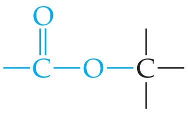
Carboxylic acids can undergo condensation reactions with alcohols to form esters:



$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH + HO{-}CH_2CH_3 \longrightarrow CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}CH_2CH_3 + H_2O \qquad [24.20]$$

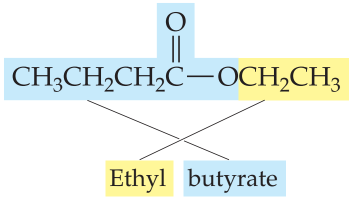
Acetic acid Ethanol Ethyl acetate

Esters are compounds in which the H atom of a carboxylic acid is replaced by a carbon-containing group:



$$-\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}\overset{|}{\underset{|}{C}}{-}$$

Figure 24.13(b) shows some commercial products containing esters. The name of any ester consists of the name of the group contributed by the alcohol followed by the name of the group contributed by the carboxylic acid, with the *-ic* replaced by *-ate*. For example, the ester formed from ethyl alcohol, CH_3CH_2OH, and butyric acid, $CH_3(CH_2)_2COOH$, is

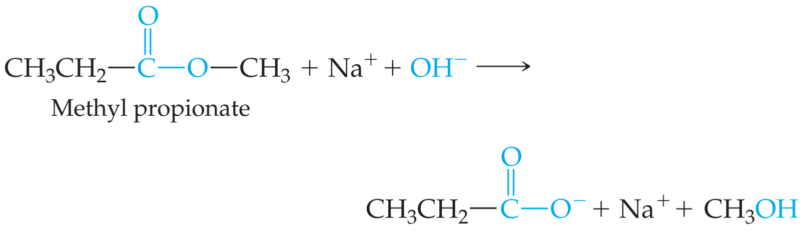


$$CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}{-}OCH_2CH_3$$

Notice that the chemical formula generally has the group originating from the acid written first, which is opposite of the way the ester is named.

Esters generally have very pleasant odors and are largely responsible for the pleasant aromas of fruit. Pentyl acetate ($CH_3COOCH_2CH_2CH_2CH_2CH_3$), for example, is responsible for the odor of bananas.

An ester treated with an acid or a base in aqueous solution is *hydrolyzed*; that is, the molecule is split into an alcohol and a carboxylic acid or its anion:



$$CH_3CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}CH_3 + Na^+ + OH^- \longrightarrow$$

Methyl propionate

$$CH_3CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^- + Na^+ + CH_3OH \qquad [24.21]$$

Sodium propionate Methanol

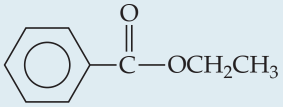
The **hydrolysis** of an ester in the presence of a base is called **saponification**, a term that comes from the Latin word for soap, *sapon*. Naturally occurring esters include fats and oils, and in making soap an animal fat or a vegetable oil is boiled with a strong base. The resultant soap consists of a mixture of salts of long-chain carboxylic acids (called fatty acids), which form during the saponification reaction. ∞ (Section 13.6)

Soap has been manufactured and used for thousands of years. Directions for making soap from cassia oil were written on a Babylonian clay tablet around 2200 B.C. For a long time, soap was made by heating animal fat with wood ashes, which contain potassium carbonate (also known as potash) and made the solution basic. (Section 16.9) The modern commercial process for making soap usually uses sodium hydroxide as the base. Using potassium hydroxide produces soft or liquid soaps.

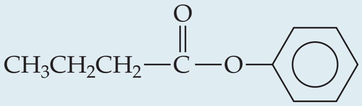
SAMPLE EXERCISE 24.6 Naming Esters and Predicting Hydrolysis Products

In a basic aqueous solution, esters react with hydroxide ion to form the salt of the carboxylic acid and the alcohol from which the ester is constituted. Name each of the following esters, and indicate the products of their reaction with aqueous base.

(a)



(b)



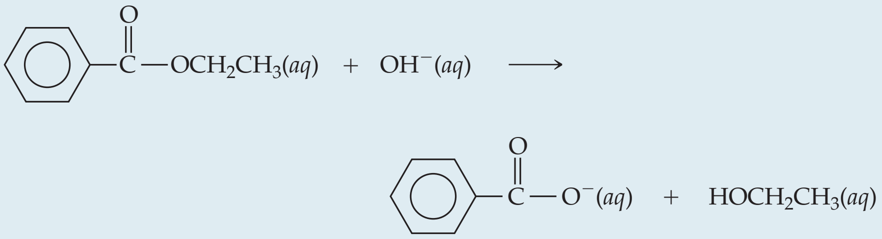
SOLUTION

Analyze We are given two esters and asked to name them and to predict the products formed when they undergo hydrolysis (split into an alcohol and carboxylate ion) in basic solution.

Plan Esters are formed by the condensation reaction between an alcohol and a carboxylic acid. To name an ester, we must analyze its structure and determine the identities of the alcohol and acid from which it is formed. We can identify the alcohol by adding an OH to the alkyl group attached to the O atom of the carboxyl (COO) group. We can identify the acid by adding an H to the O atom of the carboxyl group. We have learned that the first part of an ester name indicates the alcohol portion and the second indicates the acid portion. The name conforms to how the ester undergoes hydrolysis in base, reacting with base to form an alcohol and a carboxylate anion.

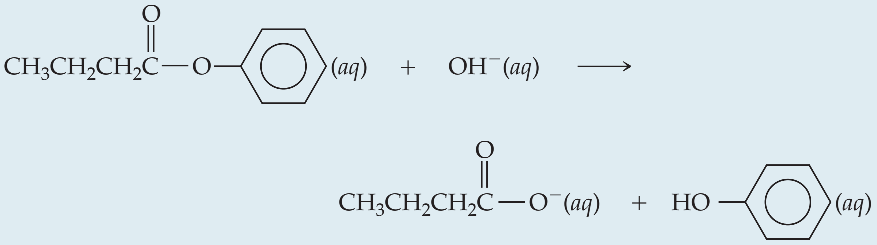
Solve

(a) This ester is derived from ethanol (CH_3CH_2OH) and benzoic acid (C_6H_5COOH). Its name is therefore ethyl benzoate. The net ionic equation for reaction of ethyl benzoate with hydroxide ion is



The products are benzoate ion and ethanol.

(b) This ester is derived from phenol (C_6H_5OH) and butanoic acid (commonly called butyric acid) ($CH_3CH_2CH_2COOH$). The residue from the phenol is called the phenyl group. The ester is therefore named phenyl butyrate. The net ionic equation for the reaction of phenyl butyrate with hydroxide ion is

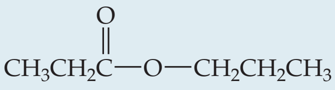


The products are butyrate ion and phenol.

PRACTICE EXERCISE

Write the condensed structural formula for the ester formed from propyl alcohol and propionic acid.

Answer:



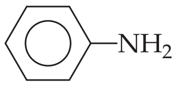
$$CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}CH_2CH_2CH_3$$

Amines and Amides

Amines are compounds in which one or more of the hydrogens of ammonia (NH_3) are replaced by an alkyl group:

$CH_3CH_2NH_2$ Ethylamine

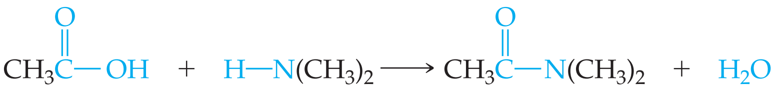
$(CH_3)_3N$ Trimethylamine



Phenylamine
Aniline

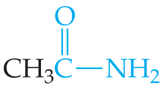
As we have seen earlier, they are the most common organic bases. (Section 16.7)

An amine with at least one H bonded to N can undergo a condensation reaction with a carboxylic acid to form an **amide**, which contains the carbonyl group (C═O) attached to N (Table 24.6):



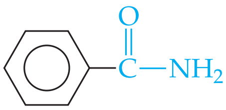
$$\mathrm{CH_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{OH} + \mathrm{H}-\mathrm{N(CH_3)_2} \longrightarrow \mathrm{CH_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{N(CH_3)_2} + \mathrm{H_2O} \qquad [24.22]$$

We may consider the amide functional group to be derived from a carboxylic acid with an NRR′ group replacing the OH of the acid, as in these examples:



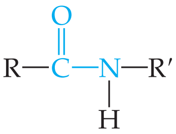
$$\mathrm{CH_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{NH_2}$$

Ethanamide
Acetamide



Phenylmethanamide
Benzamide

The amide linkage

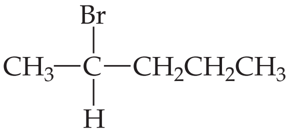


$$\mathrm{R}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}-\mathrm{R'}$$

where R and R′ are organic groups, is the key functional group in proteins, as we will see in Section 24.7.

24.5 CHIRALITY IN ORGANIC CHEMISTRY

A molecule possessing a nonsuperimposable mirror image is termed **chiral** (Greek *cheir*, “hand”). (Section 23.4) *Compounds containing carbon atoms with four different attached groups are inherently chiral.* A carbon atom with four different attached groups is called a *chiral center*. For example, consider 2-bromopentane:



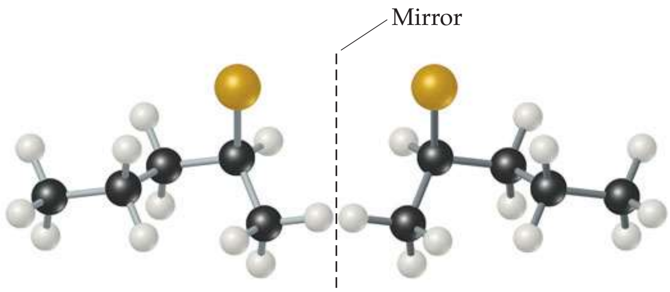
$$\mathrm{CH_3}-\underset{\mathrm{H}}{\underset{|}{\overset{\mathrm{Br}}{\overset{|}{\mathrm{C}}}}}-\mathrm{CH_2CH_2CH_3}$$

All four groups attached to C2 are different, making that carbon a chiral center. ◀ **FIGURE 24.15** illustrates the nonsuperimposable mirror images of this molecule. Imagine moving the molecule shown to the left of the mirror over to the right of the mirror. If you then turn it in every possible way, you will conclude that it cannot be superimposed on the molecule shown to the right of the mirror. Nonsuperimposable mirror images are called either *optical isomers* or *enantiomers*. (Section 23.4) Organic chemists use the labels *R* and *S* to distinguish the two forms. We need not go into the rules for deciding on the labels.

The two members of an enantiomer pair have identical physical properties and identical chemical properties when they react with nonchiral reagents. Only in a chiral environment do they

GO FIGURE

If you replace Br with CH_3, will the compound be chiral?

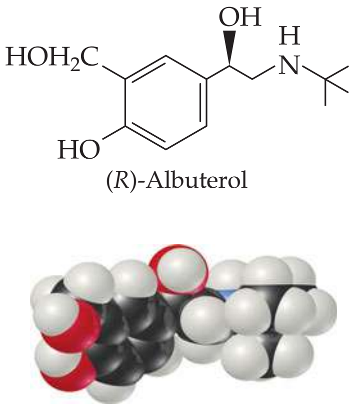


▲ **FIGURE 24.15 The two enantiomeric forms of 2-bromopentane.** The mirror-image isomers are not superimposable on each other.

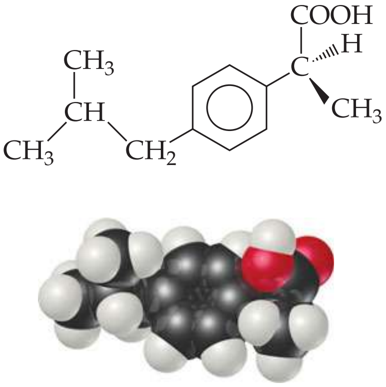
behave differently from each other. One interesting property of chiral substances is that their solutions may rotate the plane of polarized light, as explained in Section 23.4.

Chirality is common in organic substances. It is not often observed, however, because when a chiral substance is synthesized in a typical reaction, the two enantiomers are formed in precisely the same quantity. The resulting mixture is called a *racemic mixture*, and it does not rotate the plane of polarized light because the two forms rotate the light to equal extents in opposite directions. ∞ (Section 23.4)

Many drugs are chiral substances. When a drug is administered as a racemic mixture, often only one enantiomer has beneficial results. The other is either inert, or nearly so, or may even have a harmful effect. For example, the drug (*R*)-albuterol (▶ **FIGURE 24.16**) is a bronchodilator used to relieve the symptoms of asthma. The enantiomer (*S*)-albuterol is not only ineffective as a bronchodilator but also actually counters the effects of (*R*)-albuterol. As another example, the nonsteroidal analgesic ibuprofen is a chiral molecule usually sold as the racemic mixture. However, a preparation consisting of just the more active enantiomer, (*S*)-ibuprofen (▶ **FIGURE 24.17**), relieves pain and reduces inflammation more rapidly than the racemic mixture. For this reason, the chiral version of the drug may in time come to replace the racemic one.



▲ **FIGURE 24.16** **(*R*) -Albuterol.** This compound, which acts as a bronchodilator in patients with asthma, is one member of an enantiomer pair. The other member, (*S*)-albuterol, does not have the same physiological effect.



▲ **FIGURE 24.17** **(*S*)-Ibuprofen.** For relieving pain and reducing inflammation, the ability of this enantiomer far outweighs that of the (*R*) isomer.

GIVE IT SOME THOUGHT

What are the requirements on the four groups attached to a carbon atom in order that it be a chiral center?

24.6 INTRODUCTION TO BIOCHEMISTRY

The functional groups discussed in Section 24.4 generate a vast array of molecules with very specific chemical reactivities. Nowhere is this specificity more apparent than in *biochemistry*—the chemistry of living organisms.

Before we discuss specific biochemical molecules, we can make some general observations. Many biologically important molecules are quite large, because organisms build biomolecules from smaller, simpler substances readily available in the biosphere. The synthesis of large molecules requires energy because most of the reactions are endothermic. The ultimate source of this energy is the Sun. Animals have essentially no capacity for using solar energy directly, however, and so depend on plant photosynthesis to supply the bulk of their energy needs. ∞ (Section 23.3)

In addition to requiring large amounts of energy, living organisms are highly organized. In thermodynamic terms, this high degree of organization means that the entropy of living systems is much lower than that of the raw materials from which the systems formed. Thus, living systems must continuously work against the spontaneous tendency toward increased entropy.

In the "Chemistry and Life" essays that appear throughout this text, we have introduced you to some important biochemical applications of fundamental chemical ideas. The remainder of this chapter will serve as only a brief introduction to other aspects of biochemistry. Nevertheless, you will see some patterns emerging. Hydrogen bonding (Section 11.2), for example, is critical to the function of many biochemical systems, and the geometry of molecules (Section 9.1) can govern their biological importance and activity. Many of the large molecules in living systems are polymers (Section 12.8) of much smaller molecules. These **biopolymers** can be classified into three broad categories: proteins, polysaccharides (carbohydrates), and nucleic acids. Lipids are another common class of molecules in living systems, but they are usually large molecules, not biopolymers.

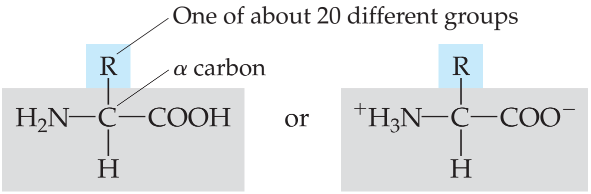
24.7 PROTEINS

Proteins are macromolecules present in all living cells. About 50% of your body's dry mass is protein. Some proteins are structural components in animal tissues; they are a key part of skin, nails, cartilage, and muscles. Other proteins catalyze reactions, transport oxygen, serve as hormones to regulate specific body processes, and perform other tasks. Whatever their function, all proteins are chemically similar, being composed of smaller molecules called *amino acids*.

Amino Acids

An **amino acid** is a molecule containing an amine group, —NH_2, and a carboxylic acid group, —COOH. The building blocks of all proteins are *α-amino acids*, where the α (alpha) indicates that the amino group is located on the carbon atom immediately adjacent to the carboxylic acid group. Thus, there is always one carbon atom between the amino group and the carboxylic acid group.

The general formula for an α-amino acid is represented by



$$H_2N-\underset{H}{\overset{R}{C}}-COOH \quad \text{or} \quad {}^{+}H_3N-\underset{H}{\overset{R}{C}}-COO^{-}$$

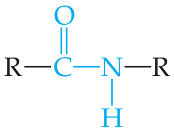
The doubly ionized form, called a *zwitterion*, usually predominates at near-neutral pH values. This form is a result of the transfer of a proton from the carboxylic acid group to the amine group. (Section 16.10: "Chemistry and Life: The Amphiprotic Behavior of Amino Acids")

Amino acids differ from one another in the nature of their R groups. Twenty-two amino acids have been identified in nature, and ▶ **FIGURE 24.18** shows the 20 of these 22 that are found in humans. Our bodies can synthesize 10 of these 20 amino acids in sufficient amounts for our needs. The other 10 must be ingested and are called *essential amino acids* because they are necessary components of our diet.

The α-carbon atom of the amino acids, which is the carbon between the amino and carboxylate groups, has four different groups attached to it. The amino acids are thus chiral (except for glycine, which has two hydrogens attached to the central carbon). For historical reasons, the two enantiomeric forms of amino acids are often distinguished by the labels D (from the Latin *dexter*, "right") and L (from the Latin *laevus*, "left"). Nearly all the chiral amino acids found in living organisms have the L configuration at the chiral center. The principal exceptions to the dominance of L amino acids in nature are the proteins that make up the cell walls of bacteria, which can contain considerable quantities of the D isomers.

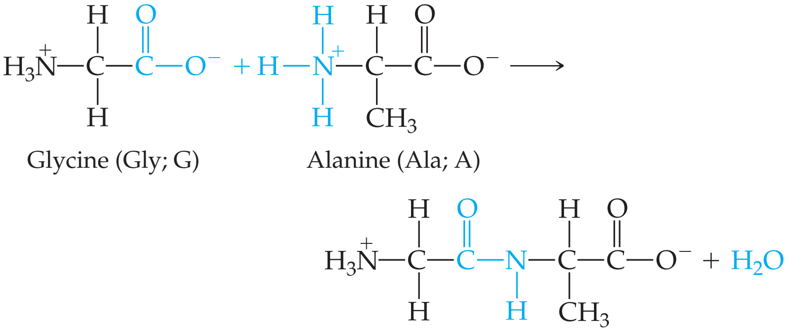
Polypeptides and Proteins

Amino acids are linked together into proteins by amide groups (Table 24.6):



$$R-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-R \qquad [24.23]$$

Each amide group is called a **peptide bond** when it is formed by amino acids. A peptide bond is formed by a condensation reaction between the carboxyl group of one amino acid and the amino group of another amino acid. Alanine and glycine, for example, form the dipeptide glycylalanine:



$$H_3\overset{+}{N}-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-O^{-} + H-\underset{H}{\overset{H}{\overset{+}{N}}}-\underset{CH_3}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-O^{-} \longrightarrow$$

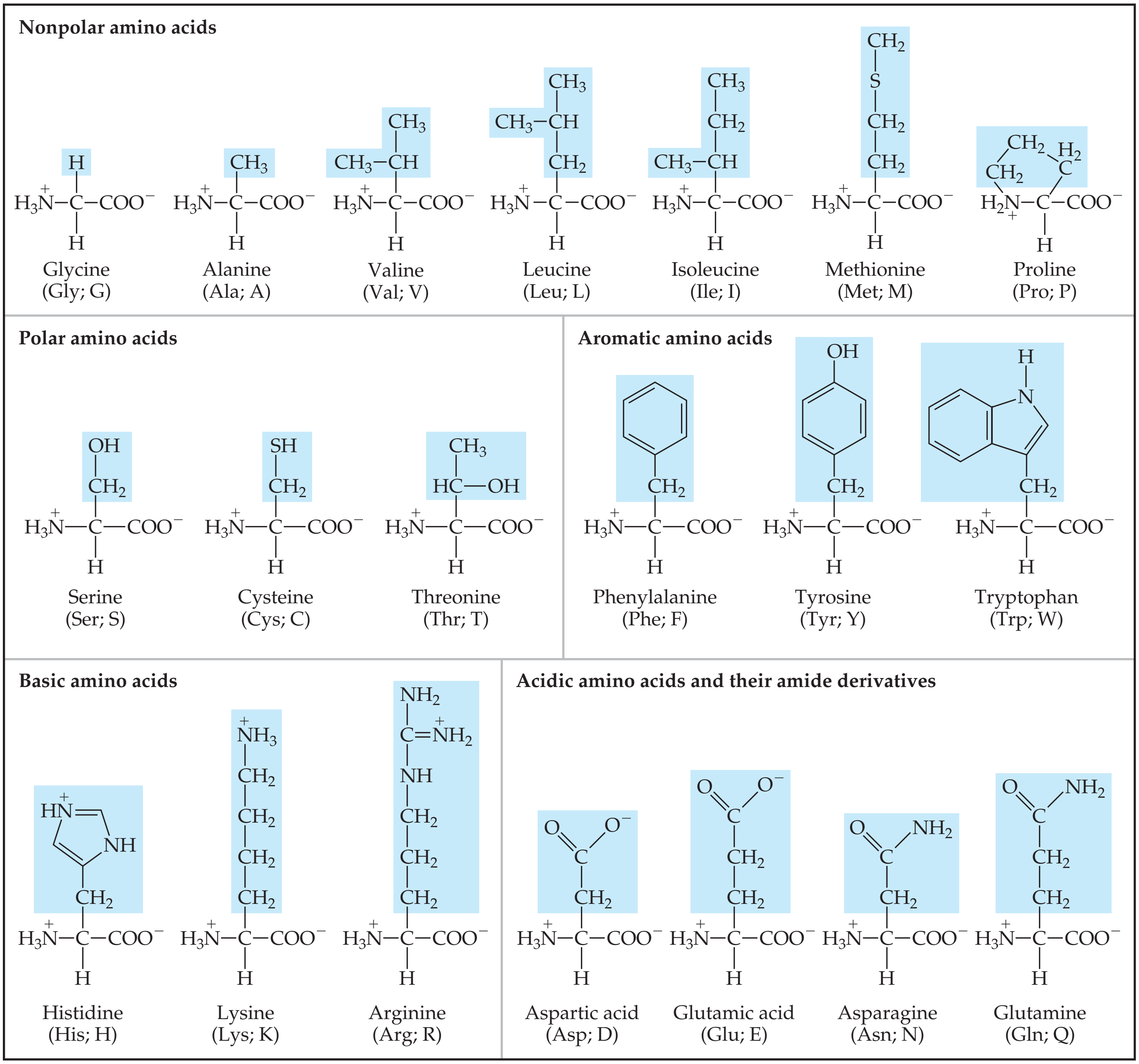
Glycine (Gly; G) Alanine (Ala; A)

$$H_3\overset{+}{N}-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-\underset{CH_3}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-O^{-} + H_2O$$

Glycylalanine (Gly–Ala; GA)

GO FIGURE

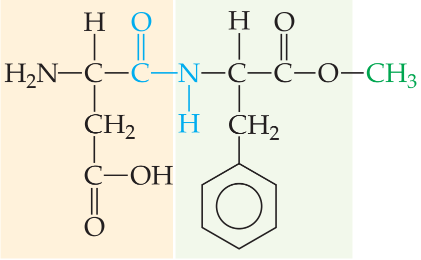
Which group of amino acids has a net positive charge at pH 7?



▲ **FIGURE 24.18** **The 20 amino acids found in the human body.** The acids are shown in the zwitterionic form in which they exist in water at near-neutral pH values.

The amino acid that furnishes the carboxyl group for peptide-bond formation is named first, with a -*yl* ending; then the amino acid furnishing the amino group is named. Using the abbreviations shown in Figure 24.18, glycylalanine can be abbreviated as either Gly-Ala or GA. In this notation, it is understood that the unreacted amino group is on the left and the unreacted carboxyl group on the right.

The artificial sweetener *aspartame* (▶ **FIGURE 24.19**) is the methyl ester of the dipeptide formed from the amino acids aspartic acid and phenylalanine.



▲ **FIGURE 24.19** **Sweet stuff.** The artificial sweetener aspartame is the methyl ester of a dipeptide.

SAMPLE EXERCISE 24.7 Drawing the Structural Formula of a Tripeptide

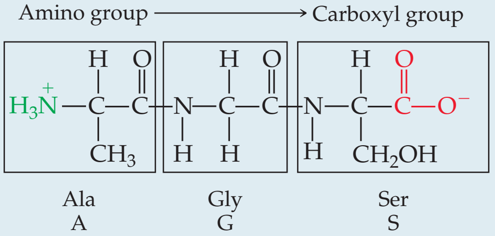
Draw the structural formula for alanylglycylserine.

SOLUTION

Analyze We are given the name of a substance with peptide bonds and asked to write its structural formula.

Plan The name of this substance suggests that three amino acids—alanine, glycine, and serine—have been linked together, forming a *tripeptide*. Note that the ending *-yl* has been added to each amino acid except for the last one, serine. By convention, the sequence of amino acids in peptides and proteins is written from the nitrogen end to the carbon end: The first-named amino acid (alanine, in this case) has a free amino group and the last-named one (serine) has a free carboxyl group.

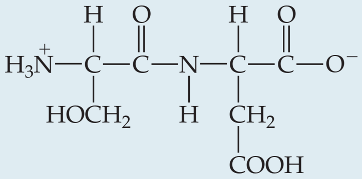
Solve We first combine the carboxyl group of alanine with the amino group of glycine to form a peptide bond and then the carboxyl group of glycine with the amino group of serine to form another peptide bond:



We can abbreviate this tripeptide as either Ala-Gly-Ser or AGS.

PRACTICE EXERCISE

Name the dipeptide



$$H_3\overset{+}{N}-\underset{HOCH_2}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-\underset{CH_2COOH}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-O^-$$

and give the two ways of writing its abbreviation.

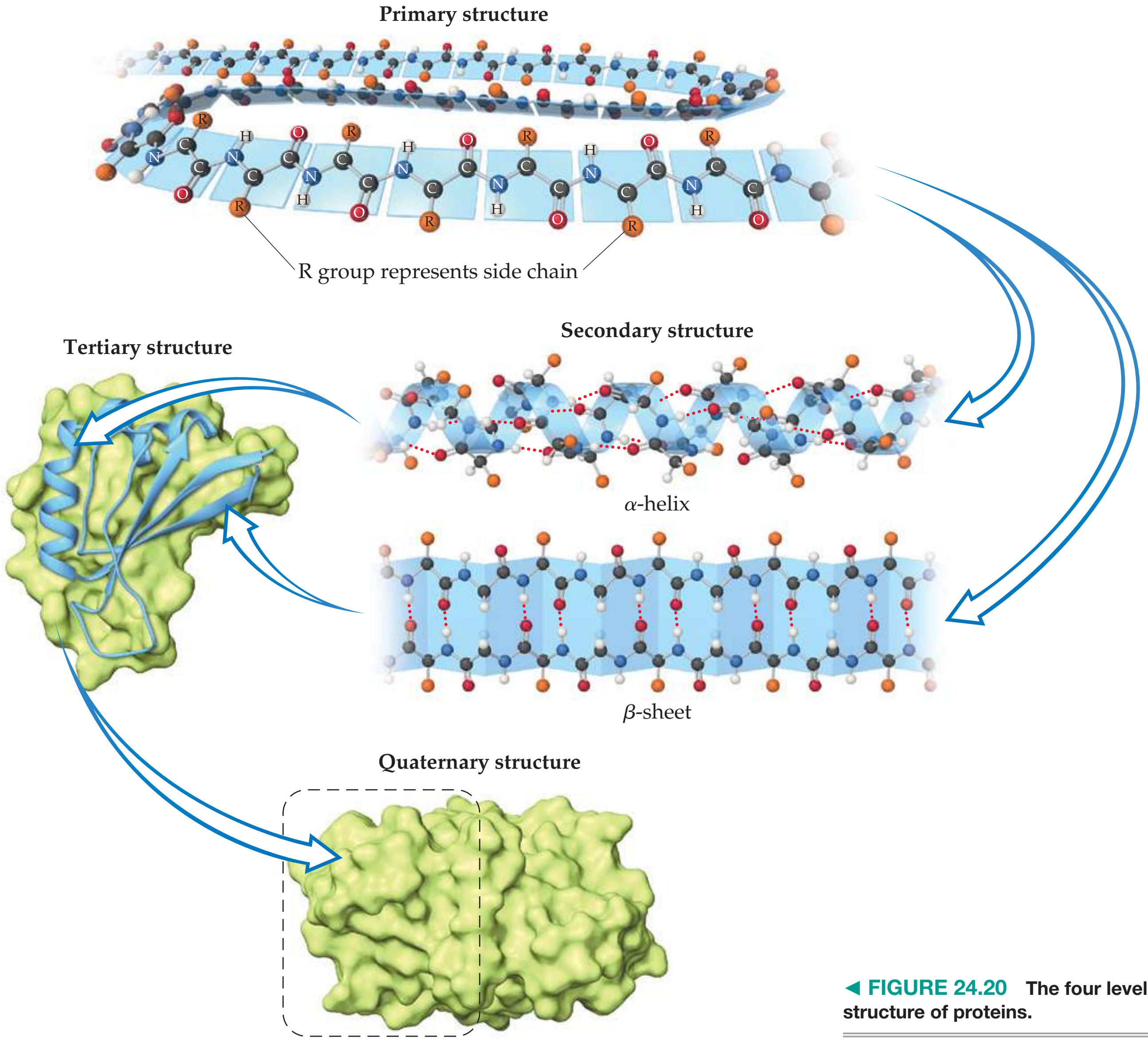
Answer: serylaspartic acid; Ser-Asp, SD.

Polypeptides are formed when a large number of amino acids are linked together by peptide bonds. Proteins are linear (that is, unbranched) polypeptide molecules with molecular weights ranging from about 6000 to over 50 million amu. Because up to 22 different amino acids are linked together in proteins and because proteins consist of hundreds of amino acids, the number of possible arrangements of amino acids within proteins is virtually limitless.

Protein Structure

The sequence of amino acids along a protein chain is called its **primary structure** and gives the protein its unique identity. A change in even one amino acid can alter the biochemical characteristics of the protein. For example, sickle-cell anemia is a genetic disorder resulting from a single replacement in a protein chain in hemoglobin. The chain that is affected contains 146 amino acids. The substitution of an amino acid with a hydrocarbon side chain for one that has an acidic functional group in the side chain alters the solubility properties of the hemoglobin, and normal blood flow is impeded. ∞ (Section 13.6: "Chemistry and Life: Sickle-Cell Anemia")

Proteins in living organisms are not simply long, flexible chains with totally random shapes. Rather, the chains self-assemble into structures based on the intermolecular forces we learned about in Chapter 11. This self-assembling leads to a protein's **secondary structure**, which refers to how segments of the protein chain are oriented in a regular pattern, as seen in ► **FIGURE 24.20**.



Primary structure

Secondary structure

Tertiary structure

Quaternary structure

◀ **FIGURE 24.20 The four levels of structure of proteins.**

One of the most important and common secondary structure arrangements is the **α-helix**. As the α-helix of Figure 24.20 shows, the helix is held in position by hydrogen bonds between amide H atoms and carbonyl O atoms. The pitch of the helix and its diameter must be such that (1) no bond angles are strained and (2) the N—H and C═O functional groups on adjacent turns are in proper position for hydrogen bonding. An arrangement of this kind is possible for some amino acids along the chain but not for others. Large protein molecules may contain segments of the chain that have the α-helical arrangement interspersed with sections in which the chain is in a random coil.

The other common secondary structure of proteins is the beta (**β**) **sheet**. Beta sheets are made of two or more strands of peptides that hydrogen-bond from an amide H in one strand to a carbonyl O in the other strand (Figure 24.20).

GIVE IT SOME THOUGHT

If you heat a protein to break the intramolecular hydrogen bonds, will you maintain the α-helical or β-sheet structure?

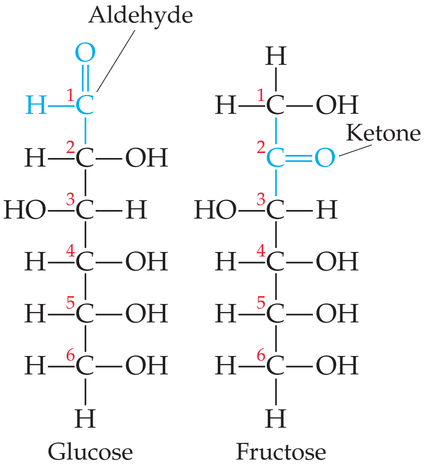
Proteins are not active biologically unless they are in a particular shape in solution. The process by which the protein adopts its biologically active shape is called **folding**. The shape of a protein in its folded form—determined by all the bends, kinks, and sections of rodlike α-helical, β-sheet, or flexible coil components—is called the **tertiary structure**.

Figure 23.14 shows the tertiary structure of myoglobin, a protein with a molecular weight of about 18,000 amu and containing one heme group. Some sections of this protein consist of α-helices.

Myoglobin is a *globular protein*, one that folds into a compact, roughly spherical shape. Globular proteins are generally soluble in water and are mobile within cells. They have nonstructural functions, such as combating the invasion of foreign objects, transporting and storing oxygen, and acting as catalysts. The *fibrous proteins* form a second class of proteins. In these substances the long coils align more or less in parallel to form long, water-insoluble fibers. Fibrous proteins provide structural integrity and strength to many kinds of tissue and are the main components of muscle, tendons, and hair. The largest known proteins, in excess of 27,000 amino acids long, are muscle proteins.

The tertiary structure of a protein is maintained by many different interactions. Certain foldings of the protein chain lead to lower-energy (more stable) arrangements than do other folding patterns. For example, a globular protein dissolved in aqueous solution folds in such a way that the nonpolar hydrocarbon portions are tucked within the molecule, away from the polar water molecules. Most of the more polar acidic and basic side chains, however, project into the solution, where they can interact with water molecules through ion–dipole, dipole–dipole, or hydrogen-bonding interactions.

Some proteins are assemblies of more than one polypeptide chain. Each chain has its own tertiary structure, and two or more of these tertiary subunits aggregate into a larger functional macromolecule. The way the tertiary subunits are arranged is called the **quaternary structure** of the protein (Figure 24.20). For example, hemoglobin, the oxygen-carrying protein of red blood cells, consists of four tertiary subunits. Each subunit contains a component called a heme with an iron atom that binds oxygen as depicted in Figure 23.15. The quaternary structure is maintained by the same types of interactions that maintain the tertiary structure.

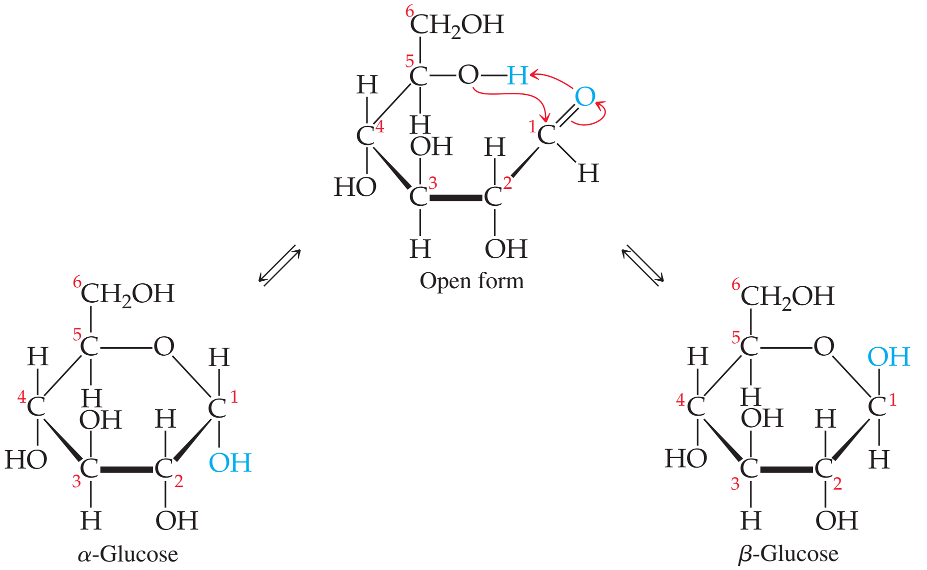


▲ FIGURE 24.21 Linear structure of the carbohydrates glucose and fructose.

24.8 CARBOHYDRATES

Carbohydrates are an important class of naturally occurring substances found in both plant and animal matter. The name **carbohydrate** ("hydrate of carbon") comes from the empirical formulas for most substances in this class, which can be written as $C_x(H_2O)_y$. For example, **glucose**, the most abundant carbohydrate, has the molecular formula $C_6H_{12}O_6$, or $C_6(H_2O)_6$. Carbohydrates are not really hydrates of carbon; rather, they are polyhydroxy aldehydes and ketones. Glucose, for example, is a six-carbon aldehyde sugar, whereas *fructose*, the sugar that occurs widely in fruit, is a six-carbon ketone sugar (◀ **FIGURE 24.21**).

The glucose molecule, having both alcohol and aldehyde functional groups and a reasonably long and flexible backbone, can form a six-member-ring structure, as shown in ▼ **FIGURE 24.22**. In fact, in an aqueous solution only a small percentage of the

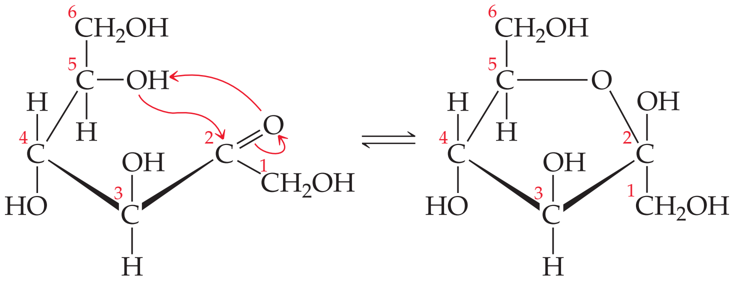


▶ FIGURE 24.22 Cyclic glucose has an α form and a β form.

glucose molecules are in the open-chain form. Although the ring is often drawn as if it were planar, the molecules are actually nonplanar because of the tetrahedral bond angles around the C and O atoms of the ring.

Figure 24.22 shows that the ring structure of glucose can have two relative orientations. In the α form the OH group on C1 and the CH_2OH group on C5 point in opposite directions, and in the β form they point in the same direction. Although the difference between the α and β forms might seem small, it has enormous biological consequences, including the vast difference in properties between starch and cellulose.

Fructose can cyclize to form either five- or six-member rings. The five-member ring forms when the C5 OH group reacts with the C2 carbonyl group:



The six-member ring results from the reaction between the C6 OH group and the C2 carbonyl group.

SAMPLE EXERCISE 24.8 Identifying Chiral Centers

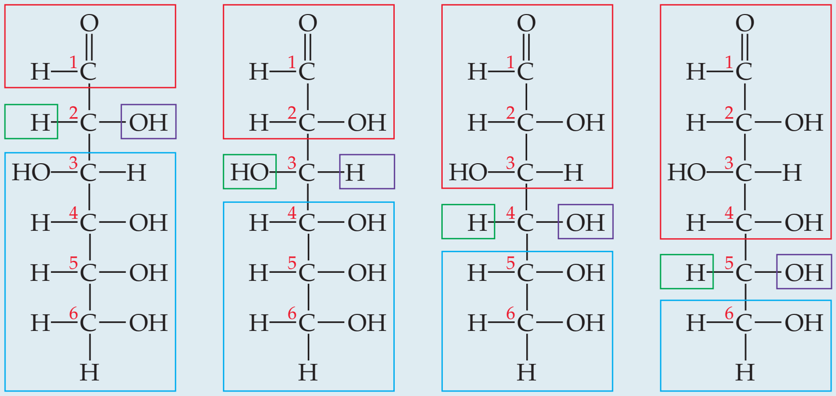
How many chiral carbon atoms are there in the open-chain form of glucose (Figure 24.21)?

SOLUTION

Analyze We are given the structure of glucose and asked to determine the number of chiral carbons in the molecule.

Plan A chiral carbon has four different groups attached (Section 24.5). We need to identify those carbon atoms in glucose.

Solve Carbons 2, 3, 4, and 5 each have four different groups attached to them:



Thus, there are four chiral carbon atoms in the glucose molecule.

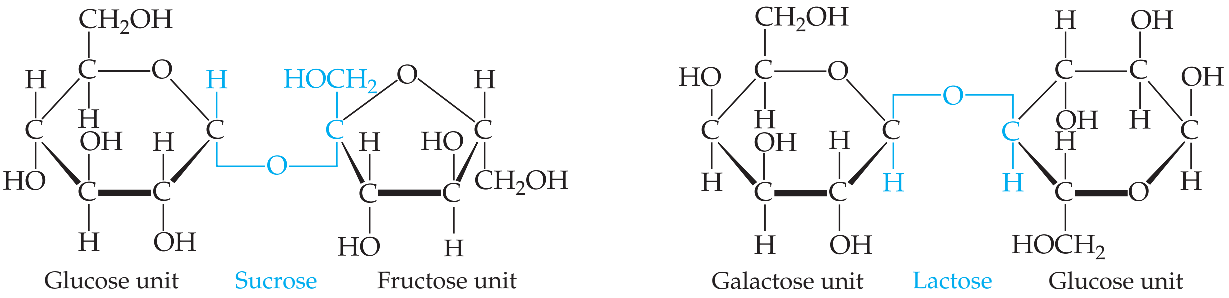
PRACTICE EXERCISE

How many chiral carbon atoms are there in the open-chain form of fructose (Figure 24.21)?

Answer: three

Disaccharides

Both glucose and fructose are examples of **monosaccharides**, simple sugars that cannot be broken into smaller molecules by hydrolysis with aqueous acids. Two monosaccharide units can be linked together by a condensation reaction to form a **disaccharide**. The structures of two common disaccharides, *sucrose* (table sugar) and *lactose* (milk sugar), are shown in ▶ **FIGURE 24.23**.



▲ **FIGURE 24.23** **Two disaccharides.**

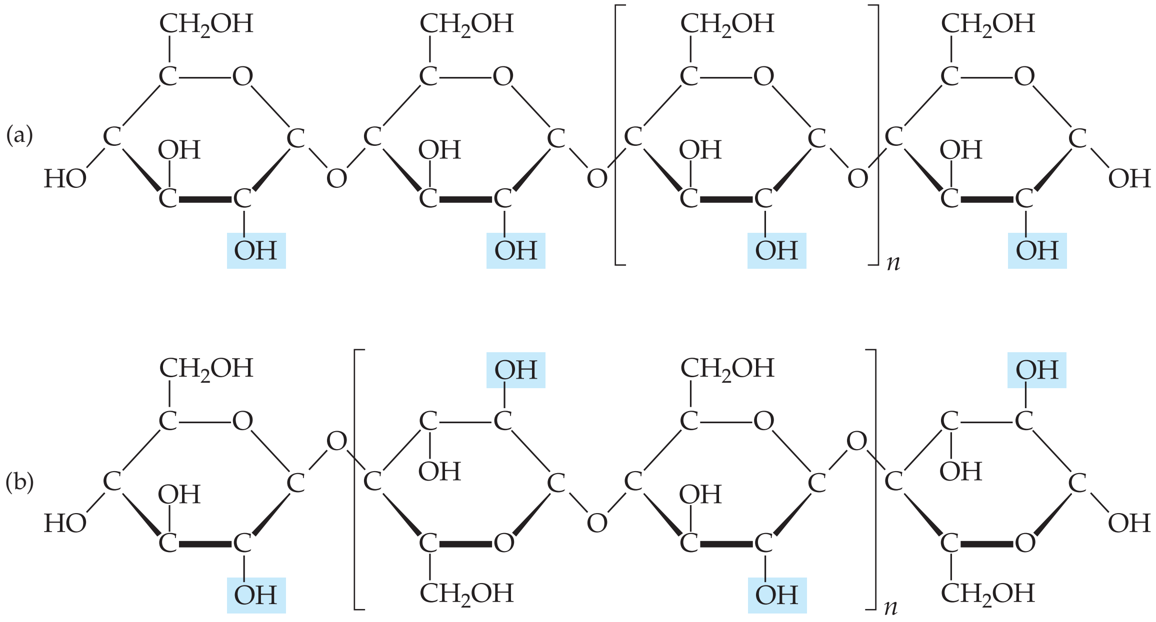
The word *sugar* makes us think of sweetness. All sugars are sweet, but they differ in the degree of sweetness we perceive when we taste them. Sucrose is about six times sweeter than lactose, slightly sweeter than glucose, but only about half as sweet as fructose. Disaccharides can be reacted with water (hydrolyzed) in the presence of an acid catalyst to form monosaccharides. When sucrose is hydrolyzed, the mixture of glucose and fructose that forms, called *invert sugar*,* is sweeter to the taste than the original sucrose. The sweet syrup present in canned fruits and candies is largely invert sugar formed from hydrolysis of added sucrose.

Polysaccharides

Polysaccharides are made up of many monosaccharide units joined together. The most important polysaccharides are starch, glycogen, and cellulose, all three of which are formed from repeating glucose units.

Starch is not a pure substance. The term refers to a group of polysaccharides found in plants. Starches serve as a major method of food storage in plant seeds and tubers. Corn, potatoes, wheat, and rice all contain substantial amounts of starch. These plant products serve as major sources of needed food energy for humans. Enzymes in the digestive system catalyze the hydrolysis of starch to glucose.

Some starch molecules are unbranched chains, whereas others are branched. ▼ **FIGURE 24.24**(a) illustrates an unbranched starch structure. Notice, in particular,



▲ **FIGURE 24.24** **Structures of (a) starch and (b) cellulose.**

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*The term *invert sugar* comes from the fact that rotation of the plane of polarized light by the glucose-fructose mixture is in the opposite direction, or inverted, from that of the sucrose solution.

that the glucose units are in the α form with the bridging oxygen atoms pointing in one direction and the CH_2OH groups pointing in the opposite direction

Glycogen is a starchlike substance synthesized in the animal body. Glycogen molecules vary in molecular weight from about 5000 to more than 5 million amu. Glycogen acts as a kind of energy bank in the body. It is concentrated in the muscles and liver. In muscles it serves as an immediate source of energy; in the liver it serves as a storage place for glucose and helps to maintain a constant glucose level in the blood.

Cellulose [Figure 24.24(b)] forms the major structural unit of plants. Wood is about 50% cellulose; cotton fibers are almost entirely cellulose. Cellulose consists of an unbranched chain of glucose units, with molecular weights averaging more than 500,000 amu. At first glance this structure looks very similar to that of starch. In cellulose, however, the glucose units are in the β form with each bridging oxygen atom pointing in the same direction as the CH_2OH group in the ring to its left.

Because the individual glucose units have different relationships to one another in starch and cellulose, enzymes that readily hydrolyze starches do not hydrolyze cellulose. Thus, you might eat a pound of cellulose and receive no caloric value from it even though the heat of combustion per unit mass is essentially the same for both cellulose and starch. A pound of starch, in contrast, would represent a substantial caloric intake. The difference is that the starch is hydrolyzed to glucose, which is eventually oxidized with release of energy. However, enzymes in the body do not readily hydrolyze cellulose, so it passes through the digestive system relatively unchanged. Many bacteria contain enzymes, called cellulases, that hydrolyze cellulose. These bacteria are present in the digestive systems of grazing animals, such as cattle, that use cellulose for food.

GIVE IT SOME THOUGHT

Which type of linkage, α or β, would you expect to join the sugar molecules of glycogen?

24.9 LIPIDS

Lipids are a diverse class of nonpolar biological molecules used by organisms for long-term energy storage (fats, oils) and as elements of biological structures (phospholipids, cell membranes, waxes).

Fats

Fats are lipids derived from glyercol and fatty acids. Glycerol is an alcohol with three OH groups. Fatty acids are carboxylic acids (RCOOH) in which R is a hydrocarbon chain, usually 16 to 19 carbon atoms in length. Glycerol and fatty acids undergo condensation reactions to form ester linkages as shown in ▶ **FIGURE 24.25**. Three fatty acid molecules join to a glycerol. Although the three fatty acids in a fat can be the same, as they are in Figure 24.25, it is also possible that a fat contains three different fatty acids.

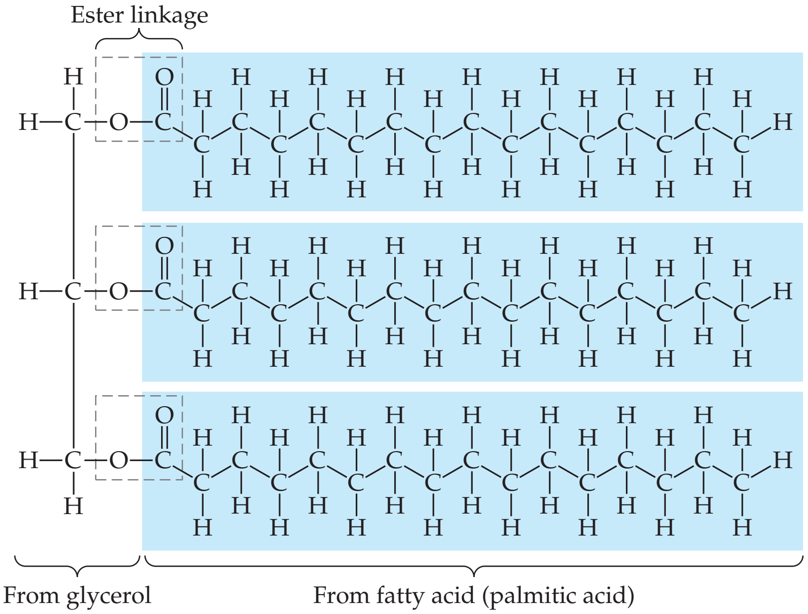
Lipids with saturated fatty acids are called saturated fats and are commonly solids at room temperature (such as butter and shortening). Unsaturated fats contain one or more double bonds in their carbon–carbon chains. The cis and trans nomenclature we learned for alkenes applies: Trans fats have H atoms on the opposite sides of the $C{=}C$ double bond, and cis fats have H atoms on the same sides of the $C{=}C$ double bond. Unsaturated fats (such as olive oil and peanut oil) are usually liquid at room temperature and are more often found in plants. For example, the major component (approximately 60 to 80%) of olive oil is oleic acid, *cis*-$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$.

Oleic acid is an example of a *monounsaturated* fatty acid, meaning it has only one carbon–carbon double bond in the chain. In contrast, *polyunsaturated* fatty acids have more than one carbon–carbon double bond in the chain.

For humans, trans fats are not nutritionally required, which is why some governments are moving to ban them in foods. How, then, do trans fats end up in our food? The process that converts unsaturated fats (such as oils) into saturated fats (such as shortening) is hydrogenation. (Section 24.3) The by-products of this hydrogenation process include trans fats.

GO FIGURE

What structural features of a fat molecule cause it to be insoluble in water?



▲ **FIGURE 24.25** **Structure of a fat.**

Some of the fatty acids essential for human health must be available in our diets because our metabolism cannot synthesize them. These essential fatty acids are ones that have the carbon–carbon double bonds either three carbons or six carbons away from the $—CH_3$ end of the chain. These are called omega-3 and omega-6 fatty acids, where *omega* refers to the last carbon in the chain (the carboxylic acid carbon is considered the first, or alpha, one).

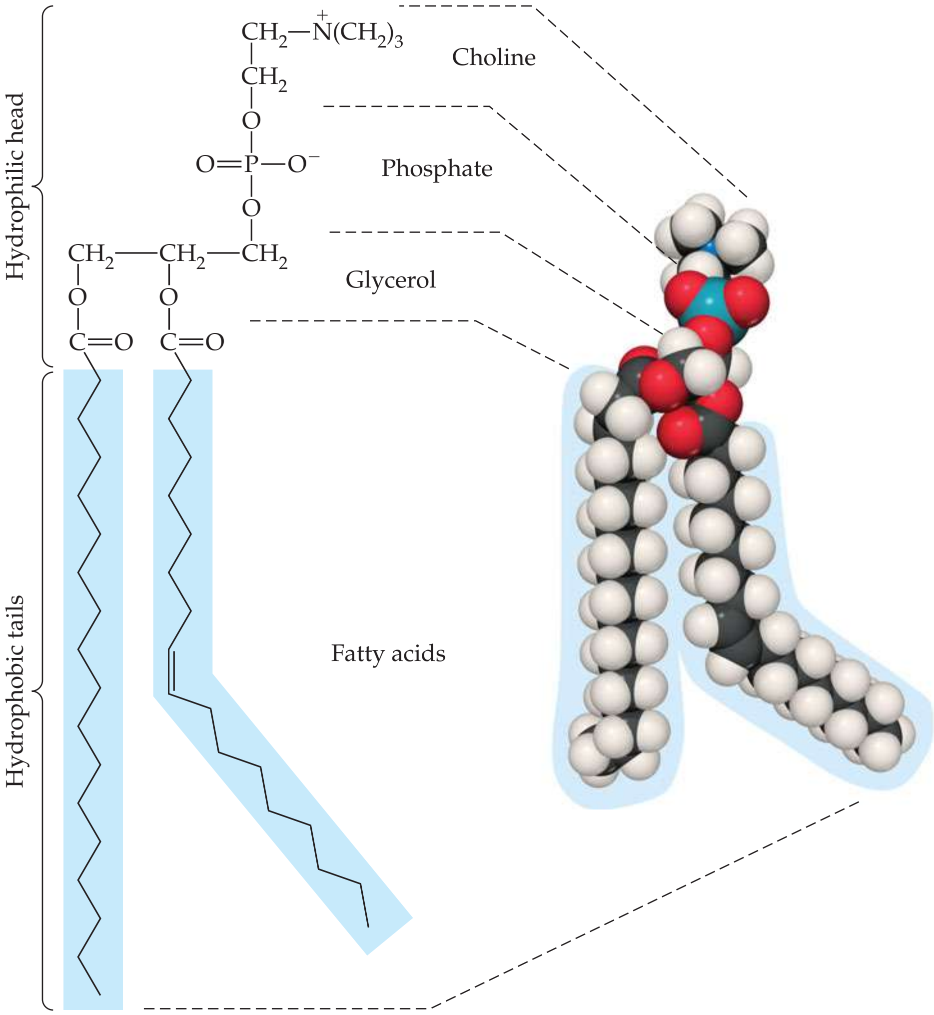
Phospholipids

Phospholipids are similar in chemical structure to fats but have only two fatty acids attached to a glycerol. The third alcohol group of glycerol is joined to a phosphate group (▶ **FIGURE 24.26**). The phosphate group can be also attached to a small charged or polar group, such as choline, as shown in the figure. The diversity in phospholipids is based on differences in their fatty acids and in the groups attached to the phosphate group.

In water, phospholipids cluster together with their charged polar heads facing the water and their nonpolar tails facing inward. The phospholipids thus form a bilayer that is a key component of cell membranes (▶ **FIGURE 24.27**).

24.10 NUCLEIC ACIDS

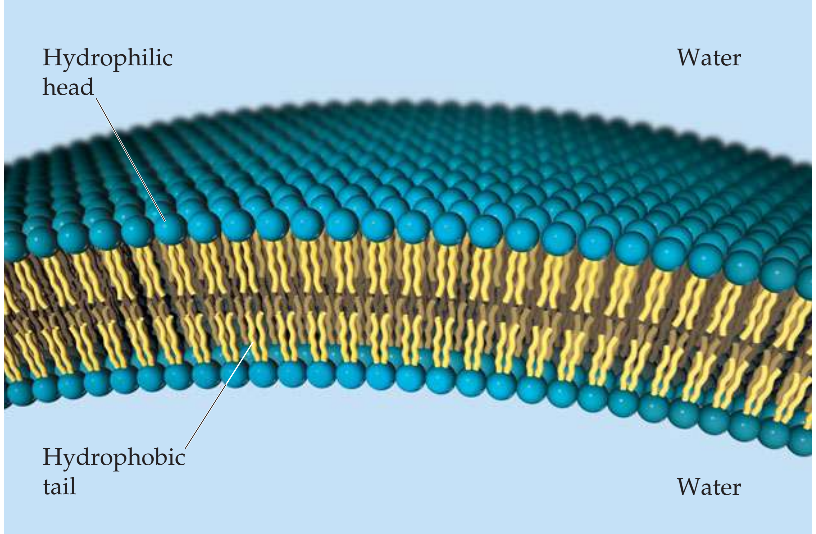
Nucleic acids are a class of biopolymers that are the chemical carriers of an organism's genetic information. **Deoxyribonucleic acids (DNA)** are huge molecules whose molecular weights may range from 6 million to 16 million amu. **Ribonucleic acids (RNA)** are smaller molecules, with molecular weights in the range of 20,000 to 40,000 amu. Whereas DNA is found primarily in the nucleus of the cell, RNA is found mostly outside the nucleus in the *cytoplasm*, the nonnuclear material enclosed by the cell membrane. DNA stores the genetic information of the cell and specifies which proteins the cell can synthesize. RNA carries the information stored by DNA out of the cell nucleus into the cytoplasm, where the information is used in protein synthesis.



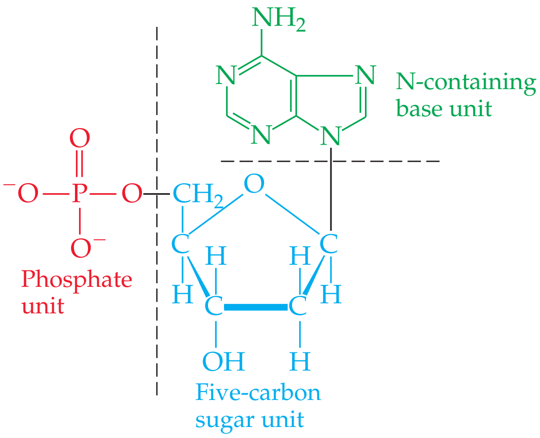
▲ **FIGURE 24.26** **Structure of a phospholipid.**

GO FIGURE

Why do phospholipids form bilayers but not monolayers in water?



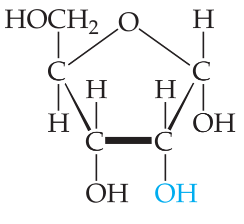
◀ **FIGURE 24.27** **The cell membrane.** Living cells are encased in membranes typically made of phospholipid bilayers. The bilayer structure is stabilized by the favorable interactions of the hydrophobic tails of the phospholipids, which point away from both the water inside the cell and the water outside the cell, while the charged head groups face the two water environments.

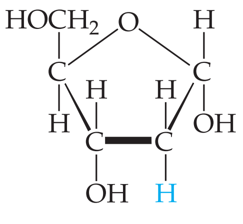


▲ **FIGURE 24.28 A nucleotide.** Structure of deoxyadenylic acid, the nucleotide formed from phosphoric acid, deoxyribose, and the organic base adenine.

The monomers of nucleic acids, called **nucleotides**, are formed from a five-carbon sugar, a nitrogen-containing organic base, and a phosphate group. An example is shown in ◀ **FIGURE 24.28**.

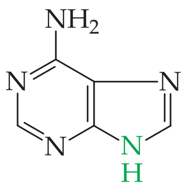
The five-carbon sugar in RNA is *ribose*, and that in DNA is *deoxyribose*:

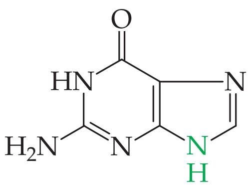

Ribose

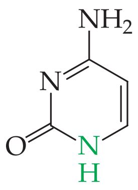

Deoxyribose

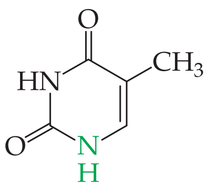
Deoxyribose differs from ribose only in having one fewer oxygen atom at carbon 2.

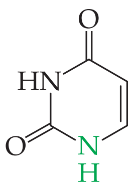
There are five nitrogen-containing bases in nucleic acids:


Adenine (A)
DNA
RNA


Guanine (G)
DNA
RNA


Cytosine (C)
DNA
RNA


Thymine (T)
DNA


Uracil (U)
RNA

The first three bases shown here are found in both DNA and RNA. Thymine occurs only in DNA, and uracil occurs only in RNA. In either nucleic acid, each base is attached to a five-carbon sugar through a bond to the nitrogen atom shown in color.

The nucleic acids RNA and DNA are *polynucleotides* formed by condensation reactions between a phosphoric acid OH group on one nucleotide and a sugar OH group on another nucleotide. Thus, the polynucleotide strand has a backbone consisting of alternating sugar and phosphate groups with the bases extending off the chain as side groups (◀ **FIGURE 24.29**).

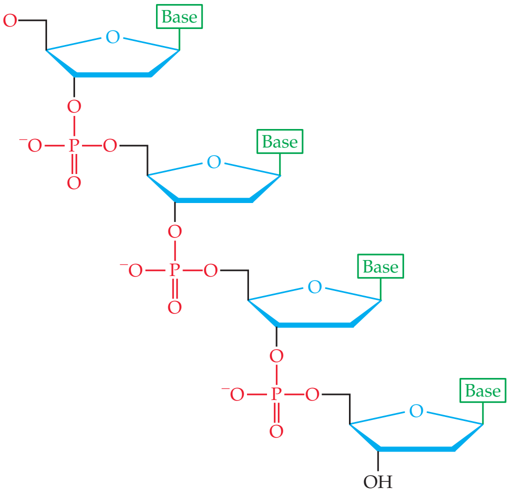
The DNA strands wind together in a **double helix** (▶ **FIGURE 24.30**). The two strands are held together by attractions between bases (represented by T, A, C, and G). These attractions involve dispersion forces, dipole–dipole forces, and hydrogen bonds. ∞ (Section 11.2) As shown in ▶ **FIGURE 24.31**, the structures of thymine and adenine make them perfect partners for hydrogen bonding. Likewise, cytosine and guanine form ideal hydrogen-bonding partners. We say that thymine and adenine are *complementary* to each other and cytosine and guanine are *complementary* to each other. In the double-helix structure, therefore, each thymine on one strand is opposite an adenine on the other strand, and each cytosine is opposite a guanine. The double-helix structure with complementary bases on the two strands is the key to understanding how DNA functions.

The two strands of DNA unwind during cell division, and new complementary strands are constructed on the unraveling strands (▶ **FIGURE 24.32**). This process results in two identical double-helix DNA structures, each containing one strand from the original structure and one new strand. This replication allows genetic information to be transmitted when cells divide.

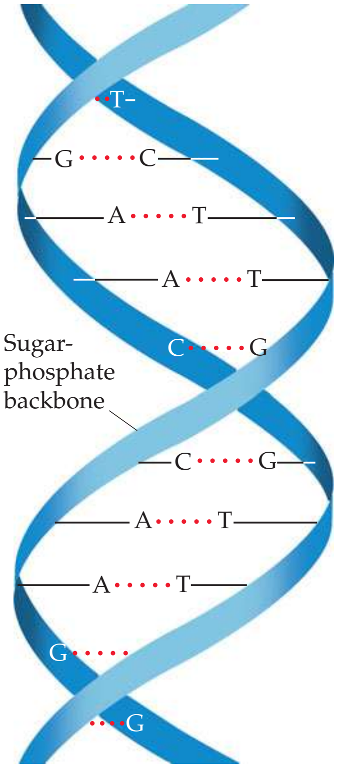
The structure of DNA is also the key to understanding protein synthesis, the means by which viruses infect cells, and many other problems of central importance to modern biology. These themes are beyond the scope of this book. If you take courses in the life sciences, however, you will learn a good deal about such matters.

GO FIGURE

Is DNA positively charged, negatively charged, or neutral in aqueous solution at pH 7?



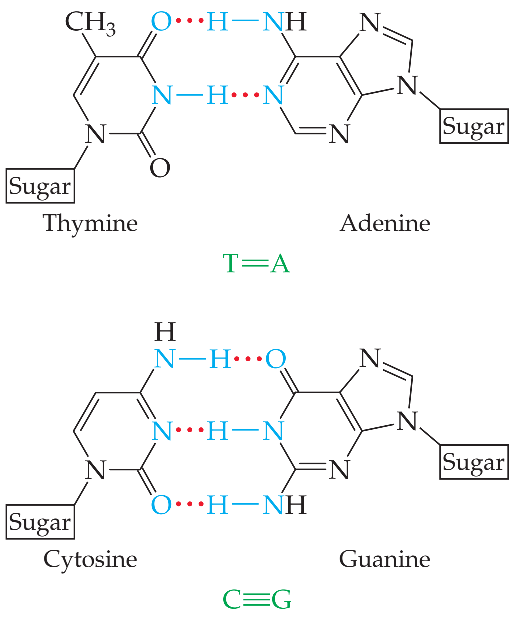
▲ **FIGURE 24.29 A polynucleotide.** Because the sugar in each nucleotide is deoxyribose, this polynucleotide is of the form found in DNA.



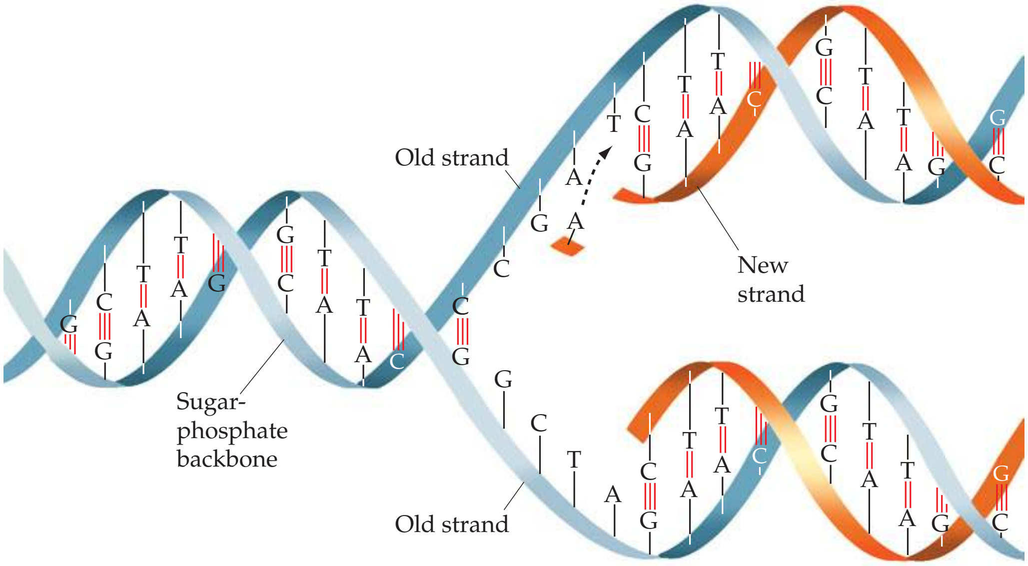
▲ **FIGURE 24.30** **The DNA double helix.**

GO FIGURE

Which pair of complementary bases, AT or GC, would you expect to bind more strongly?



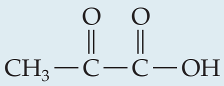
▲ **FIGURE 24.31** **Hydrogen bonding between complementary bases.**



◀ **FIGURE 24.32** **DNA replication.** The original DNA double helix partially unwinds, and new nucleotides line up on each strand in complementary fashion. Hydrogen bonds help align the new nucleotides with the original DNA chain. When the new nucleotides are joined by condensation reactions, two identical double-helix DNA molecules result.

SAMPLE INTEGRATIVE EXERCISE Putting Concepts Together

Pyruvic acid,



$$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OH$$

is formed in the body from carbohydrate metabolism. In muscles, it is reduced to lactic acid in the course of exertion. The acid-dissociation constant for pyruvic acid is 3.2×10^{-3}. (**a**) Why does pyruvic acid have a higher acid-dissociation constant than acetic acid? (**b**) Would you expect pyruvic acid to exist primarily as the neutral acid or as dissociated ions in muscle tissue, assuming a pH of about 7.4 and an acid concentration of $2 \times 10^{-4}\ M$? (**c**) What would you predict for the solubility properties of pyruvic acid? Explain. (**d**) What is the hybridization of each carbon atom in pyruvic acid? **(e)** Assuming H atoms as the reducing agent, write a balanced chemical equation for the reduction of pyruvic acid to lactic acid (Figure 24.14). (Although H atoms do not exist as such in biochemical systems, biochemical reducing agents deliver hydrogen for such reductions.)

SOLUTION

(a) The acid-dissociation constant for pyruvic acid should be somewhat greater than that of acetic acid because the carbonyl function on the α-carbon atom of pyruvic acid exerts an electron-withdrawing effect on the carboxylic acid group. In the $C-O-H$ bond system the electrons are shifted from H, facilitating loss of the H as a proton. ∞ (Section 16.10)

(b) To determine the extent of ionization, we first set up the ionization equilibrium and equilibrium-constant expression. Using HPv as the symbol for the acid, we have

$$\text{HPv} \rightleftharpoons \text{H}^+ + \text{Pv}^-$$

$$K_a = \frac{[\text{H}^+][\text{Pv}^-]}{[\text{HPv}]} = 3.2 \times 10^{-3}$$

Let $[\text{Pv}^-] = x$. Then the concentration of undissociated acid is $2 \times 10^{-4} - x$. The concentration of $[\text{H}^+]$ is fixed at 4.0×10^{-8} (the antilog of the pH value). Substituting, we obtain

$$3.2 \times 10^{-3} = \frac{[4.0 \times 10^{-8}][x]}{[2 \times 10^{-4} - x]}$$

Solving for x, we obtain $x[3.2 \times 10^{-3} + 4.0 \times 10^{-8}] = 6.4 \times 10^{-7}$.

The second term in the brackets is negligible compared to the first, so

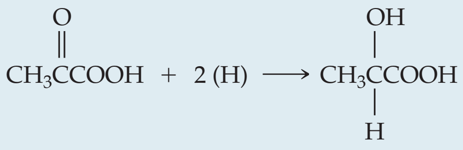
$$x = [\text{Pv}^-] = 6.4 \times 10^{-7}/3.2 \times 10^{-3} = 2 \times 10^{-4}\,M$$

This is the initial concentration of acid, which means that essentially all the acid has dissociated. We might have expected this result because the acid is quite dilute and the acid-dissociation constant is fairly high.

(c) Pyruvic acid should be quite soluble in water because it has polar functional groups and a small hydrocarbon component. It is miscible with water, ethanol, and diethyl ether.

(d) The methyl group carbon has sp^3 hybridization. The carbon of the carbonyl group has sp^2 hybridization because of the double bond to oxygen. Similarly, the carboxylic acid carbon is sp^2 hybridized.

(e) The balanced chemical equation for this reaction is



$$CH_3\overset{\overset{O}{\|}}{C}COOH + 2\,(H) \longrightarrow CH_3\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}COOH$$

Essentially, the ketonic functional group has been reduced to an alcohol.

STRATEGIES IN CHEMISTRY

WHAT NOW?

If you are reading this box, you have made it to the end of our text. We congratulate you on the tenacity and dedication that you have exhibited to make it this far!

As an epilogue, we offer the ultimate study strategy in the form of a question: What do you plan to do with the knowledge of chemistry that you have gained thus far in your studies? Many of you will enroll in additional courses in chemistry as part of your required curriculum. For others, this will be the last formal course in chemistry that you will take. Regardless of the career path you plan to take—whether it is chemistry, one of the biomedical fields, engineering, the liberal arts, or another field—we hope that this text has increased your appreciation of the chemistry in the world around you. If you pay attention, you will be aware of encounters with chemistry on a daily basis, from food and pharmaceutical labels to gasoline pumps, sports equipment to news reports.

We have also tried to give you a sense that chemistry is a dynamic, continuously changing science. Research chemists synthesize new compounds, develop new reactions, uncover chemical properties that were previously unknown, find new applications for known compounds, and refine theories. The understanding of biological systems in terms of the underlying chemistry has become increasingly important as new levels of complexity are uncovered. You may wish to participate in the fascinating venture of chemical research by taking part in an undergraduate research program. Given all the answers that chemists seem to have, you may be surprised at the large number of questions that they still find to ask.

Finally, we hope you have enjoyed using this textbook. We certainly enjoyed putting so many of our thoughts about chemistry on paper. We truly believe it to be the central science, one that benefits all who learn about it and from it.

CHAPTER SUMMARY AND KEY TERMS

INTRODUCTION AND SECTION 24.1 This chapter introduces **organic chemistry**, which is the study of carbon compounds (typically compounds containing carbon–carbon bonds), and **biochemistry**, which is the study of the chemistry of living organisms. We have encountered many aspects of organic chemistry in earlier chapters. Carbon forms four bonds in its stable compounds. The $\mathrm{C{-}C}$ single bonds and the $\mathrm{C{-}H}$ bonds tend to have low reactivity. Those bonds that have a high electron density (such as multiple bonds or bonds with an atom of high electronegativity) tend to be the sites of reactivity in an organic compound. These sites of reactivity are called **functional groups**.

SECTION 24.2 The simplest types of organic compounds are hydrocarbons, those composed of only carbon and hydrogen. There are four major kinds of hydrocarbons: alkanes, alkenes, alkynes, and aromatic hydrocarbons. **Alkanes** are composed of only $\mathrm{C{-}H}$ and $\mathrm{C{-}C}$ single bonds. **Alkenes** contain one or more carbon–carbon double bonds. **Alkynes** contain one or more carbon–carbon triple bonds. **Aromatic hydrocarbons** contain cyclic arrangements of carbon atoms bonded through both σ and delocalized π bonds. Alkanes are saturated hydrocarbons; the others are unsaturated.

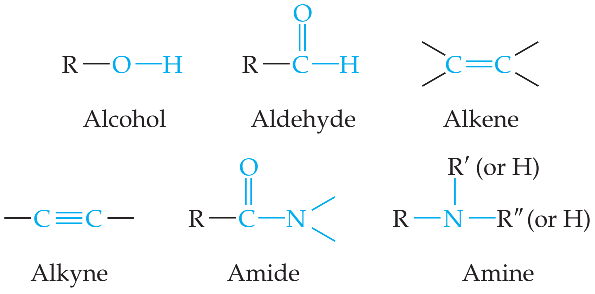
Alkanes may form straight-chain, branched-chain, and cyclic arrangements. Isomers are substances that possess the same molecular formula but differ in the arrangements of atoms. In **structural isomers** the bonding arrangements of the atoms differ. Different isomers are given different systematic names. The naming of hydrocarbons is based on the longest continuous chain of carbon atoms in the structure. The locations of **alkyl groups**, which branch off the chain, are specified by numbering along the carbon chain.

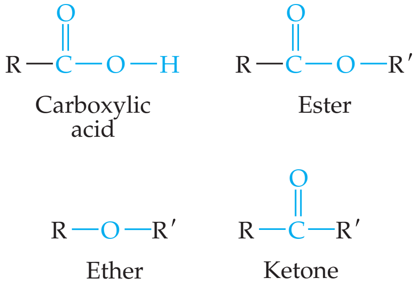
Alkanes with ring structures are called **cycloalkanes**. Alkanes are relatively unreactive. They do, however, undergo combustion in air, and their chief use is as sources of heat energy produced by combustion.

SECTION 24.3 The names of alkenes and alkynes are based on the longest continuous chain of carbon atoms that contains the multiple bond, and the location of the multiple bond is specified by a numerical prefix. Alkenes exhibit not only structural isomerism but geometric (*cis-trans*) isomerism as well. In **geometric isomers** the bonds are the same, but the molecules have different geometries. Geometric isomerism is possible in alkenes because rotation about the $\mathrm{C{=}C}$ double bond is restricted.

Alkenes and alkynes readily undergo **addition reactions** to the carbon–carbon multiple bonds. Additions of acids, such as HBr, proceed via a rate-determining step in which a proton is transferred to one of the alkene or alkyne carbon atoms. Addition reactions are difficult to carry out with aromatic hydrocarbons, but **substitution reactions** are easily accomplished in the presence of catalysts.

SECTION 24.4 The chemistry of organic compounds is dominated by the nature of their functional groups. The functional groups we have considered are





R, R′, and R″ represent hydrocarbon groups—for example, methyl (CH_3) or phenyl (C_6H_5).

Alcohols are hydrocarbon derivatives containing one or more OH groups. **Ethers** are formed by a condensation reaction of two molecules of alcohol. Several functional groups contain the **carbonyl** ($\mathrm{C{=}O}$) **group**, including **aldehydes**, **ketones**, **carboxylic acids**, **esters**, and **amides**. Aldehydes and ketones can be produced by oxidation of certain alcohols. Further oxidation of the aldehydes produces carboxylic acids. Carboxylic acids can form esters by a condensation reaction with alcohols, or they can form amides by a condensation reaction with amines. Esters undergo **hydrolysis** (**saponification**) in the presence of strong bases.

SECTION 24.5 Molecules that possess nonsuperimposable mirror images are termed **chiral**. The two nonsuperimposable forms of a chiral molecule are called *enantiomers*. In carbon compounds a chiral center is created when all four groups bonded to a central carbon atom are different, as in 2-bromobutane. Many of the molecules occurring in living systems, such as the amino acids, are chiral and exist in nature in only one enantiomeric form. Many drugs of importance in human medicine are chiral, and the enantiomers may produce very different biochemical effects. For this reason, synthesis of only the effective isomers of chiral drugs has become a high priority.

SECTIONS 24.6 AND 24.7 Many of the molecules that are essential for life are large natural polymers that are constructed from smaller molecules called monomers. Three of these **biopolymers** are considered in this chapter: proteins, polysaccharides (carbohydrates), and nucleic acids.

Proteins are polymers of **amino acids**. They are the major structural materials in animal systems. All naturally occurring proteins are formed from 22 amino acids, although only 20 are common. The amino acids are linked by **peptide bonds**. A **polypeptide** is a polymer formed by linking many amino acids by peptide bonds.

Amino acids are chiral substances. Usually only one of the enantiomers is found to be biologically active. Protein structure is determined by the sequence of amino acids in the chain (its **primary structure**), the coiling or stretching of the chain (its **secondary structure**), and the overall shape of the complete molecule (its **tertiary structure**). Two important secondary structures are the **α-helix** and the **β sheet**. The process by which a protein assumes its biologically active tertiary structure is called **folding**. Sometimes several proteins aggregate together to form a **quaternary structure**.

SECTIONS 24.8 AND 24.9 **Carbohydrates**, which are polyhydroxy aldehydes and ketones, are the major structural constituents of plants and are a source of energy in both plants and animals. **Glucose** is the most common **monosaccharide**, or simple sugar. Two monosaccharides can be linked together by means of a condensation reaction to form a **disaccharide**. **Polysaccharides** are complex carbohydrates made up of many monosaccharide units joined together. The three most important polysaccharides are **starch**, which is found in plants; **glycogen**, which is found in mammals; and **cellulose**, which is also found in plants.

Lipids are compounds derived from glycerol and fatty acids and include fats and **phospholipids**. Fatty acids can be *saturated, unsaturated, cis,* or *trans* depending on their chemical formulas and structures.

SECTION 24.10 **Nucleic acids** are biopolymers that carry the genetic information necessary for cell reproduction; they also control cell development through control of protein synthesis. The building blocks of these biopolymers are **nucleotides**. There are two types of nucleic acids, the **ribonucleic acids (RNA)** and the **deoxyribonucleic acids (DNA)**. These substances consist of a polymeric backbone of alternating phosphate and ribose or deoxyribose sugar groups with organic bases attached to the sugar molecules. The DNA polymer is a double-stranded helix (**double helix**) held together by hydrogen bonding between matching organic bases situated across from one another on the two strands. The hydrogen bonding between specific base pairs is the key to gene replication and protein synthesis.

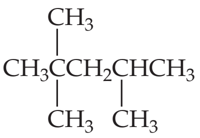
KEY SKILLS

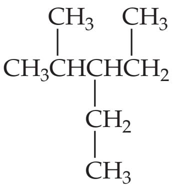
- Distinguish among alkanes, alkenes, alkynes, and aromatic hydrocarbons. (Section 24.2)
- Draw hydrocarbon structures based on their names and name hydrocarbons based on their structures. (Sections 24.2 and 24.3)
- Distinguish between addition reactions and substitution reactions. (Section 24.3)
- Know the structures of the functional groups: alkene, alkyne, alcohol, carbonyl, ether, aldehyde, ketone, carboxylic acid, amine, amide. (Section 24.4)
- Understand what makes a compound chiral and be able to recognize a chiral substance. (Section 24.5)
- Recognize the amino acids and understand how they form peptides and proteins via amide bond formation. (Section 24.7)
- Understand the differences among the primary, secondary, tertiary, and quaternary structures of proteins. (Section 24.7)
- Be able to explain the difference between α-helix and β-sheet peptide and protein structures. (Section 24.7)
- Understand the distinction between starch and cellulose structures. (Section 24.8)
- Classify molecules as saccharides or lipids based on their structures. (Sections 24.8 and 24.9)
- Understand the difference between a saturated and unsaturated fat. (Section 24.9)
- Understand the structure of nucleic acids and the role played by complementary bases in DNA replication. (Section 24.10)

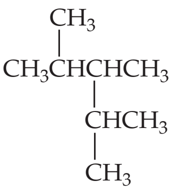
EXERCISES

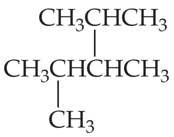
VISUALIZING CONCEPTS

24.1 All the structures shown here have the molecular formula C_8H_{18}. Which structures are the same molecule? (*Hint:* One way to answer this question is to determine the chemical name for each structure.) [Section 24.2]

(a)

$\mathrm{CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2\underset{CH_3}{C}HCH_3}$

(b)

$\mathrm{CH_3\overset{CH_3}{C}H\underset{\underset{CH_3}{CH_2}}{C}H\overset{CH_3}{C}H_2}$

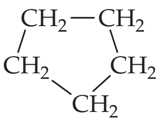
(c)

$\mathrm{CH_3\overset{CH_3}{C}H\underset{\underset{CH_3}{CHCH_3}}{C}HCH_3}$

(d)

$\mathrm{CH_3\underset{CH_3}{C}H\overset{CH_3CHCH_3}{C}HCH_3}$

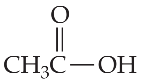
24.2 Which of these molecules is unsaturated? [Section 24.3]

$\mathrm{CH_3CH_2CH_2CH_3}$

(a)



(b)

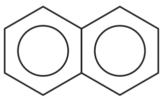

$\mathrm{CH_3\overset{O}{\overset{\|}{C}}-OH}$

(c)

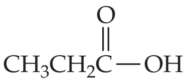
$\mathrm{CH_3CH{=}CHCH_3}$

(d)

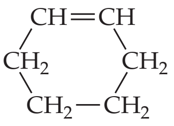
24.3 Which of these molecules most readily undergoes an addition reaction? [Section 24.3]



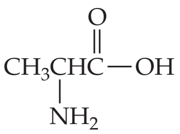
(a)


$\mathrm{CH_3CH_2\overset{O}{\overset{\|}{C}}-OH}$

(b)

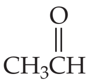


(c)


$\mathrm{CH_3\underset{NH_2}{C}H\overset{O}{\overset{\|}{C}}-OH}$

(d)

24.4 Which of these compounds would you expect to have the highest boiling point? Explain. [Section 24.4]


$\mathrm{CH_3\overset{O}{\overset{\|}{C}}H}$

(a)

$\mathrm{CH_3CH_2OH}$

(b)

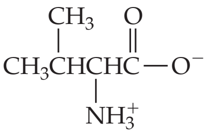
$\mathrm{CH_3C{\equiv}CH}$

(c)


$\mathrm{H\overset{O}{\overset{\|}{C}}OCH_3}$

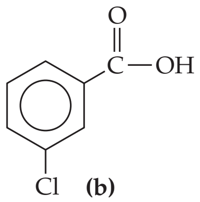
(d)

24.5 Which of these compounds can be a member of an isomer pair? In each case where isomerism is possible, identify the type or types of isomerism. [Sections 24.2, 24.4]



$\mathrm{CH_3\overset{\overset{CH_3}{|}}{C}H\underset{\underset{NH_3^+}{|}}{C}H\overset{\overset{O}{\|}}{C}{-}O^-}$

(a)



(b)

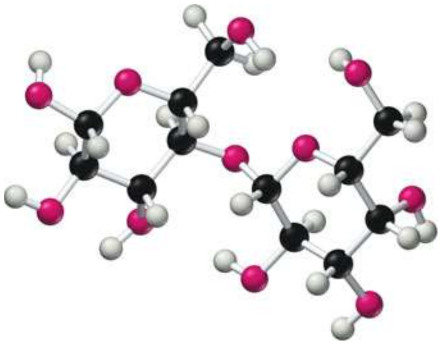
$\mathrm{CH_3CH_2CH{=}CHCH_3}$

(c)

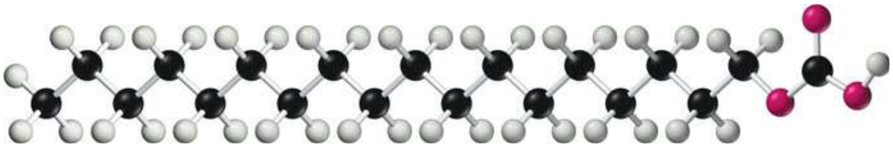
$\mathrm{CH_3CH_2CH_3}$

(d)

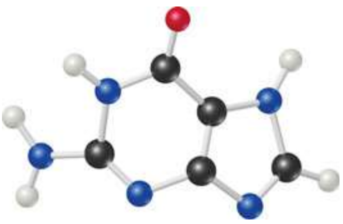
24.6 From examination of the molecular models i-v, choose the substance that (**a**) can be hydrolyzed to form a solution containing glucose, (**b**) is capable of forming a zwitterion, (**c**) is one of the four bases present in DNA, (**d**) reacts with an acid to form an ester, (**e**) is a lipid. [Sections 24.6–24.10]



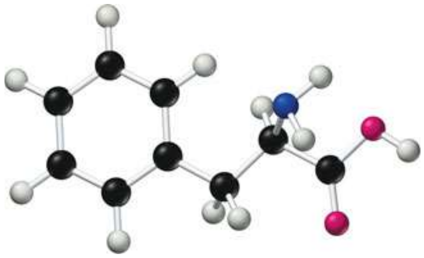
(i)



(ii)



(iii)



(iv)

(v)

INTRODUCTION TO ORGANIC COMPOUNDS; HYDROCARBONS (sections 24.1 and 24.2)

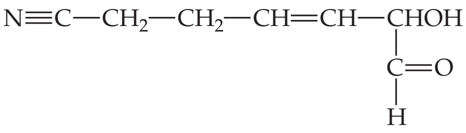
24.7 What are the characteristic hybrid orbitals employed by (**a**) carbon in an alkane, (**b**) carbon in a double bond in an alkene, (**c**) carbon in the benzene ring, (**d**) carbon in a triple bond in an alkyne?

24.8 What are the approximate bond angles (**a**) about carbon in an alkane, (**b**) about a doubly bonded carbon atom in an alkene, (**c**) about a triply bonded carbon atom in an alkyne?

24.9 Predict the ideal values for the bond angles about each carbon atom in the following molecule. Indicate the hybridization of orbitals for each carbon.

$$\mathrm{CH_3CCCH_2COOH}$$

24.10 Identify the carbon atom(s) in the structure shown that has (have) each of the following hybridizations: (**a**) sp^3, (**b**) sp, (**c**) sp^2.



$\mathrm{N{\equiv}C{-}CH_2{-}CH_2{-}CH{=}CH{-}\underset{\underset{\underset{\underset{H}{|}}{C{=}O}}{|}}{C}HOH}$

24.11 Are carbon monoxide or ammonia considered organic molecules? Why or why not?

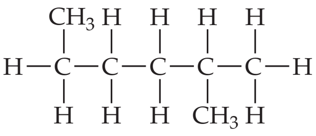
24.12 Organic compounds containing C—O and C—Cl bonds are more reactive than simple alkane hydrocarbons. Considering the comparative values of C—H, C—C, C—O, and C—Cl bond enthalpies (Table 8.4), why is this so?

24.13 (**a**) What is the difference between a straight-chain and branched-chain alkane? (**b**) What is the difference between an alkane and an alkyl group?

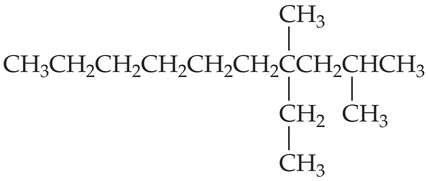
24.14 What structural features help us identify a compound as (**a**) an alkane, (**b**) a cycloalkane, (**c**) an alkene, (**d**) an alkyne, (**e**) a saturated hydrocarbon, (**f**) an aromatic hydrocarbon?

24.15 Give the the name or condensed structural formula, as appropriate:

(a)

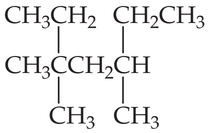


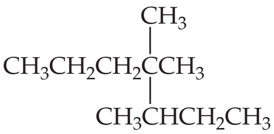
$$\begin{array}{ccccccccccc} & & \mathrm{CH_3} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} \\ & & | & & | & & | & & | & & | \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - \mathrm{H} \\ & & | & & | & & | & & | & & | \\ & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{CH_3} & & \mathrm{H} \end{array}$$

(b) 
$CH_3CH_2CH_2CH_2CH_2CH_2\overset{CH_3}{\underset{\underset{CH_3}{CH_2}}{C}}CH_2\underset{CH_3}{CH}CH_3$

(c) 2-methylheptane
(d) 4-ethyl-2,3-dimethyloctane
(e) 1,2-dimethylcyclohexane

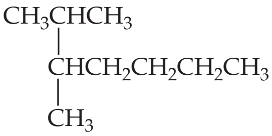
24.16 Give the name or condensed structural formula, as appropriate:

(a) 
$CH_3\overset{CH_3CH_2}{\underset{CH_3}{C}}CH_2\overset{CH_2CH_3}{\underset{CH_3}{CH}}$

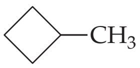
(b) 
$CH_3CH_2CH_2\overset{CH_3}{\underset{CH_3CHCH_2CH_3}{C}}CH_3$

(c) 2,5,6-trimethylnonane
(d) 3-propyl-4,5-methyldecane
(e) 1-ethyl-3-methylcyclohexane

24.17 Give the name or condensed structural formula, as appropriate:

(a) 
$CH_3\underset{\underset{CH_3}{CHCH_2CH_2CH_2CH_3}}{CH}CH_3$

(b) 2,2-dimethylpentane
(c) 4-ethyl-1,1-dimethylcyclohexane
(d) $(CH_3)_2CHCH_2CH_2C(CH_3)_3$
(e) $CH_3CH_2CH(C_2H_5)CH_2CH_2CH_2CH_3$

24.18 Give the name or condensed structural formula, as appropriate:
(a) 3-phenylpentane
(b) 2,3-dimethylhexane
(c) 2-ethyl-2-methylhepane
(d) $CH_3CH_2CH(CH_3)CH_2CH(CH_3)_2$
(e) 

24.19 What is the octane number of a mixture that is 35% heptane and 65% isooctane?

24.20 Describe two ways in which the octane number of a gasoline consisting of alkanes can be increased.

ALKENES, ALKYNES, AND AROMATIC HYDROCARBONS (section 24.3)

24.21 **(a)** Why are alkanes said to be saturated? **(b)** Is C_4H_6 a saturated hydrocarbon? Why or why not?

24.22 **(a)** Is the compound $CH_3CH{=}CH_2$ saturated or unsaturated? Explain. **(b)** What is wrong with the formula $CH_3CH_2CH{=}CH_3$?

24.23 Give the molecular formula of a hydrocarbon containing five carbon atoms that is **(a)** an alkane, **(b)** a cycloalkane, **(c)** an alkene, **(d)** an alkyne. Which are saturated and which are unsaturated hydrocarbons?

24.24 Give the molecular formula of a cyclic alkane, a cyclic alkene, a linear alkyne, and an aromatic hydrocarbon that in each case contains six carbon atoms. Which are saturated and which are unsaturated hydrocarbons?

24.25 Enediynes are a class of compounds that include some antibiotic drugs. Draw the structure of an "enediyne" fragment that contains six carbons in a row. (*Hint: di* means "two.")

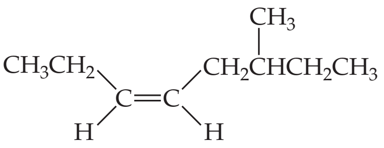
24.26 Give the general formula for any cyclic alkene, that is, a cyclic hydrocarbon with one double bond.

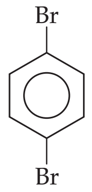
24.27 Write the condensed structural formulas for as many alkenes and alkynes as you can think of that have the molecular formula C_6H_{10}.

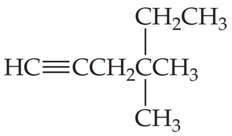
24.28 Draw all the possible noncyclic structural isomers of C_5H_{10}. Name each compound.

24.29 Name or write the condensed structural formula for the following compounds:

(a) *trans* -2-pentene
(b) 2,5-dimethyl-4-octene

(c) 

(d) 

(e) 
$HC\equiv CCH_2\overset{CH_2CH_3}{\underset{CH_3}{C}}CH_3$

24.30 Name or write the condensed structural formula for the following compounds:
(a) 4-methyl-2-pentene
(b) *cis*-2,5-dimethyl-3-hexene
(c) ortho-dimethylbenzene
(d) $HC\equiv CCH_2CH_3$
(e) *trans*-$CH_3CH{=}CHCH_2CH_2CH_2CH_3$

24.31 Why is geometric isomerism possible for alkenes but not for alkanes and alkynes?

24.32 Draw all structural and geometric isomers of butene and name them.

24.33 Indicate whether each of the following molecules is capable of geometrical (cis-trans) isomerism. For those that are, draw the structures: **(a)** 1,1-dichloro-1-butene, **(b)** 2,4-dichloro-2-butene, **(c)** 1,4-dichlorobenzene, **(d)** 4,5-dimethyl-2-pentyne.

24.34 Draw the three distinct geometric isomers of 2,4-hexadiene.

24.35 **(a)** What is the difference between a substitution reaction and an addition reaction? Which one is commonly observed with alkenes and which one with aromatic hydrocarbons? **(b)** Using condensed structural formulas, write the balanced equation for the addition reaction of 2-pentene with Br_2 and name the resulting compound. (**c**) Write a balanced chemical equation for the substitution reaction of Cl_2 with benzene to make *para*-dichlorobenzene in the presence of $FeCl_3$ as a catalyst.

24.36 Using condensed structural formulas, write a balanced chemical equation for each of the following reactions: (**a**) hydrogenation of cyclohexene; (**b**) addition of H_2O to *trans*-2-pentene using H_2SO_4 as a catalyst (two products); (**c**) reaction of 2-chloropropane with benzene in the presence of $AlCl_3$.

24.37 (**a**) When cyclopropane is treated with HI, 1-iodopropane is formed. A similar type of reaction does not occur with cyclopentane or cyclohexane. How do you account for the reactivity of cyclopropane? (**b**) Suggest a method of preparing ethylbenzene, starting with benzene and ethylene as the only organic reagents.

24.38 (**a**) One test for the presence of an alkene is to add a small amount of bromine, a red-brown liquid, and look for the disappearance of the red-brown color. This test does not work for detecting the presence of an aromatic hydrocarbon. Explain. (**b**) Write a series of reactions leading to *para*-bromoethylbenzene, beginning with benzene and using other reagents as needed. What isomeric side products might also be formed?

24.39 The rate law for addition of Br_2 to an alkene is first order in Br_2 and first order in the alkene. Does this fact prove that the mechanism of addition of Br_2 to an alkene proceeds in the same manner as for addition of HBr? Explain.

24.40 Describe the intermediate that is thought to form in the addition of a hydrogen halide to an alkene, using cyclohexene as the alkene in your description.

24.41 The molar heat of combustion of gaseous cyclopropane is -2089 kJ/mol; that for gaseous cyclopentane is -3317 kJ/mol. Calculate the heat of combustion per CH_2 group in the two cases, and account for the difference.

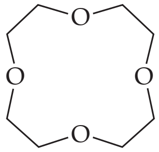
24.42 The heat of combustion of decahydronaphthalene ($C_{10}H_{18}$) is -6286 kJ/mol. The heat of combustion of naphthalene ($C_{10}H_8$) is -5157 kJ/mol. [In both cases $CO_2(g)$ and $H_2O(l)$ are the products.] Using these data and data in Appendix C, calculate the heat of hydrogenation of naphthalene. Does this value provide any evidence for aromatic character in naphthalene?

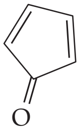
FUNCTIONAL GROUPS AND CHIRALITY (sections 24.4 and 24.5)

24.43 Identify the functional groups in each of the following compounds:

(a) $H_3C—CH_2—OH$

(c) 
$H_3C—\overset{H}{N}—CH_2CH{=}CH_2$

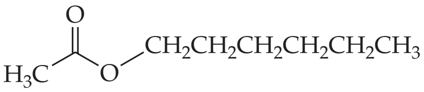
(b) 

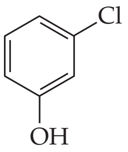
(d) 

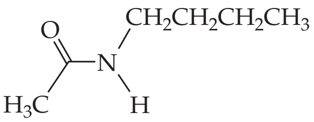
(e) $CH_3CH_2CH_2CH_2CHO$

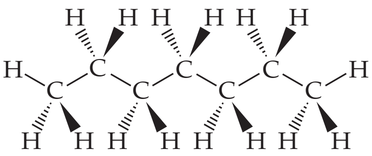
(f) $CH_3C{\equiv}CCH_2COOH$

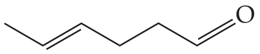
24.44 Identify the functional groups in each of the following compounds:

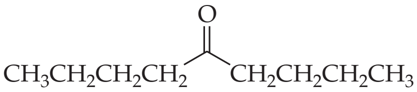
(a) 

(b) 

(c) 

(d) 

(e) 

(f) 
$CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_3$

24.45 Give the structural formula for (**a**) an aldehyde that is an isomer of acetone, (**b**) an ether that is an isomer of 1-propanol.

24.46 (**a**) Give the empirical formula and structural formula for a cyclic ether containing four carbon atoms in the ring. (**b**) Write the structural formula for a straight-chain compound that is a structural isomer of your answer to part (a).

24.47 The IUPAC name for a carboxylic acid is based on the name of the hydrocarbon with the same number of carbon atoms. The ending *-oic* is appended, as in ethanoic acid, which is the IUPAC name for acetic acid. Draw the structure of the following acids: (**a**) methanoic acid, (**b**) pentanoic acid, (**c**) 2-chloro-3-methyldecanoic acid.

24.48 Aldehydes and ketones can be named in a systematic way by counting the number of carbon atoms (including the carbonyl carbon) that they contain. The name of the aldehyde or ketone is based on the hydrocarbon with the same number of carbon atoms. The ending *-al* for aldehyde or *-one* for ketone is added as appropriate. Draw the structural formulas for the following aldehydes or ketones: (**a**) propanal, (**b**) 2-pentanone, (**c**) 3-methyl-2-butanone, (**d**) 2-methylbutanal.

24.49 Draw the condensed structure of the compounds formed by condensation reactions between (**a**) benzoic acid and ethanol, (**b**) ethanoic acid and methylamine, (**c**) acetic acid and phenol. Name the compound in each case.

24.50 Draw the condensed structures of the compounds formed from (**a**) butanoic acid and methanol, (**b**) benzoic acid and 2-propanol, (**c**) propanoic acid and dimethylamine. Name the compound in each case.

24.51 Write a balanced chemical equation using condensed structural formulas for the saponification (base hydrolysis) of (**a**) methyl propionate, (**b**) phenyl acetate.

24.52 Write a balanced chemical equation using condensed structural formulas for (**a**) the formation of butyl propionate from the appropriate acid and alcohol, (**b**) the saponification (base hydrolysis) of methyl benzoate.

24.53 Would you expect pure acetic acid to be a strongly hydrogen-bonded substance? How do the melting and boiling points of the substance (16.7 °C and 118 °C) support your answer?

24.54 Acetic anhydride is formed from acetic acid in a condensation reaction that involves the removal of a molecule of water from between two acetic acid molecules. Write the chemical equation for this process, and show the structure of acetic anhydride.

24.55 Write the condensed structural formula for each of the following compounds: (**a**) 2-pentanol, (**b**) 1,2-propanediol, (**c**) ethyl acetate, (**d**) diphenyl ketone, (**e**) methyl ethyl ether.

24.56 Write the condensed structural formula for each of the following compounds: (**a**) 2-ethyl-1-hexanol, (**b**) methyl phenyl ketone, (**c**) *para*-bromobenzoic acid, (**d**) ethyl butyl ether, (**e**) *N*, *N*-dimethylbenzamide.

24.57 Draw the structure for 2-bromo-2-chloro-3-methylpentane, and indicate any chiral carbons in the molecule.

24.58 Does 3-chloro-3-methylhexane have optical isomers? Why or why not?

PROTEINS (section 24.7)

24.59 (**a**) What is an α-amino acid? (**b**) How do amino acids react to form proteins? (**c**) Draw the bond that links amino acids together in proteins. What is this called?

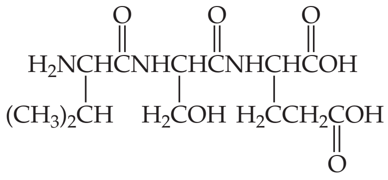
24.60 What properties of the side chains (R groups) of amino acids are important in affecting the amino acids' overall biochemical behavior? Give examples to illustrate your reply.

24.61 Draw the two possible dipeptides formed by condensation reactions between leucine and tryptophan.

24.62 Write a chemical equation for the formation of methionyl glycine from the constituent amino acids.

24.63 (**a**) Draw the condensed structure of the tripeptide Gly-Gly-His. (**b**) How many different tripeptides can be made from the amino acids glycine and histidine? Give the abbreviations for each of these tripeptides, using the three-letter and one-letter codes for the amino acids.

24.64 (**a**) What amino acids would be obtained by hydrolysis of the following tripeptide?



$$\mathrm{H_2N\underset{(CH_3)_2CH}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}NH\underset{H_2COH}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}NH\underset{H_2CCH_2\underset{\underset{O}{\|}}{C}OH}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}OH}$$

(**b**) How many different tripeptides can be made from glycine, serine, and glutamic acid? Give the abbreviation for each of these tripeptides, using the three-letter codes and one-letter codes for the amino acids.

24.65 (**a**) Describe the primary, secondary, and tertiary structures of proteins. (**b**) *Quaternary structures* of proteins arise if two or more smaller polypeptides or proteins associate with each other to make an overall much larger protein structure. The association is due to the same hydrogen bonding, electrostatic, and dispersion forces we have seen before. Hemoglobin, the protein used to transport oxygen molecules in our blood, is an example of a protein that has quaternary structure. Hemoglobin is a tetramer; it is made of four smaller polypeptides, two "alphas" and two "betas." (These names do not imply anything about the number of alpha-helices or beta sheets in the individual polypeptides.) What kind of experiments would provide sound evidence that hemoglobin exists as a tetramer and not as one enormous polypeptide chain? You may need to look into the chemical literature to discover techniques that chemists and biochemists use to make these decisions.

24.66 What is the difference between the α-helix and β-sheet secondary structures in proteins?

CARBOHYDRATES AND LIPIDS (sections 24.8 and 24.9)

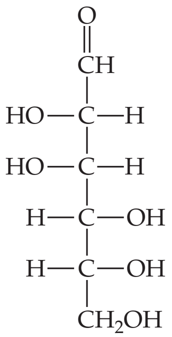
24.67 In your own words, define the following terms: (**a**) carbohydrate, (**b**) monosaccharide, (**c**) disaccharide, (**d**) polysaccharide.

24.68 What is the difference between α-glucose and β-glucose? Show the condensation of two glucose molecules to form a disaccharide with an α linkage; with a β linkage.

24.69 What is the empirical formula of cellulose? What is the unit that forms the basis of the cellulose polymer? What form of linkage joins these monomeric units?

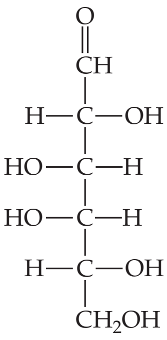
24.70 What is the empirical formula of glycogen? What is the unit that forms the basis of the glycogen polymer? What form of linkage joins these monomeric units?

24.71 The structural formula for the linear form of D-mannose is



(**a**) How many chiral carbons are present in the molecule? (**b**) Draw the structure of the six-member-ring form of this sugar.

24.72 The structural formula for the linear form of galactose is



(**a**) How many chiral carbons are present in the molecule? (**b**) Draw the structure of the six-member-ring form of this sugar.

24.73 Describe the chemical structures of lipids and phospholipids. Why can phospholipids form a bilayer in water?

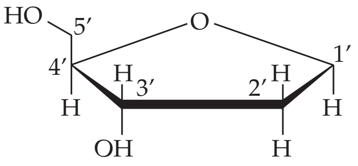
24.74 Using data from Table 8.4 on bond enthalpies, show that the more C—H bonds a molecule has compared to C—O and O—H bonds, the more energy it can store.

NUCLEIC ACIDS (section 24.10)

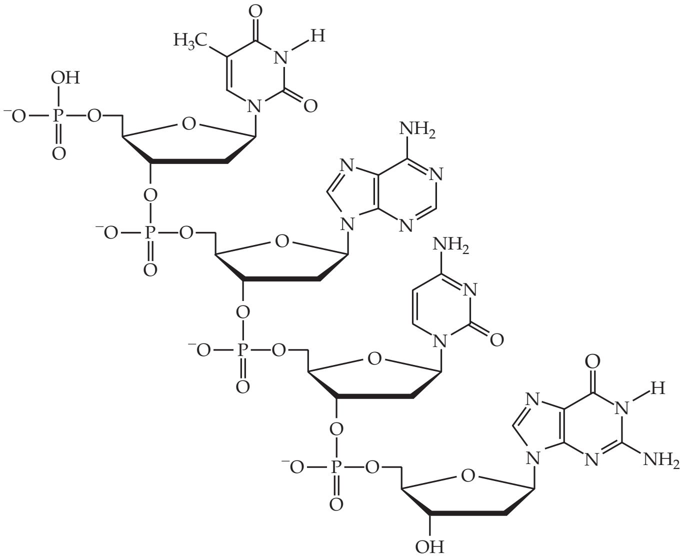
24.75 Adenine and guanine are members of a class of molecules known as *purines*; they have two rings in their structure. Thymine and cytosine, on the other hand, are *pyrimidines*, and have only one ring in their structure. Predict which have larger dispersion forces in aqueous solution, the purines or the pyrimidines.

24.76 A nucleoside consists of an organic base of the kind shown in Section 24.10, bound to ribose or deoxyribose. Draw the structure for deoxyguanosine, formed from guanine and deoxyribose.

24.77 Just as the amino acids in a protein are listed in the order from the amine end to the carboxylic acid end (the *protein sequence*), the bases in nucleic acids are listed in the order 5′ to 3′, where the numbers refer to the position of the carbons in the sugars (shown here for deoxyribose):



The base is attached to the sugar at the 1′ carbon. The 5′ end of a DNA sequence is a phosphate of an OH group, and the 3′ end of a DNA sequence is the OH group. What is the DNA sequence for the molecule shown here?



24.78 When samples of double-stranded DNA are analyzed, the quantity of adenine present equals that of thymine. Similarly, the quantity of guanine equals that of cytosine. Explain the significance of these observations.

24.79 Imagine a single DNA strand containing a section with the following base sequence: 5′-GCATTGGC-3′. What is the base sequence of the complementary strand? (The two strands of DNA will come together in an *antiparallel* fashion; that is, 5′-TAG-3′ will bind to 3′-ATC-5′.)

24.80 Explain the chemical differences between DNA and RNA.

ADDITIONAL EXERCISES

24.81 Draw the condensed structural formulas for two different molecules with the formula C_3H_4O.

24.82 How many structural isomers are there for a five-member straight carbon chain with one double bond? For a six-member straight carbon chain with two double bonds?

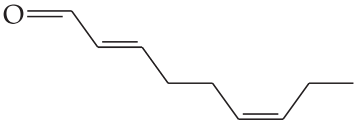
24.83 Draw the condensed structural formulas for the cis and trans isomers of 2-pentene. Can cyclopentene exhibit cis-trans isomerism? Explain.

24.84 If a molecule is an "ene-one," what functional groups must it have?

24.85 Write the structural formulas for as many alcohols as you can think of that have empirical formula C_3H_6O.

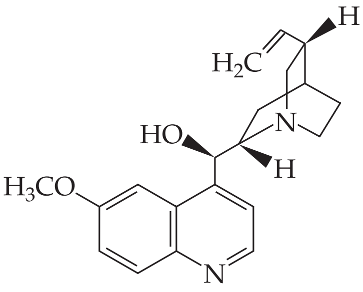
24.86 Identify each of the functional groups in these molecules:

(a)



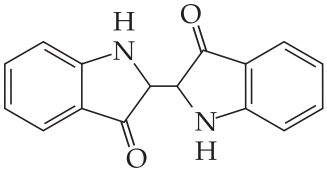
(Responsible for the odor of cucumbers)

(b)



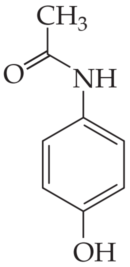
(Quinine — an antimalarial drug)

(c)



(Indigo — a blue dye)

(d)

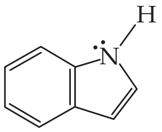


(Acetaminophen — aka Tylenol)

24.87 Write a condensed structural formula for each of the following: **(a)** an acid with the formula $C_4H_8O_2$, **(b)** a cyclic ketone with the formula C_5H_8O, **(c)** a dihydroxy compound with the formula $C_3H_8O_2$, **(d)** a cyclic ester with the formula $C_5H_8O_2$.

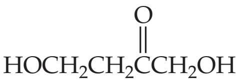
24.88 Although carboxylic acids and alcohols both contain an —OH group, one is acidic in water and the other is not. Explain the difference.

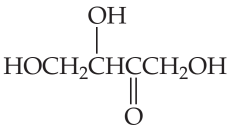
[24.89] Indole smells terrible in high concentrations but has a pleasant floral-like odor when highly diluted. Its structure is

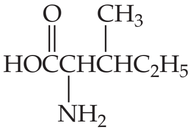


The molecule is planar, and the nitrogen is a very weak base, with $K_b = 2 \times 10^{-12}$. Explain how this information indicates that the indole molecule is aromatic.

24.90 Locate the chiral carbon atoms, if any, in each molecule:

(a) 
$\mathrm{HOCH_2CH_2\overset{O}{\overset{\|}{C}}CH_2OH}$

(b) 
$\mathrm{HOCH_2\overset{OH}{\overset{|}{C}}H\underset{O}{\underset{\|}{C}}CH_2OH}$

(c) 
$\mathrm{HO\overset{O}{\overset{\|}{C}}\underset{NH_2}{\underset{|}{C}}H\overset{CH_3}{\overset{|}{C}}HC_2H_5}$

24.91 Which of the following peptides have a net positive charge at pH 7? **(a)** Gly-Ser-Lys, **(b)** Pro-Leu-Ile, **(c)** Phe-Tyr-Asp.

24.92 Glutathione is a tripeptide found in most living cells. Partial hydrolysis yields Cys-Gly and Glu-Cys. What structures are possible for glutathione?

24.93 Monosaccharides can be categorized in terms of the number of carbon atoms (pentoses have five carbons and hexoses have six carbons) and according to whether they contain an aldehyde (*aldo-* prefix, as in aldopentose) or ketone group (*keto-* prefix, as in ketopentose). Classify glucose and fructose in this way.

24.94 Can a DNA strand bind to a complementary RNA strand? Explain.

INTEGRATIVE EXERCISES

24.95 Explain why the boiling point of ethanol (78 °C) is much higher than that of its isomer, dimethyl ether (−25 °C), and why the boiling point of CH_2F_2 (−52 °C) is far above that of CH_4 (−128 °C).

[24.96] An unknown organic compound is found on elemental analysis to contain 68.1% carbon, 13.7% hydrogen, and 18.2% oxygen by mass. It is slightly soluble in water. Upon careful oxidation it is converted into a compound that behaves chemically like a ketone and contains 69.7% carbon, 11.7% hydrogen, and 18.6% oxygen by mass. Indicate two or more reasonable structures for the unknown.

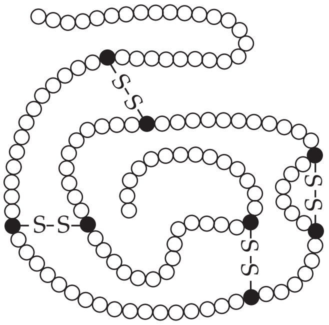
24.97 An organic compound is analyzed and found to contain 66.7% carbon, 11.2% hydrogen, and 22.1% oxygen by mass. The compound boils at 79.6 °C. At 100 °C and 0.970 atm, the vapor has a density of 2.28 g/L. The compound has a carbonyl group and cannot be oxidized to a carboxylic acid. Suggest a structure for the compound.

[24.98] An unknown substance is found to contain only carbon and hydrogen. It is a liquid that boils at 49 °C at 1 atm pressure. Upon analysis it is found to contain 85.7% carbon and 14.3% hydrogen by mass. At 100 °C and 735 torr, the vapor of this unknown has a density of 2.21 g/L. When it is dissolved in hexane solution and bromine water is added, no reaction occurs. What is the identity of the unknown compound?

24.99 The standard free energy of formation of solid glycine is −369 kJ/mol, whereas that of solid glycylglycine is −488 kJ/mol. What is $\Delta G°$ for the condensation of glycine to form glycylglycine?

24.100 A typical amino acid with one amino group and one carboxylic acid group, such as serine (Figure 24.18), can exist in water in several ionic forms. **(a)** Suggest the forms of the amino acid at low pH and at high pH. **(b)** Amino acids generally have two pK_a values, one in the range of 2 to 3 and the other in the range of 9 to 10. Serine, for example, has pK_a values of 2.19 and 9.21. Using species such as acetic acid and ammonia as models, suggest the origin of the two pK_a values. **(c)** Glutamic acid is an amino acid that has three pK_a's: 2.10, 4.07, and 9.47. Draw the structure of glutamic acid, and assign each pK_a to the appropriate part of the molecule.

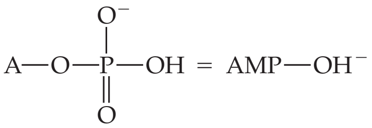
[24.101] The protein ribonuclease A in its native, or most stable, form is folded into a compact globular shape:



Native ribonuclease A

(a) Does the native form have a lower or higher free energy than the denatured form, in which the protein is an extended chain? **(b)** What is the sign of the entropy change in going from the denatured to the folded form? **(c)** In the native form, the molecule has four —S—S— bonds that bridge parts of the chain. What effect do you predict these four linkages to have on the free energy and entropy of the native form relative to the free energy and entropy of a hypothetical folded structure that does not have any —S—S— linkages? Explain. **(d)** A gentle reducing agent converts the four —S—S— linkages in ribonuclease A to eight —S—H bonds. What effect do you predict this conversion to have on the tertiary structure and entropy of the protein? **(e)** Which amino acid must be present for —SH bonds to exist in ribonuclease A?

24.102 The monoanion of adenosine monophosphate (AMP) is an intermediate in phosphate metabolism:


$$\mathrm{A{-}O{-}\overset{O^-}{\overset{|}{\underset{O}{\underset{\|}{P}}}}{-}OH = AMP{-}OH^-}$$

where A = adenosine. If the pK_a for this anion is 7.21, what is the ratio of $[\mathrm{AMP{-}OH^-}]$ to $[\mathrm{AMP{-}O^{2-}}]$ in blood at pH 7.4?

APPENDIX A

MATHEMATICAL OPERATIONS

A.1 EXPONENTIAL NOTATION

The numbers used in chemistry are often either extremely large or extremely small. Such numbers are conveniently expressed in the form

$$N \times 10^n$$

where N is a number between 1 and 10, and n is the exponent. Some examples of this *exponential notation*, which is also called *scientific notation*, follow.

1,200,000 is 1.2×10^6 (read "one point two times ten to the sixth power")

0.000604 is 6.04×10^{-4} (read "six point zero four times ten to the negative fourth power")

A positive exponent, as in the first example, tells us how many times a number must be multiplied by 10 to give the long form of the number:

$$\begin{aligned} 1.2 \times 10^6 &= 1.2 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \quad \text{(six tens)} \\ &= 1{,}200{,}000 \end{aligned}$$

It is also convenient to think of the *positive exponent* as the number of places the decimal point must be moved to the *left* to obtain a number greater than 1 and less than 10. For example, if we begin with 3450 and move the decimal point three places to the left, we end up with 3.45×10^3.

In a related fashion, a negative exponent tells us how many times we must divide a number by 10 to give the long form of the number.

$$6.04 \times 10^{-4} = \frac{6.04}{10 \times 10 \times 10 \times 10} = 0.000604$$

It is convenient to think of the *negative exponent* as the number of places the decimal point must be moved to the *right* to obtain a number greater than 1 but less than 10. For example, if we begin with 0.0048 and move the decimal point three places to the right, we end up with 4.8×10^{-3}.

In the system of exponential notation, with each shift of the decimal point one place to the right, the exponent *decreases* by 1:

$$4.8 \times 10^{-3} = 48 \times 10^{-4}$$

Similarly, with each shift of the decimal point one place to the left, the exponent *increases* by 1:

$$4.8 \times 10^{-3} = 0.48 \times 10^{-2}$$

Many scientific calculators have a key labeled EXP or EE, which is used to enter numbers in exponential notation. To enter the number 5.8×10^3 on such a calculator, the key sequence is

$$\boxed{5}\boxed{\cdot}\boxed{8}\boxed{\text{EXP}}\ (\text{or } \boxed{\text{EE}})\ \boxed{3}$$

On some calculators the display will show 5.8, then a space, followed by 03, the exponent. On other calculators, a small 10 is shown with an exponent 3.

To enter a negative exponent, use the key labeled +/−. For example, to enter the number 8.6×10^{-5}, the key sequence is

$$\boxed{8}\boxed{\cdot}\boxed{6}\boxed{\text{EXP}}\boxed{+/-}\boxed{5}$$

When entering a number in exponential notation, do not key in the 10 if you use the EXP or EE button.

In working with exponents, it is important to recall that $10^0 = 1$. The following rules are useful for carrying exponents through calculations.

1. **Addition and Subtraction** In order to add or subtract numbers expressed in exponential notation, the powers of 10 must be the same.

$$\begin{aligned}(5.22 \times 10^4) + (3.21 \times 10^2) &= (522 \times 10^2) + (3.21 \times 10^2)\\ &= 525 \times 10^2 \quad \text{(3 significant figures)}\\ &= 5.25 \times 10^4\\ (6.25 \times 10^{-2}) - (5.77 \times 10^{-3}) &= (6.25 \times 10^{-2}) - (0.577 \times 10^{-2})\\ &= 5.67 \times 10^{-2} \quad \text{(3 significant figures)}\end{aligned}$$

When you use a calculator to add or subtract, you need not be concerned with having numbers with the same exponents because the calculator automatically takes care of this matter.

2. **Multiplication and Division** When numbers expressed in exponential notation are multiplied, the exponents are added; when numbers expressed in exponential notation are divided, the exponent of the denominator is subtracted from the exponent of the numerator.

$$\begin{aligned}(5.4 \times 10^2)(2.1 \times 10^3) &= (5.4)(2.1) \times 10^{2+3}\\ &= 11 \times 10^5\\ &= 1.1 \times 10^6\\ (1.2 \times 10^5)(3.22 \times 10^{-3}) &= (1.2)(3.22) \times 10^{5+(-3)} = 3.9 \times 10^2\\ \frac{3.2 \times 10^5}{6.5 \times 10^2} &= \frac{3.2}{6.5} \times 10^{5-2} = 0.49 \times 10^3 = 4.9 \times 10^2\\ \frac{5.7 \times 10^7}{8.5 \times 10^{-2}} &= \frac{5.7}{8.5} \times 10^{7-(-2)} = 0.67 \times 10^9 = 6.7 \times 10^8\end{aligned}$$

3. **Powers and Roots** When numbers expressed in exponential notation are raised to a power, the exponents are multiplied by the power. When the roots of numbers expressed in exponential notation are taken, the exponents are divided by the root.

$$\begin{aligned}(1.2 \times 10^5)^3 &= (1.2)^3 \times 10^{5\times 3}\\ &= 1.7 \times 10^{15}\\ \sqrt[3]{2.5 \times 10^6} &= \sqrt[3]{2.5} \times 10^{6/3}\\ &= 1.3 \times 10^2\end{aligned}$$

Scientific calculators usually have keys labeled x^2 and $\sqrt{x}$ for squaring and taking the square root of a number, respectively. To take higher powers or roots, many calculators have y^x and $\sqrt[x]{y}$ (or INV y^x) keys. For example, to perform the operation $\sqrt[3]{7.5 \times 10^{-4}}$ on such a calculator, you would key in 7.5×10^{-4}, press the $\sqrt[x]{y}$ key (or the INV and then the y^x keys), enter the root, 3, and finally press = . The result is 9.1×10^{-2}.

SAMPLE EXERCISE 1 Using Exponential Notation

Perform each of the following operations, using your calculator where possible:

(a) Write the number 0.0054 in standard exponential notation.
(b) $(5.0 \times 10^{-2}) + (4.7 \times 10^{-3})$
(c) $(5.98 \times 10^{12})(2.77 \times 10^{-5})$
(d) $\sqrt[4]{1.75 \times 10^{-12}}$

SOLUTION

(a) Because we move the decimal point three places to the right to convert 0.0054 to 5.4, the exponent is -3:

$$5.4 \times 10^{-3}$$

Scientific calculators are generally able to convert numbers to exponential notation using one or two keystrokes; frequently "SCI" for "scientific notation" will convert a number into exponential notation. Consult your instruction manual to see how this operation is accomplished on your calculator.
(b) To add these numbers longhand, we must convert them to the same exponent.

$$(5.0 \times 10^{-2}) + (0.47 \times 10^{-2}) = (5.0 + 0.47) \times 10^{-2} = 5.5 \times 10^{-2}$$

(Note that the result has only two significant figures.) To perform this operation on a calculator, we enter the first number, strike the + key, then enter the second number and strike the = key.
(c) Performing this operation longhand, we have

$$(5.98 \times 2.77) \times 10^{12-5} = 16.6 \times 10^{7} = 1.66 \times 10^{8}$$

On a scientific calculator, we enter 5.98×10^{12}, press the × key, enter 2.77×10^{-5}, and press the = key.
(d) To perform this operation on a calculator, we enter the number, press the $\sqrt[x]{y}$ key (or the INV and y^x keys), enter 4, and press the = key. The result is 1.15×10^{-3}.

PRACTICE EXERCISE

Perform the following operations:

(a) Write 67,000 in exponential notation, showing two significant figures.
(b) $(3.378 \times 10^{-3}) - (4.97 \times 10^{-5})$
(c) $(1.84 \times 10^{15})(7.45 \times 10^{-2})$
(d) $(6.67 \times 10^{-8})^3$

Answers: **(a)** 6.7×10^{4}, **(b)** 3.328×10^{-3}, **(c)** 2.47×10^{16}, **(d)** 2.97×10^{-22}

A.2 LOGARITHMS

Common Logarithms

The common, or base-10, logarithm (abbreviated log) of any number is the power to which 10 must be raised to equal the number. For example, the common logarithm of 1000 (written log 1000) is 3 because raising 10 to the third power gives 1000.

$$10^3 = 1000, \text{ therefore, } \log 1000 = 3$$

Further examples are

$$\log 10^5 = 5$$
$$\log 1 = 0 \qquad \text{Remember that } 10^0 = 1$$
$$\log 10^{-2} = -2$$

In these examples the common logarithm can be obtained by inspection. However, it is not possible to obtain the logarithm of a number such as 31.25 by inspection. The logarithm of 31.25 is the number x that satisfies the following relationship:

$$10^x = 31.25$$

Most electronic calculators have a key labeled LOG that can be used to obtain logarithms. For example, on many calculators we obtain the value of log 31.25 by entering 31.25 and pressing the LOG key. We obtain the following result:

$$\log 31.25 = 1.4949$$

Notice that 31.25 is greater than 10 (10^1) and less than 100 (10^2). The value for log 31.25 is accordingly between log 10 and log 100, that is, between 1 and 2.

Significant Figures and Common Logarithms

For the common logarithm of a measured quantity, the number of digits after the decimal point equals the number of significant figures in the original number. For example, if 23.5 is a measured quantity (three significant figures), then $\log 23.5 = 1.371$ (three significant figures after the decimal point).

Antilogarithms

The process of determining the number that corresponds to a certain logarithm is known as obtaining an *antilogarithm*. It is the reverse of taking a logarithm. For example, we saw previously that $\log 23.5 = 1.371$. This means that the antilogarithm of 1.371 equals 23.5.

$$\log 23.5 = 1.371$$
$$\text{antilog } 1.371 = 23.5$$

The process of taking the antilog of a number is the same as raising 10 to a power equal to that number.

$$\text{antilog } 1.371 = 10^{1.371} = 23.5$$

Many calculators have a key labeled 10^x that allows you to obtain antilogs directly. On others, it will be necessary to press a key labeled INV (for *inverse*), followed by the LOG key.

Natural Logarithms

Logarithms based on the number e are called natural, or base e, logarithms (abbreviated ln). The natural log of a number is the power to which e (which has the value 2.71828...) must be raised to equal the number. For example, the natural log of 10 equals 2.303.

$$e^{2.303} = 10, \text{ therefore } \ln 10 = 2.303$$

Your calculator probably has a key labeled LN that allows you to obtain natural logarithms. For example, to obtain the natural log of 46.8, you enter 46.8 and press the LN key.

$$\ln 46.8 = 3.846$$

The natural antilog of a number is e raised to a power equal to that number. If your calculator can calculate natural logs, it will also be able to calculate natural antilogs. On some calculators there is a key labeled e^x that allows you to calculate natural antilogs directly; on others, it will be necessary to first press the INV key followed by the LN key. For example, the natural antilog of 1.679 is given by

$$\text{Natural antilog } 1.679 = e^{1.679} = 5.36$$

The relation between common and natural logarithms is as follows:

$$\ln a = 2.303 \log a$$

Notice that the factor relating the two, 2.303, is the natural log of 10, which we calculated earlier.

Mathematical Operations Using Logarithms

Because logarithms are exponents, mathematical operations involving logarithms follow the rules for the use of exponents. For example, the product of z^a and z^b (where z is any number) is given by

$$z^a \cdot z^b = z^{(a+b)}$$

Similarly, the logarithm (either common or natural) of a product equals the *sum* of the logs of the individual numbers.

$$\log ab = \log a + \log b \qquad \ln ab = \ln a + \ln b$$

For the log of a quotient,

$$\log(a/b) = \log a - \log b \qquad \ln(a/b) = \ln a - \ln b$$

Using the properties of exponents, we can also derive the rules for the logarithm of a number raised to a certain power.

$$\log a^n = n \log a \qquad \ln a^n = n \ln a$$

$$\log a^{1/n} = (1/n) \log a \qquad \ln a^{1/n} = (1/n) \ln a$$

pH Problems

One of the most frequent uses for common logarithms in general chemistry is in working pH problems. The pH is defined as $-\log[H^+]$, where $[H^+]$ is the hydrogen ion concentration of a solution. ∞ (Section 16.4) The following sample exercise illustrates this application.

SAMPLE EXERCISE 2 Using Logarithms

(a) What is the pH of a solution whose hydrogen ion concentration is 0.015 *M*?

(b) If the pH of a solution is 3.80, what is its hydrogen ion concentration?

SOLUTION

1. We are given the value of $[H^+]$. We use the LOG key of our calculator to calculate the value of $\log[H^+]$. The pH is obtained by changing the sign of the value obtained. (Be sure to change the sign *after* taking the logarithm.)

$$[H^+] = 0.015$$

$$\log[H^+] = -1.82 \qquad \text{(2 significant figures)}$$

$$\text{pH} = -(-1.82) = 1.82$$

2. To obtain the hydrogen ion concentration when given the pH, we must take the antilog of $-$pH.

$$\text{pH} = -\log[H^+] = 3.80$$

$$\log[H^+] = -3.80$$

$$[H^+] = \text{antilog}(-3.80) = 10^{-3.80} = 1.6 \times 10^{-4}\ M$$

PRACTICE EXERCISE

Perform the following operations: **(a)** $\log(2.5 \times 10^{-5})$, **(b)** ln 32.7, **(c)** antilog -3.47, **(d)** $e^{-1.89}$.
Answers: **(a)** -4.60, **(b)** 3.487, **(c)** 3.4×10^{-4}, **(d)** 1.5×10^{-1}

A.3 QUADRATIC EQUATIONS

An algebraic equation of the form $ax^2 + bx + c = 0$ is called a *quadratic equation*. The two solutions to such an equation are given by the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Many calculators today can calculate the solutions to a quadratic equation with one or two keystrokes. Most of the time, x corresponds to the concentration of a chemical species in solution. Only one of the solutions will be a positive number, and that is the one you should use; a "negative concentration" has no physical meaning.

SAMPLE EXERCISE 3 Using the Quadratic Formula

Find the values of x that satisfy the equation $2x^2 + 4x = 1$.

SOLUTION

To solve the given equation for x, we must first put it in the form

$$ax^2 + bx + c = 0$$

and then use the quadratic formula. If

$$2x^2 + 4x = 1$$

then

$$2x^2 + 4x - 1 = 0$$

Using the quadratic formula, where $a = 2$, $b = 4$, and $c = -1$, we have

$$x = \frac{-4 \pm \sqrt{(4)(4) - 4(2)(-1)}}{2(2)}$$

$$= \frac{-4 \pm \sqrt{16 + 8}}{4} = \frac{-4 \pm \sqrt{24}}{4} = \frac{-4 \pm 4.899}{4}$$

The two solutions are

$$x = \frac{0.899}{4} = 0.225 \quad \text{and} \quad x = \frac{-8.899}{4} = -2.225$$

If this was a problem in which x represented a concentration, we would say $x = 0.225$ (in the appropriate units), since a negative number for concentration has no physical meaning.

TABLE A.1 • Interrelation between Pressure and Temperature

Temperature (°C)	Pressure (atm)
20.0	0.120
30.0	0.124
40.0	0.128
50.0	0.132

A.4 GRAPHS

Often the clearest way to represent the interrelationship between two variables is to graph them. Usually, the variable that is being experimentally varied, called the *independent variable*, is shown along the horizontal axis (x-axis). The variable that responds to the change in the independent variable, called the *dependent variable*, is then shown along the vertical axis (y-axis). For example, consider an experiment in which we vary the temperature of an enclosed gas and measure its pressure. The independent variable is temperature, and the dependent variable is pressure. The data shown in ◀ **TABLE A.1** can be obtained by means of this experiment. These data are shown graphically in ◀ **FIGURE A.1**. The relationship between temperature and pressure is linear. The equation for any straight-line graph has the form

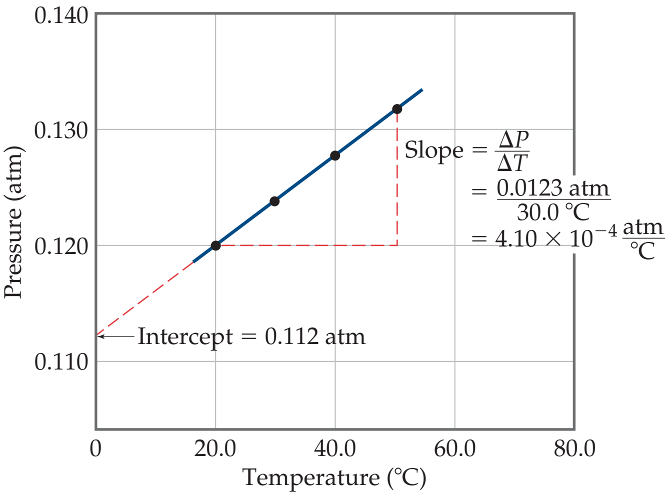
$$y = mx + b$$

where m is the slope of the line and b is the intercept with the y-axis. In the case of Figure A.1, we could say that the relationship between temperature and pressure takes the form

$$P = mT + b$$

where P is pressure in atm and T is temperature in °C. As shown in Figure A.1, the slope is 4.10×10^{-4} atm/°C, and the intercept—the point where the line crosses the y-axis—is 0.112 atm. Therefore, the equation for the line is

$$P = \left(4.10 \times 10^{-4} \frac{\text{atm}}{°\text{C}}\right)T + 0.112 \text{ atm}$$



▲ **FIGURE A.1** A graph of pressure versus temperature yields a straight line for the data.

A.5 STANDARD DEVIATION

The standard deviation from the mean, s, is a common method for describing precision in experimentally determined data. We define the standard deviation as

$$s = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \overline{x})^2}{N - 1}}$$

where N is the number of measurements, $\overline{x}$ is the average (also called the mean) of the measurements, and x_i represents the individual measurements. Electronic calculators with built-in statistical functions can calculate s directly by inputting the individual measurements.

A smaller value of s indicates a higher precision, meaning that the data are more closely clustered around the average. The standard deviation has statistical significance. If a large number of measurements is made, 68% of the measured values is expected to be within one standard deviation of the average, assuming only random errors are associated with the measurements.

SAMPLE EXERCISE 4 Calculating an Average and Standard Deviation

The percent carbon in a sugar is measured four times: 42.01%, 42.28%, 41.79%, and 42.25%. Calculate **(a)** the average and **(b)** the standard deviation for these measurements.

SOLUTION

(a) The average is found by adding the quantities and dividing by the number of measurements:

$$\overline{x} = \frac{42.01 + 42.28 + 41.79 + 42.25}{4} = \frac{168.33}{4} = 42.08$$

(b) The standard deviation is found using the preceding equation:

$$s = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \overline{x})^2}{N - 1}}$$

Let's tabulate the data so the calculation of $\sum_{i=1}^{N}(x_i - \overline{x})^2$ can be seen clearly.

Percent C	**Difference between Measurement and Average, $(x_i - \overline{x})$**	**Square of Difference, $(x_i - \overline{x})^2$**
42.01	$42.01 - 42.08 = -0.07$	$(-0.07)^2 = 0.005$
42.28	$42.28 - 42.08 = 0.20$	$(0.20)^2 = 0.040$
41.79	$41.79 - 42.08 = -0.29$	$(-0.29)^2 = 0.084$
42.25	$42.25 - 42.08 = 0.17$	$(0.17)^2 = 0.029$

The sum of the quantities in the last column is

$$\sum_{i=1}^{N}(x_i - \overline{x})^2 = 0.005 + 0.040 + 0.084 + 0.029 = 0.16$$

Thus, the standard deviation is

$$s = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \overline{x})^2}{N - 1}} = \sqrt{\frac{0.16}{4 - 1}} = \sqrt{\frac{0.16}{3}} = \sqrt{0.053} = 0.23$$

Based on these measurements, it would be appropriate to represent the measured percent carbon as 42.08 ± 0.23.

APPENDIX B

PROPERTIES OF WATER

Density: 0.99987 g/mL at 0 °C
1.00000 g/mL at 4 °C
0.99707 g/mL at 25 °C
0.95838 g/mL at 100 °C

Heat (enthalpy) of fusion: 6.008 kJ/mol at 0 °C

Heat (enthalpy) of vaporization: 44.94 kJ/mol at 0 °C
44.02 kJ/mol at 25 °C
40.67 kJ/mol at 100 °C

Ion-product constant, K_w: 1.14×10^{-15} at 0 °C
1.01×10^{-14} at 25 °C
5.47×10^{-14} at 50 °C

Specific heat: 2.092 J/g-K = 2.092 J/g·°C for ice at −3 °C
4.184 J/g-K = 4.184 J/g·°C for water at 25 °C
1.841 J/g-K = 1.841 J/g·°C for steam at 100 °C

Vapor Pressure (torr) at Different Temperatures

T(°C)	P	*T*(°C)	P	*T*(°C)	P	*T*(°C)	P
0	4.58	21	18.65	35	42.2	92	567.0
5	6.54	22	19.83	40	55.3	94	610.9
10	9.21	23	21.07	45	71.9	96	657.6
12	10.52	24	22.38	50	92.5	98	707.3
14	11.99	25	23.76	55	118.0	100	760.0
16	13.63	26	25.21	60	149.4	102	815.9
17	14.53	27	26.74	65	187.5	104	875.1
18	15.48	28	28.35	70	233.7	106	937.9
19	16.48	29	30.04	80	355.1	108	1004.4
20	17.54	30	31.82	90	525.8	110	1074.6

APPENDIX C

THERMODYNAMIC QUANTITIES FOR SELECTED SUBSTANCES AT 298.15 K (25 °C)

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol-K)
Aluminum			
$Al(s)$	0	0	28.32
$AlCl_3(s)$	−705.6	−630.0	109.3
$Al_2O_3(s)$	−1669.8	−1576.5	51.00
Barium			
$Ba(s)$	0	0	63.2
$BaCO_3(s)$	−1216.3	−1137.6	112.1
$BaO(s)$	−553.5	−525.1	70.42
Beryllium			
$Be(s)$	0	0	9.44
$BeO(s)$	−608.4	−579.1	13.77
$Be(OH)_2(s)$	−905.8	−817.9	50.21
Bromine			
$Br(g)$	111.8	82.38	174.9
$Br^-(aq)$	−120.9	−102.8	80.71
$Br_2(g)$	30.71	3.14	245.3
$Br_2(l)$	0	0	152.3
$HBr(g)$	−36.23	−53.22	198.49
Calcium			
$Ca(g)$	179.3	145.5	154.8
$Ca(s)$	0	0	41.4
$CaCO_3(s$, calcite)	−1207.1	−1128.76	92.88
$CaCl_2(s)$	−795.8	−748.1	104.6
$CaF_2(s)$	−1219.6	−1167.3	68.87
$CaO(s)$	−635.5	−604.17	39.75
$Ca(OH)_2(s)$	−986.2	−898.5	83.4
$CaSO_4(s)$	−1434.0	−1321.8	106.7
Carbon			
$C(g)$	718.4	672.9	158.0
$C(s$, diamond)	1.88	2.84	2.43
$C(s$, graphite)	0	0	5.69
$CCl_4(g)$	−106.7	−64.0	309.4
$CCl_4(l)$	−139.3	−68.6	214.4
$CF_4(g)$	−679.9	−635.1	262.3
$CH_4(g)$	−74.8	−50.8	186.3
$C_2H_2(g)$	226.77	209.2	200.8
$C_2H_4(g)$	52.30	68.11	219.4
$C_2H_6(g)$	−84.68	−32.89	229.5
$C_3H_8(g)$	−103.85	−23.47	269.9
$C_4H_{10}(g)$	−124.73	−15.71	310.0
$C_4H_{10}(l)$	−147.6	−15.0	231.0
$C_6H_6(g)$	82.9	129.7	269.2
$C_6H_6(l)$	49.0	124.5	172.8
$CH_3OH(g)$	−201.2	−161.9	237.6
$CH_3OH(l)$	−238.6	−166.23	126.8
$C_2H_5OH(g)$	−235.1	−168.5	282.7
$C_2H_5OH(l)$	−277.7	−174.76	160.7
$C_6H_{12}O_6(s)$	−1273.02	−910.4	212.1
$CO(g)$	−110.5	−137.2	197.9
$CO_2(g)$	−393.5	−394.4	213.6
$CH_3COOH(l)$	−487.0	−392.4	159.8
Cesium			
$Cs(g)$	76.50	49.53	175.6
$Cs(l)$	2.09	0.03	92.07
$Cs(s)$	0	0	85.15
$CsCl(s)$	−442.8	−414.4	101.2
Chlorine			
$Cl(g)$	121.7	105.7	165.2
$Cl(aq)$	−167.2	−131.2	56.5
$Cl_2(g)$	0	0	222.96
$HCl(aq)$	−167.2	−131.2	56.5
$HCl(g)$	−92.30	−95.27	186.69
Chromium			
$Cr(g)$	397.5	352.6	174.2
$Cr(s)$	0	0	23.6
$Cr_2O_3(s)$	−1139.7	−1058.1	81.2
Cobalt			
$Co(g)$	439	393	179
$Co(s)$	0	0	28.4
Copper			
$Cu(g)$	338.4	298.6	166.3
$Cu(s)$	0	0	33.30

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol-K)
$CuCl_2(s)$	−205.9	−161.7	108.1
$CuO(s)$	−156.1	−128.3	42.59
$Cu_2O(s)$	−170.7	−147.9	92.36
Fluorine			
$F(g)$	80.0	61.9	158.7
$F(aq)$	−332.6	−278.8	−13.8
$F_2(g)$	0	0	202.7
$HF(g)$	−268.61	−270.70	173.51
Hydrogen			
$H(g)$	217.94	203.26	114.60
$H^+(aq)$	0	0	0
$H^+(g)$	1536.2	1517.0	108.9
$H_2(g)$	0	0	130.58
Iodine			
$I(g)$	106.60	70.16	180.66
$I^-(aq)$	−55.19	−51.57	111.3
$I_2(g)$	62.25	19.37	260.57
$I_2(s)$	0	0	116.73
$HI(g)$	25.94	1.30	206.3
Iron			
$Fe(g)$	415.5	369.8	180.5
$Fe(s)$	0	0	27.15
$Fe^{2+}(aq)$	−87.86	−84.93	113.4
$Fe^{3+}(aq)$	−47.69	−10.54	293.3
$FeCl_2(s)$	−341.8	−302.3	117.9
$FeCl_3(s)$	−400	−334	142.3
$FeO(s)$	−271.9	−255.2	60.75
$Fe_2O_3(s)$	−822.16	−740.98	89.96
$Fe_3O_4(s)$	−1117.1	−1014.2	146.4
$FeS_2(s)$	−171.5	−160.1	52.92
Lead			
$Pb(s)$	0	0	68.85
$PbBr_2(s)$	−277.4	−260.7	161
$PbCO_3(s)$	−699.1	−625.5	131.0
$Pb(NO_3)_2(aq)$	−421.3	−246.9	303.3
$Pb(NO_3)_2(s)$	−451.9	—	—
$PbO(s)$	−217.3	−187.9	68.70
Lithium			
$Li(g)$	159.3	126.6	138.8
$Li(s)$	0	0	29.09
$Li^+(aq)$	−278.5	−273.4	12.2
$Li^+(g)$	685.7	648.5	133.0
$LiCl(s)$	−408.3	−384.0	59.30
Magnesium			
$Mg(g)$	147.1	112.5	148.6
$Mg(s)$	0	0	32.51
$MgCl_2(s)$	−641.6	−592.1	89.6
$MgO(s)$	−601.8	−569.6	26.8
$Mg(OH)_2(s)$	−924.7	−833.7	63.24
Manganese			
$Mn(g)$	280.7	238.5	173.6
$Mn(s)$	0	0	32.0
$MnO(s)$	−385.2	−362.9	59.7
$MnO_2(s)$	−519.6	−464.8	53.14
$MnO_4^-(aq)$	−541.4	−447.2	191.2
Mercury			
$Hg(g)$	60.83	31.76	174.89
$Hg(l)$	0	0	77.40
$HgCl_2(s)$	−230.1	−184.0	144.5
$Hg_2Cl_2(s)$	−264.9	−210.5	192.5
Nickel			
$Ni(g)$	429.7	384.5	182.1
$Ni(s)$	0	0	29.9
$NiCl_2(s)$	−305.3	−259.0	97.65
$NiO(s)$	−239.7	−211.7	37.99
Nitrogen			
$N(g)$	472.7	455.5	153.3
$N_2(g)$	0	0	191.50
$NH_3(aq)$	−80.29	−26.50	111.3
$NH_3(g)$	−46.19	−16.66	192.5
$NH_4^+(aq)$	−132.5	−79.31	113.4
$N_2H_4(g)$	95.40	159.4	238.5
$NH_4CN(s)$	0.0	—	—
$NH_4Cl(s)$	−314.4	−203.0	94.6
$NH_4NO_3(s)$	−365.6	−184.0	151
$NO(g)$	90.37	86.71	210.62
$NO_2(g)$	33.84	51.84	240.45
$N_2O(g)$	81.6	103.59	220.0
$N_2O_4(g)$	9.66	98.28	304.3
$NOCl(g)$	52.6	66.3	264
$HNO_3(aq)$	−206.6	−110.5	146
$HNO_3(g)$	−134.3	−73.94	266.4
Oxygen			
$O(g)$	247.5	230.1	161.0
$O_2(g)$	0	0	205.0
$O_3(g)$	142.3	163.4	237.6
$OH^-(aq)$	−230.0	−157.3	−10.7
$H_2O(g)$	−241.82	−228.57	188.83
$H_2O(l)$	−285.83	−237.13	69.91
$H_2O_2(g)$	−136.10	−105.48	232.9
$H_2O_2(l)$	−187.8	−120.4	109.6
Phosphorus			
$P(g)$	316.4	280.0	163.2
$P_2(g)$	144.3	103.7	218.1

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol-K)
$P_4(g)$	58.9	24.4	280
$P_4(s, \text{red})$	−17.46	−12.03	22.85
$P_4(s, \text{white})$	0	0	41.08
$PCl_3(g)$	−288.07	−269.6	311.7
$PCl_3(l)$	−319.6	−272.4	217
$PF_5(g)$	−1594.4	−1520.7	300.8
$PH_3(g)$	5.4	13.4	210.2
$P_4O_6(s)$	−1640.1	—	—
$P_4O_{10}(s)$	−2940.1	−2675.2	228.9
$POCl_3(g)$	−542.2	−502.5	325
$POCl_3(l)$	−597.0	−520.9	222
$H_3PO_4(aq)$	−1288.3	−1142.6	158.2
Potassium			
$K(g)$	89.99	61.17	160.2
$K(s)$	0	0	64.67
$KCl(s)$	−435.9	−408.3	82.7
$KClO_3(s)$	−391.2	−289.9	143.0
$KClO_3(aq)$	−349.5	−284.9	265.7
$K_2CO_3(s)$	−1150.18	−1064.58	155.44
$KNO_3(s)$	−492.70	−393.13	132.9
$K_2O(s)$	−363.2	−322.1	94.14
$KO_2(s)$	−284.5	−240.6	122.5
$K_2O_2(s)$	−495.8	−429.8	113.0
$KOH(s)$	−424.7	−378.9	78.91
$KOH(aq)$	−482.4	−440.5	91.6
Rubidium			
$Rb(g)$	85.8	55.8	170.0
$Rb(s)$	0	0	76.78
$RbCl(s)$	−430.5	−412.0	92
$RbClO_3(s)$	−392.4	−292.0	152
Scandium			
$Sc(g)$	377.8	336.1	174.7
$Sc(s)$	0	0	34.6
Selenium			
$H_2Se(g)$	29.7	15.9	219.0
Silicon			
$Si(g)$	368.2	323.9	167.8
$Si(s)$	0	0	18.7
$SiC(s)$	−73.22	−70.85	16.61
$SiCl_4(l)$	−640.1	−572.8	239.3
$SiO_2(s, \text{quartz})$	−910.9	−856.5	41.84
Silver			
$Ag(s)$	0	0	42.55
$Ag^+(aq)$	105.90	77.11	73.93
$AgCl(s)$	−127.0	−109.70	96.11
$Ag_2O(s)$	−31.05	−11.20	121.3
$AgNO_3(s)$	−124.4	−33.41	140.9
Sodium			
$Na(g)$	107.7	77.3	153.7
$Na(s)$	0	0	51.45
$Na^+(aq)$	−240.1	−261.9	59.0
$Na^+(g)$	609.3	574.3	148.0
$NaBr(aq)$	−360.6	−364.7	141.00
$NaBr(s)$	−361.4	−349.3	86.82
$Na_2CO_3(s)$	−1130.9	−1047.7	136.0
$NaCl(aq)$	−407.1	−393.0	115.5
$NaCl(g)$	−181.4	−201.3	229.8
$NaCl(s)$	−410.9	−384.0	72.33
$NaHCO_3(s)$	−947.7	−851.8	102.1
$NaNO_3(aq)$	−446.2	−372.4	207
$NaNO_3(s)$	−467.9	−367.0	116.5
$NaOH(aq)$	−469.6	−419.2	49.8
$NaOH(s)$	−425.6	−379.5	64.46
$Na_2SO_4(s)$	−1387.1	−1270.2	149.6
Strontium			
$SrO(s)$	−592.0	−561.9	54.9
$Sr(g)$	164.4	110.0	164.6
Sulfur			
$S(s, \text{rhombic})$	0	0	31.88
$S_8(g)$	102.3	49.7	430.9
$SO_2(g)$	−296.9	−300.4	248.5
$SO_3(g)$	−395.2	−370.4	256.2
$SO_4^{2-}(aq)$	−909.3	−744.5	20.1
$SOCl_2(l)$	−245.6	—	—
$H_2S(g)$	−20.17	−33.01	205.6
$H_2SO_4(aq)$	−909.3	−744.5	20.1
$H_2SO_4(l)$	−814.0	−689.9	156.1
Titanium			
$Ti(g)$	468	422	180.3
$Ti(s)$	0	0	30.76
$TiCl_4(g)$	−763.2	−726.8	354.9
$TiCl_4(l)$	−804.2	−728.1	221.9
$TiO_2(s)$	−944.7	−889.4	50.29
Vanadium			
$V(g)$	514.2	453.1	182.2
$V(s)$	0	0	28.9
Zinc			
$Zn(g)$	130.7	95.2	160.9
$Zn(s)$	0	0	41.63
$ZnCl_2(s)$	−415.1	−369.4	111.5
$ZnO(s)$	−348.0	−318.2	43.9

APPENDIX D

AQUEOUS EQUILIBRIUM CONSTANTS

TABLE D.1 • Dissociation Constants for Acids at 25 °C

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Acetic acid	CH_3COOH (or $HC_2H_3O_2$)	1.8×10^{-5}		
Arsenic acid	H_3AsO_4	5.6×10^{-3}	1.0×10^{-7}	3.0×10^{-12}
Arsenous acid	H_3AsO_3	5.1×10^{-10}		
Ascorbic acid	$H_2C_6H_6O_6$	8.0×10^{-5}	1.6×10^{-12}	
Benzoic acid	C_6H_5COOH (or $HC_7H_5O_2$)	6.3×10^{-5}		
Boric acid	H_3BO_3	5.8×10^{-10}		
Butanoic acid	C_3H_7COOH (or $HC_4H_7O_2$)	1.5×10^{-5}		
Carbonic acid	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Chloroacetic acid	$CH_2ClCOOH$ (or $HC_2H_2O_2Cl$)	1.4×10^{-3}		
Chlorous acid	$HClO_2$	1.1×10^{-2}		
Citric acid	$HOOCC(OH)\ (CH_2COOH)_2$ (or $H_3C_6H_5O_7$)	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Cyanic acid	$HCNO$	3.5×10^{-4}		
Formic acid	$HCOOH$ (or $HCHO_2$)	1.8×10^{-4}		
Hydroazoic acid	HN_3	1.9×10^{-5}		
Hydrocyanic acid	HCN	4.9×10^{-10}		
Hydrofluoric acid	HF	6.8×10^{-4}		
Hydrogen chromate ion	$HCrO_4^-$	3.0×10^{-7}		
Hydrogen peroxide	H_2O_2	2.4×10^{-12}		
Hydrogen selenate ion	$HSeO_4^-$	2.2×10^{-2}		
Hydrogen sulfide	H_2S	9.5×10^{-8}	1×10^{-19}	
Hypobromous acid	$HBrO$	2.5×10^{-9}		
Hypochlorous acid	$HClO$	3.0×10^{-8}		
Hypoiodous acid	HIO	2.3×10^{-11}		
Iodic acid	HIO_3	1.7×10^{-1}		
Lactic acid	$CH_3CH(OH)COOH$ (or $HC_3H_5O_3$)	1.4×10^{-4}		
Malonic acid	$CH_2(COOH)_2$ (or $H_2C_3H_2O_4$)	1.5×10^{-3}	2.0×10^{-6}	
Nitrous acid	HNO_2	4.5×10^{-4}		
Oxalic acid	$(COOH)_2$ (or $H_2C_2O_4$)	5.9×10^{-2}	6.4×10^{-5}	
Paraperiodic acid	H_5IO_6	2.8×10^{-2}	5.3×10^{-9}	
Phenol	C_6H_5OH (or HC_6H_5O)	1.3×10^{-10}		
Phosphoric acid	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Propionic acid	C_2H_5COOH (or $HC_3H_5O_2$)	1.3×10^{-5}		
Pyrophosphoric acid	$H_4P_2O_7$	3.0×10^{-2}	4.4×10^{-3}	2.1×10^{-7}
Selenous acid	H_2SeO_3	2.3×10^{-3}	5.3×10^{-9}	
Sulfuric acid	H_2SO_4	Strong acid	1.2×10^{-2}	
Sulfurous acid	H_2SO_3	1.7×10^{-2}	6.4×10^{-8}	
Tartaric acid	$HOOC(CHOH)_2COOH$ (or $H_2C_4H_4O_6$)	1.0×10^{-3}		

TABLE D.2 • Dissociation Constants for Bases at 25 °C

Name	Formula	K_b
Ammonia	NH_3	1.8×10^{-5}
Aniline	$C_6H_5NH_2$	4.3×10^{-10}
Dimethylamine	$(CH_3)_2NH$	5.4×10^{-4}
Ethylamine	$C_2H_5NH_2$	6.4×10^{-4}
Hydrazine	H_2NNH_2	1.3×10^{-6}
Hydroxylamine	$HONH_2$	1.1×10^{-8}
Methylamine	CH_3NH_2	4.4×10^{-4}
Pyridine	C_5H_5N	1.7×10^{-9}
Trimethylamine	$(CH_3)_3N$	6.4×10^{-5}

TABLE D.3 • Solubility-Product Constants for Compounds at 25 °C

Name	Formula	K_{sp}	Name	Formula	K_{sp}
Barium carbonate	$BaCO_3$	5.0×10^{-9}	Lead(II) fluoride	PbF_2	3.6×10^{-8}
Barium chromate	$BaCrO_4$	2.1×10^{-10}	Lead(II) sulfate	$PbSO_4$	6.3×10^{-7}
Barium fluoride	BaF_2	1.7×10^{-6}	Lead(II) sulfide*	PbS	3×10^{-28}
Barium oxalate	BaC_2O_4	1.6×10^{-6}	Magnesium hydroxide	$Mg(OH)_2$	1.8×10^{-11}
Barium sulfate	$BaSO_4$	1.1×10^{-10}	Magnesium carbonate	$MgCO_3$	3.5×10^{-8}
Cadmium carbonate	$CdCO_3$	1.8×10^{-14}	Magnesium oxalate	MgC_2O_4	8.6×10^{-5}
Cadmium hydroxide	$Cd(OH)_2$	2.5×10^{-14}	Manganese(II) carbonate	$MnCO_3$	5.0×10^{-10}
Cadmium sulfide*	CdS	8×10^{-28}	Manganese(II) hydroxide	$Mn(OH)_2$	1.6×10^{-13}
Calcium carbonate (calcite)	$CaCO_3$	4.5×10^{-9}	Manganese(II) sulfide*	MnS	2×10^{-53}
Calcium chromate	$CaCrO_4$	4.5×10^{-9}	Mercury(I) chloride	Hg_2Cl_2	1.2×10^{-18}
Calcium fluoride	CaF_2	3.9×10^{-11}	Mercury(I) iodide	Hg_2I_2	$1.1 \times 10^{-1.1}$
Calcium hydroxide	$Ca(OH)_2$	6.5×10^{-6}	Mercury(II) sulfide*	HgS	2×10^{-53}
Calcium phosphate	$Ca_3(PO_4)_2$	2.0×10^{-29}	Nickel(II) carbonate	$NiCO_3$	1.3×10^{-7}
Calcium sulfate	$CaSO_4$	2.4×10^{-5}	Nickel(II) hydroxide	$Ni(OH)_2$	6.0×10^{-16}
Chromium(III) hydroxide	$Cr(OH)_3$	1.6×10^{-30}	Nickel(II) sulfide*	NiS	3×10^{-20}
Cobalt(II) carbonate	$CoCO_3$	1.0×10^{-10}	Silver bromate	$AgBrO_3$	5.5×10^{-13}
Cobalt(II) hydroxide	$Co(OH)_2$	1.3×10^{-15}	Silver bromide	$AgBr$	5.0×10^{-13}
Cobalt(II) sulfide*	CoS	5×10^{-22}	Silver carbonate	Ag_2CO_3	8.1×10^{-12}
Copper(I) bromide	$CuBr$	5.3×10^{-9}	Silver chloride	$AgCl$	1.8×10^{-10}
Copper(II) carbonate	$CuCO_3$	2.3×10^{-10}	Silver chromate	Ag_2CrO_4	1.2×10^{-12}
Copper(II) hydroxide	$Cu(OH)_2$	4.8×10^{-20}	Silver iodide	AgI	8.3×10^{-17}
Copper(II) sulfide*	CuS	6×10^{-37}	Silver sulfate	Ag_2SO_4	1.5×10^{-5}
Iron(II) carbonate	$FeCO_3$	2.1×10^{-11}	Silver sulfide*	Ag_2S	6×10^{-51}
Iron(II) hydroxide	$Fe(OH)_2$	7.9×10^{-16}	Strontium carbonate	$SrCO_3$	9.3×10^{-10}
Lanthanum fluoride	LaF_3	2×10^{-19}	Tin(II) sulfide*	SnS	1×10^{-26}
Lanthanum iodate	$La(IO_3)_3$	7.4×10^{-14}	Zinc carbonate	$ZnCO_3$	1.0×10^{-10}
Lead(II) carbonate	$PbCO_3$	7.4×10^{-14}	Zinc hydroxide	$Zn(OH)_2$	3.0×10^{-16}
Lead(II) chloride	$PbCl_2$	1.7×10^{-5}	Zinc oxalate	ZnC_2O_4	2.7×10^{-8}
Lead(II) chromate	$PbCrO_4$	2.8×10^{-13}	Zinc sulfide*	ZnS	2×10^{-25}

*For a solubility equilibrium of the type $MS(s) + H_2O(l) \rightleftharpoons M^{2+}(aq) + HS^{-}(aq) + OH^{-}(aq)$

APPENDIX E

STANDARD REDUCTION POTENTIALS AT 25 °C

Half-Reaction	$E°$(V)
$Ag^{+}(aq) + e^{-} \longrightarrow Ag(s)$	+0.799
$AgBr(s) + e^{-} \longrightarrow Ag(s) + Br^{-}(aq)$	+0.095
$AgCl(s) + e^{-} \longrightarrow Ag(s) + Cl^{-}(aq)$	+0.222
$Ag(CN)_2^{-}(aq) + e^{-} \longrightarrow Ag(s) + 2\,CN^{-}(aq)$	−0.31
$Ag_2CrO_4(s) + 2\,e^{-} \longrightarrow 2\,Ag(s) + CrO_4^{2-}(aq)$	+0.446
$AgI(s) + e^{-} \longrightarrow Ag(s) + I^{-}(aq)$	−0.151
$Ag(S_2O_3)_2^{3-}(aq) + e^{-} \longrightarrow Ag(s) + 2\,S_2O_3^{2-}(aq)$	+0.01
$Al^{3+}(aq) + 3\,e^{-} \longrightarrow Al(s)$	−1.66
$H_3AsO_4(aq) + 2\,H^{+}(aq) + 2\,e^{-} \longrightarrow H_3AsO_3(aq) + H_2O(l)$	+0.559
$Ba^{2+}(aq) + 2\,e^{-} \longrightarrow Ba(s)$	−2.90
$BiO^{+}(aq) + 2\,H^{+}(aq) + 3\,e^{-} \longrightarrow Bi(s) + H_2O(l)$	+0.32
$Br_2(l) + 2\,e^{-} \longrightarrow 2\,Br^{-}(aq)$	+1.065
$2\,BrO_3^{-}(aq) + 12\,H^{+}(aq) + 10\,e^{-} \longrightarrow Br_2(l) + 6\,H_2O(l)$	+1.52
$2\,CO_2(g) + 2\,H^{+}(aq) + 2\,e^{-} \longrightarrow H_2C_2O_4(aq)$	−0.49
$Ca^{2+}(aq) + 2\,e^{-} \longrightarrow Ca(s)$	−2.87
$Cd^{2+}(aq) + 2\,e^{-} \longrightarrow Cd(s)$	−0.403
$Ce^{4+}(aq) + e^{-} \longrightarrow Ce^{3+}(aq)$	+1.61
$Cl_2(g) + 2\,e^{-} \longrightarrow 2\,Cl^{-}(aq)$	+1.359
$2\,HClO(aq) + 2\,H^{+}(aq) + 2\,e^{-} \longrightarrow Cl_2(g) + 2\,H_2O(l)$	+1.63
$ClO^{-}(aq) + H_2O(l) + 2\,e^{-} \longrightarrow Cl^{-}(aq) + 2\,OH^{-}(aq)$	+0.89
$2\,ClO_3^{-}(aq) + 12\,H^{+}(aq) + 10\,e^{-} \longrightarrow Cl_2(g) + 6\,H_2O(l)$	+1.47
$Co^{2+}(aq) + 2\,e^{-} \longrightarrow Co(s)$	−0.277
$Co^{3+}(aq) + e^{-} \longrightarrow Co^{2+}(aq)$	+1.842
$Cr^{3+}(aq) + 3\,e^{-} \longrightarrow Cr(s)$	−0.74
$Cr^{3+}(aq) + e^{-} \longrightarrow Cr^{2+}(aq)$	−0.41
$CrO_7^{2-}(aq) + 14\,H^{+}(aq) + 6\,e^{-} \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$	+1.33
$CrO_4^{2-}(aq) + 4\,H_2O(l) + 3\,e^{-} \longrightarrow Cr(OH)_3(s) + 5\,OH^{-}(aq)$	−0.13
$Cu^{2+}(aq) + 2\,e^{-} \longrightarrow Cu(s)$	+0.337
$Cu^{2+}(aq) + e^{-} \longrightarrow Cu^{+}(aq)$	+0.153
$Cu^{+}(aq) + e^{-} \longrightarrow Cu(s)$	+0.521
$CuI(s) + e^{-} \longrightarrow Cu(s) + I^{-}(aq)$	−0.185
$F_2(g) + 2\,e^{-} \longrightarrow 2\,F^{-}(aq)$	+2.87
$Fe^{2+}(aq) + 2\,e^{-} \longrightarrow Fe(s)$	−0.440
$Fe^{3+}(aq) + e^{-} \longrightarrow Fe^{2+}(aq)$	+0.771
$Fe(CN)_6^{3-}(aq) + e^{-} \longrightarrow Fe(CN)_6^{4-}(aq)$	+0.36
$2\,H^{+}(aq) + 2\,e^{-} \longrightarrow H_2(g)$	0.000
$2\,H_2O(l) + 2\,e^{-} \longrightarrow H_2(g) + 2\,OH^{-}(aq)$	−0.83
$HO_2^{-}(aq) + H_2O(l) + 2\,e^{-} \longrightarrow 3\,OH^{-}(aq)$	+0.88
$H_2O_2(aq) + 2\,H^{+}(aq) + 2\,e^{-} \longrightarrow 2\,H_2O(l)$	+1.776
$Hg_2^{2+}(aq) + 2\,e^{-} \longrightarrow 2\,Hg(l)$	+0.789
$2\,Hg^{2+}(aq) + 2\,e^{-} \longrightarrow Hg_2^{2+}(aq)$	+0.920
$Hg^{2+}(aq) + 2\,e^{-} \longrightarrow Hg(l)$	+0.854
$I_2(s) + 2\,e^{-} \longrightarrow 2\,I^{-}(aq)$	+0.536
$2\,IO_3^{-}(aq) + 12\,H^{+}(aq) + 10\,e^{-} \longrightarrow I_2(s) + 6\,H_2O(l)$	+1.195
$K^{+}(aq) + e^{-} \longrightarrow K(s)$	−2.925
$Li^{+}(aq) + e^{-} \longrightarrow Li(s)$	−3.05
$Mg^{2+}(aq) + 2\,e^{-} \longrightarrow Mg(s)$	−2.37
$Mn^{2+}(aq) + 2\,e^{-} \longrightarrow Mn(s)$	−1.18
$MnO_2(s) + 4\,H^{+}(aq) + 2\,e^{-} \longrightarrow Mn^{2+}(aq) + 2\,H_2O(l)$	+1.23
$MnO_4^{-}(aq) + 8\,H^{+}(aq) + 5\,e^{-} \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$	+1.51
$MnO_4^{-}(aq) + 2\,H_2O(l) + 3\,e^{-} \longrightarrow MnO_2(s) + 4\,OH^{-}(aq)$	+0.59
$HNO_2(aq) + H^{+}(aq) + e^{-} \longrightarrow NO(g) + H_2O(l)$	+1.00
$N_2(g) + 4\,H_2O(l) + 4\,e^{-} \longrightarrow 4\,OH^{-}(aq) + N_2H_4(aq)$	−1.16
$N_2(g) + 5\,H^{+}(aq) + 4\,e^{-} \longrightarrow N_2H_5^{+}(aq)$	−0.23
$NO_3^{-}(aq) + 4\,H^{+}(aq) + 3\,e^{-} \longrightarrow NO(g) + 2\,H_2O(l)$	+0.96
$Na^{+}(aq) + e^{-} \longrightarrow Na(s)$	−2.71
$Ni^{2+}(aq) + 2\,e^{-} \longrightarrow Ni(s)$	−0.28
$O_2(g) + 4\,H^{+}(aq) + 4\,e^{-} \longrightarrow 2\,H_2O(l)$	+1.23
$O_2(g) + 2\,H_2O(l) + 4\,e^{-} \longrightarrow 4\,OH^{-}(aq)$	+0.40
$O_2(g) + 2\,H^{+}(aq) + 2\,e^{-} \longrightarrow H_2O_2(aq)$	+0.68
$O_3(g) + 2\,H^{+}(aq) + 2\,e^{-} \longrightarrow O_2(g) + H_2O(l)$	+2.07
$Pb^{2+}(aq) + 2\,e^{-} \longrightarrow Pb(s)$	−0.126
$PbO_2(s) + HSO_4^{-}(aq) + 3\,H^{+}(aq) + 2\,e^{-} \longrightarrow PbSO_4(s) + 2\,H_2O(l)$	+1.685
$PbSO_4(s) + H^{+}(aq) + 2\,e^{-} \longrightarrow Pb(s) + HSO_4^{-}(aq)$	−0.356
$PtCl_4^{2-}(aq) + 2\,e^{-} \longrightarrow Pt(s) + 4\,Cl^{-}(aq)$	+0.73
$S(s) + 2\,H^{+}(aq) + 2\,e^{-} \longrightarrow H_2S(g)$	+0.141
$H_2SO_3(aq) + 4\,H^{+}(aq) + 4\,e^{-} \longrightarrow S(s) + 3\,H_2O(l)$	+0.45
$HSO_4^{-}(aq) + 3\,H^{+}(aq) + 2\,e^{-} \longrightarrow H_2SO_3(aq) + H_2O(l)$	+0.17
$Sn^{2+}(aq) + 2\,e^{-} \longrightarrow Sn(s)$	−0.136
$Sn^{4+}(aq) + 2\,e^{-} \longrightarrow Sn^{2+}(aq)$	+0.154
$VO_2^{+}(aq) + 2\,H^{+}(aq) + e^{-} \longrightarrow VO^{2+}(aq) + H_2O(l)$	+1.00
$Zn^{2+}(aq) + 2\,e^{-} \longrightarrow Zn(s)$	−0.763

ANSWERS TO SELECTED EXERCISES

CHAPTER 1

1.1 (a) Pure element: i (b) mixture of elements: v, vi (c) pure compound: iv (d) mixture of an element and a compound: ii, iii **1.3** This kind of separation based on solubility differences is called *extraction*. The insoluble grounds are then separated from the coffee solution by *filtration*. **1.5** (a) The aluminum sphere is lightest, then nickel, then silver. (b) The platinum sphere is largest, then gold, then lead. **1.7** (a) 7.5 cm; two significant figures (sig figs) (b) 72 mi/hr (inner scale, two significant figures) or 115 km/hr (outer scale, three significant figures) **1.9** Arrange the conversion factor so that the given unit cancels and the desired unit is in the correct position. **1.11** (a) Heterogeneous mixture (b) homogeneous mixture (heterogeneous if there are undissolved particles) (c) pure substance (d) pure substance. **1.13** (a) S (b) Au (c) K (d) Cl (e) Cu (f) uranium (g) nickel (h) sodium (i) aluminum (j) silicon **1.15** C is a compound; it contains both carbon and oxygen. A is a compound; it contains at least carbon and oxygen. B is not defined by the data given; it is probably also a compound because few elements exist as white solids. **1.17** Physical properties: silvery white; lustrous; melting point = 649 °C; boiling point = 1105 °C; density at 20 °C = 1.738 g/cm^3; pounded into sheets; drawn into wires; good conductor. Chemical properties: burns in air; reacts with Cl_2. **1.19** (a) Chemical (b) physical (c) physical (d) chemical (e) chemical **1.21** (a) Add water to dissolve the sugar; filter this mixture, collecting the sand on the filter paper and the sugar water in the flask. Evaporate water from the flask to recover solid sugar. (b) Allow the mixture to settle so that there are two distinct layers. Carefully pour off most of the top oil layer. After the layers reform, use a dropper to remove any remaining oil. Vinegar is in the original vessel and oil is in a second container. **1.23** (a) 1×10^{-1} (b) 1×10^{-2} (c) 1×10^{-15} (d) 1×10^{-6} (e) 1×10^{6} (f) 1×10^{3} (g) 1×10^{-9} (h) 1×10^{-3} (i) 1×10^{-12} **1.25** (a) 22 °C (b) 422.1 °F (c) 506 K (d) 107 °C (e) 1644 K (f) −459.67 °F **1.27** (a) 1.62 g/mL. Tetrachloroethylene, 1.62 g/mL, is more dense than water, 1.00 g/mL; tetrachloroethylene will sink rather than float on water. (b) 11.7 g **1.29** (a) Calculated density = 0.86 g/mL. The substance is probably toluene, density = 0.866 g/mL. (b) 40.4 mL ethylene glycol (c) 1.11×10^{3} g nickel **1.31** 28 Pg **1.33** Exact: (c), (d), and (f) **1.35** (a) 3 (b) 2 (c) 5 (d) 3 (e) 5 (f) 1 **1.37** (a) 1.025×10^{2} (b) 6.570×10^{5} (c) 8.543×10^{-3} (d) 2.579×10^{-4} (e) -3.572×10^{-2} **1.39** (a) 17.00 (b) 812.0 (c) 8.23×10^{3} (d) 8.69×10^{-2} **1.41** 5 significant figures

1.43 (a) $\dfrac{1 \times 10^{-3}\ \text{m}}{1\ \text{mm}} \times \dfrac{1\ \text{nm}}{1 \times 10^{-9}\ \text{m}}$ (b) $\dfrac{1 \times 10^{-3}\ \text{g}}{1\ \text{mg}} \times \dfrac{1\ \text{kg}}{1000\ \text{g}}$

(c) $\dfrac{1000\ \text{m}}{1\ \text{km}} \times \dfrac{1\ \text{cm}}{1 \times 10^{-2}\ \text{m}} \times \dfrac{1\ \text{in.}}{2.54\ \text{cm}} \times \dfrac{1\ \text{ft}}{12\ \text{in.}}$ (d) $\dfrac{(2.54)^3\ \text{cm}^3}{1^3\ \text{in.}^3}$

1.45 (a) 54.7 km/hr (b) 1.3×10^{3} gal (c) 46.0 m (d) 0.984 in/hr **1.47** (a) 4.32×10^{5} s (b) 88.5 m (c) \$0.499/L (d) 46.6 km/hr (e) 1.420 L/s (f) 707.9 cm^3 **1.49** (a) 1.2×10^{2} L (b) 5×10^{2} mg (c) 19.9 mi/gal (2×10^{1} mi/gal for 1 significant figure) (d) 26 mL/g (3×10^{1} mL/g for 1 significant figure) **1.51** 64 kg air **1.53** 14-in. shoe < 57-cm string < 1.1-m pipe **1.55** \$6 × 10^{4} **1.59** 8.47 g O; the *law of constant composition* **1.62** (a) Volume (b) area (c) volume (d) density (e) time (f) length (g) temperature **1.65** (a) 1.13×10^{5} quarters (b) 6.41×10^{5} g (c) \$2.83 × 10^{4} (d) 4.13×10^{8} stacks **1.68** The most dense liquid, Hg, will sink; the least dense, cyclohexane, will float; H_2O will be in the middle. **1.71** density of solid = 1.63 g/mL **1.74** (a) Density of peat = 0.13 g/cm^3, density of soil = 2.5 g/cm^3. It is not correct to say that peat is "lighter" than topsoil. Volumes must be specified in order to compare masses. (b) Buy 16 bags of peat (more than 15 are needed). (Results to 1 significant figure are not meaningful.) **1.77** The inner diameter of the tube is 1.13 cm. **1.79** The separation is successful if two distinct spots are seen on the paper. To quantify the characteristics of the separation, calculate a reference value for each spot: distance traveled by spot/distance traveled by solvent. If the values for the two spots are fairly different, the separation is successful.

CHAPTER 2

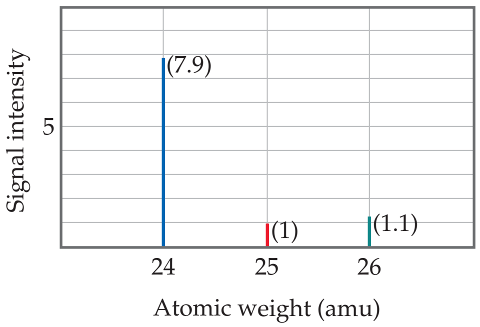
2.1 (a) The path of the charged particle bends because the particle is repelled by the negatively charged plate and attracted to the positively charged plate. (b) (−) (c) increase (d) decrease **2.4** The particle is an ion. ${}^{32}_{16}S^{2-}$ **2.6** Formula: IF_5; name: iodine pentafluoride; the compound is molecular. **2.9** Postulate 4 of the atomic theory states that the relative number and kinds of atoms in a compound are constant, regardless of the source. Therefore, 1.0 g of pure water should always contain the same relative amounts of hydrogen and oxygen, no matter where or how the sample is obtained. **2.11** (a) 0.5711 g O/1 g N; 1.142 g O/1 g N; 2.284 g O/1 g N; 2.855 g O/1 g N (b) The numbers in part (a) obey the *law of multiple proportions*. Multiple proportions arise because atoms are the indivisible entities combining, as stated in Dalton's atomic theory. **2.13** (1) Electric and magnetic fields deflected the rays in the same way they would deflect negatively charged particles. (2) A metal plate exposed to cathode rays acquired a negative charge. **2.15** (a) Most of the volume of an atom is empty space in which electrons move. Most alpha particles passed through this space. (b) The few alpha particles that hit the massive, positively charged gold nuclei were strongly repelled and deflected back in the direction they came from. (c) Because the Be nuclei have a smaller volume and a smaller positive charge than the Au nuclei, fewer alpha particles will be scattered and fewer will be strongly back scattered. **2.17** (a) 0.135 nm; 1.35×10^{2} or 135 pm (b) 3.70×10^{6} Au atoms (c) 1.03×10^{-23} cm^3 **2.19** (a) Proton, neutron, electron (b) proton = 1+, neutron = 0, electron = 1− (c) The neutron is most massive. (The neutron and proton have very similar masses.) (d) The electron is least massive. **2.21** (a) Atomic number is the number of protons in the nucleus of an atom. Mass number is the total number of nuclear particles, protons plus neutrons, in an atom. (b) mass number **2.23** (a) ${}^{40}Ar$: 18 p, 22 n, 18 e (b) ${}^{65}Zn$: 30 p, 35 n, 30 e (c) ${}^{70}Ga$: 31 p, 39 n, 31 e (d) ${}^{80}Br$: 35 p, 45 n, 35 e (e) ${}^{184}W$: 74 p, 110 n, 74 e (f) ${}^{243}Am$: 95 p, 148 n, 95e

2.25

Symbol	${}^{52}Cr$	${}^{55}Mn$	${}^{112}Cd$	${}^{222}Rn$	${}^{207}Pb$
Protons	24	25	48	86	82
Neutrons	28	30	64	136	125
Electrons	24	25	48	86	82
Mass no.	52	55	112	222	207

2.27 (a) ${}^{196}_{78}Pt$ (b) ${}^{84}_{36}Kr$ (c) ${}^{75}_{33}As$ (d) ${}^{24}_{12}Mg$ **2.29** (a) ${}^{12}_{6}C$ (b) Atomic weights are average atomic masses, the sum of the mass of each naturally occurring isotope of an element times its fractional abundance. Each B atom will have the mass of one of the naturally occurring isotopes, while the "atomic weight" is an average value. **2.31** 63.55 amu **2.33** (a) In Thomson's cathode-ray experiments and in mass spectrometry, a stream of charged particles is passed through the poles of a magnet. The charged particles are deflected by the magnetic field according to their mass and charge. (b) The *x*-axis label is atomic weight, and the *y*-axis label is signal intensity. (c) Uncharged particles are not deflected in a magnetic field. The effect of the magnetic field on charged moving particles is the basis of their separation by mass. **2.35** (a) average atomic mass = 24.31 amu

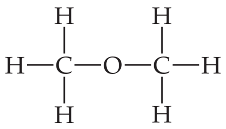
(b)



2.37 (a) Cr, 24 (metal) (b) He, 2 (nonmetal) (c) P, 15 (nonmetal) (d) Zn, 30 (metal) (e) Mg, 12 (metal) (f) Br, 35 (nonmetal) (g) As, 33 (metalloid) **2.39** (a) K, alkali metals (metal) (b) I, halogens (nonmetal) (c) Mg, alkaline earth metals (metal) (d) Ar, noble gases (nonmetal) (e) S, chalcogens (nonmetal) **2.41** An empirical formula shows the simplest mole ratio of elements in a compound. A molecular formula shows the exact number and kinds of atoms in a molecule. A structural formula shows which atoms are attached to which. **2.43** (a) $AlBr_3$ (b) C_4H_5 (c) C_2H_4O (d) P_2O_5 (e) C_3H_2Cl (f) BNH_2 **2.45** (a) 6 (b) 6 (c) 12

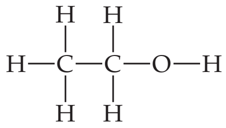
2.47

(a) C_2H_6O,



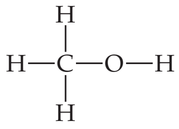
$$\begin{array}{ccccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & - & C & - & O & - & C & - & H \\ & & | & & & & | & & \\ & & H & & & & H & & \end{array}$$

(b) C_2H_6O,



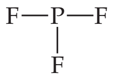
$$\begin{array}{ccccccccc} & & H & & H & & & & \\ & & | & & | & & & & \\ H & - & C & - & C & - & O & - & H \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array}$$

(c) CH_4O,



$$\begin{array}{ccccccc} & & H & & & & \\ & & | & & & & \\ H & - & C & - & O & - & H \\ & & | & & & & \\ & & H & & & & \end{array}$$

(d) PF_3,



$$\begin{array}{ccccc} F & - & P & - & F \\ & & | & & \\ & & F & & \end{array}$$

2.49

Symbol	$^{59}Co^{3+}$	$^{80}Se^{2-}$	$^{192}Os^{2+}$	$^{200}Hg^{2+}$
Protons	27	34	76	80
Neutrons	32	46	116	120
Electrons	24	36	74	78
Net Charge	3+	2−	2+	2+

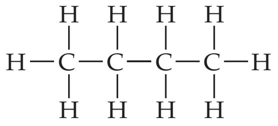
2.51 (a) Mg^{2+} (b) Al^{3+} (c) K^+ (d) S^{2-} (e) F^- **2.53** (a) GaF_3, gallium(III) fluoride (b) LiH, lithium hydride (c) AlI_3, aluminum iodide (d) K_2S, potassium sulfide **2.55** (a) $CaBr_2$ (b) K_2CO_3 (c) $Al(CH_3COO)_3$ (d) $(NH_4)_2SO_4$ (e) $Mg_3(PO_4)_2$

2.57

Ion	K^+	NH_4^+	Mg^{2+}	Fe^{3+}
Cl^-	KCl	NH_4Cl	$MgCl_2$	$FeCl_3$
OH^-	KOH	NH_4OH	$Mg(OH)_2$	$Fe(OH)_3$
CO_3^{2-}	K_2CO_3	$(NH_4)_2CO_3$	$MgCO_3$	$Fe_2(CO_3)_3$
PO_4^{3-}	K_3PO_4	$(NH_4)_3PO_4$	$Mg_3(PO_4)_2$	$FePO_4$

2.59 Molecular: (a) B_2H_6 (b) CH_3OH (f) NOCl (g) NF_3. Ionic: (c) $LiNO_3$ (d) Sc_2O_3 (e) CsBr (h) Ag_2SO_4 **2.61** (a) ClO_2^- (b) Cl^- (c) ClO_3^- (d) ClO_4^- (e) ClO^- **2.63** (a) calcium, 2+; oxide, 2− (b) sodium, 1+; sulfate, 2− (c) potassium, 1+; perchlorate, 1− (d) iron, 2+, nitrate, 1− (e) chromium, 3+; hydroxide, 1− **2.65** (a) lithium oxide (b) iron(III) chloride (ferric chloride) (c) sodium hypochlorite (d) calcium sulfite (e) copper(II) hydroxide (cupric hydroxide) (f) iron(II) nitrate (ferrous nitrate) (g) calcium acetate (h) chromium(III) carbonate (chromic carbonate) (i) potassium chromate (j) ammonium sulfate **2.67** (a) $Al(OH)_3$ (b) K_2SO_4 (c) Cu_2O (d) $Zn(NO_3)_2$ (e) $HgBr_2$ (f) $Fe_2(CO_3)_3$ (g) NaBrO **2.69** (a) Bromic acid (b) hydrobromic acid (c) phosphoric acid (d) HClO (e) HIO_3 (f) H_2SO_3 **2.71** (a) Sulfur hexafluoride (b) iodine pentafluoride (c) xenon trioxide (d) N_2O_4 (e) HCN (f) P_4S_6 **2.73** (a) $ZnCO_3$, ZnO, CO_2 (b) HF, SiO_2, SiF_4, H_2O (c) SO_2, H_2O, H_2SO_3 (d) PH_3 (e) $HClO_4$, Cd, $Cd(ClO_4)_2$ (f) VBr_3 **2.75** (a) A hydrocarbon is a compound composed of the elements hydrogen and carbon only.

(b)

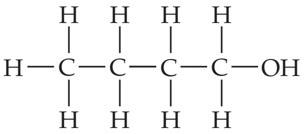


$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

Molecular: C_4H_{10}
Empirical: C_2H_5

2.77 (a) Functional groups are groups of specific atoms that are constant from one molecule to the next. (b) —OH

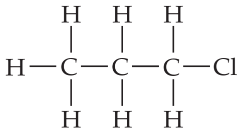
(c)



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & OH \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

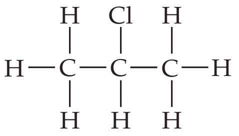
2.79

(a, b)



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & Cl \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

1-chloropropane



$$\begin{array}{ccccccccc} & & H & & Cl & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

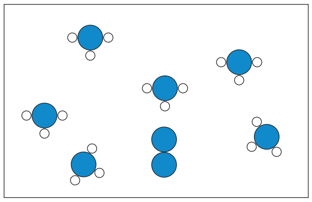
2-chloropropane

2.82 (a) 2 protons, 1 neutron, 2 electrons (b) tritium, ^3H, is more massive. (c) A precision of 1×10^{-27} g would be required to differentiate between $^3H^+$ and $^3He^+$. **2.84** Arrangement A, 4.1×10^{14} atoms/cm^2 (b) Arrangement B, 4.7×10^{14} atoms/cm^2 (c) The ratio of atoms going from arrangement B to arrangement A is 1.2 to 1. In three dimensions, arrangement B leads to a greater density for Rb metal. **2.87** (a) $^{16}_{8}O$, $^{17}_{8}O$, $^{18}_{8}O$ (b) All isotopes are atoms of the same element, oxygen, with the same atomic number, 8 protons in the nucleus and 8 electrons. We expect their electron arrangements to be the same and their chemical properties to be very similar. Each has a different number of neutrons, a different mass number, and a different atomic mass. **2.90** (a) $^{69}_{31}Ga$, 31 protons, 38 neutrons; $^{71}_{31}Ga$, 31 protons, 40 neutrons (b) $^{69}_{31}Ga$, 60.3%, $^{71}_{31}Ga$, 39.7%. **2.93** (a) 5 significant figures (b) An electron is 0.05444% of the mass of an ^1H atom. **2.96** Strontium is an alkaline earth metal, similar in chemical properties to calcium and magnesium. Harmful strontium closely mimics essential calcium and magnesium, then behaves badly when the body tries to use it as it uses calcium and magnesium. **2.98** (a) Nickel(II) oxide, 2+ (b) manganese(IV) oxide, 4+ (c) chromium(III) oxide, 3+ (d) molybdenum(VI) oxide, 6+ **2.101** (a) Perbromate ion (b) selenite ion (c) AsO_4^{3-} (d) $HTeO_4^-$ **2.104** (a) Potassium nitrate (b) sodium carbonate (c) calcium oxide (d) hydrochloric acid (e) magnesium sulfate (f) magnesium hydroxide

CHAPTER 3

3.1 Equation (a) best fits the diagram. **3.3** (a) NO_2 (b) No, because we have no way of knowing whether the empirical and molecular formulas are the same. NO_2 represents the simplest ratio of atoms in a molecule but not the only possible molecular formula. **3.5** (a) $C_2H_5NO_2$ (b) 75.0 g/mol (c) 225 g glycine (d) Mass %N in glycine is 18.7%.

3.7



$N_2 + 3\,H_2 \longrightarrow 2\,NH_3$. Eight N atoms (4 N_2 molecules) require 24 H atoms (12 H_2 molecules) for complete reaction. Only 9 H_2 molecules are available, so H_2 is the limiting reactant. Nine H_2 molecules (18 H atoms) determine that 6 NH_3 molecules are produced. One N_2 molecule is in excess. **3.9** (a) Conservation of mass (b) Subscripts in chemical formulas should not be changed when balancing equations, because changing the subscript changes the identity of the compound (*law of constant composition*). (c) $H_2O(l)$, $H_2O(g)$, $NaCl(aq)$, $NaCl(s)$

3.11 (a) $2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g)$
(b) $N_2O_5(g) + H_2O(l) \longrightarrow 2\,HNO_3(aq)$
(c) $CH_4(g) + 4\,Cl_2(g) \longrightarrow CCl_4(l) + 4\,HCl(g)$
(d) $Al_4C_3(s) + 12\,H_2O(l) \longrightarrow 4\,Al(OH)_3(s) + 3\,CH_4(g)$
(e) $2\,C_5H_{10}O_2(l) + 13\,O_2(g) \longrightarrow 10\,CO_2(g) + 10\,H_2O(g)$
(f) $2\,Fe(OH)_3(s) + 3\,H_2SO_4(aq) \longrightarrow Fe_2(SO_4)_3(aq) + 6\,H_2O(l)$
(g) $Mg_3N_2(s) + 4\,H_2SO_4(aq) \longrightarrow 3\,MgSO_4(aq) + (NH_4)_2SO_4(aq)$

3.13 (a) $CaC_2(s) + 2\,H_2O(l) \longrightarrow Ca(OH)_2(aq) + C_2H_2(g)$
(b) $2\,KClO_3(s) \xrightarrow{\Delta} 2\,KCl(s) + 3\,O_2(g)$
(c) $Zn(s) + H_2SO_4(aq) \longrightarrow ZnSO_4(aq) + H_2(g)$
(d) $PCl_3(l) + 3\,H_2O(l) \longrightarrow H_3PO_3(aq) + 3\,HCl(aq)$
(e) $3\,H_2S(g) + 2\,Fe(OH)_3(s) \longrightarrow Fe_2S_3(s) + 6\,H_2O(g)$

3.15 (a) Determine the formula by balancing the positive and negative charges in the ionic product. All ionic compounds are solids.
$2\,Na(s) + Br_2(l) \longrightarrow 2\,NaBr(s)$ (b) The second reactant is $O_2(g)$. The products are $CO_2(g)$ and $H_2O(l)$.
$2\,C_6H_6(l) + 15\,O_2(g) \longrightarrow 12\,CO_2(g) + 6\,H_2O(l)$

3.17 (a) $Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$
(b) $BaCO_3(s) \xrightarrow{\Delta} BaO(s) + CO_2(g)$
(c) $C_8H_8(l) + 10\,O_2(g) \longrightarrow 8\,CO_2(g) + 4\,H_2O(l)$
(d) $C_2H_6O(g) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 3\,H_2O(l)$

3.19 (a) $2\,C_3H_6(g) + 9\,O_2(g) \longrightarrow 6\,CO_2(g) + 6\,H_2O(g)$ combustion
(b) $NH_4NO_3(s) \longrightarrow N_2O(g) + 2\,H_2O(g)$ decomposition
(c) $C_5H_6O(l) + 6\,O_2(g) \longrightarrow 5\,CO_2(g) + 3\,H_2O(g)$ combustion
(d) $N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$ combination
(e) $K_2O(s) + H_2O(l) \longrightarrow 2\,KOH(aq)$ combination

3.21 (a) 63.0 amu (b) 158.0 amu (c) 310.3 amu (d) 60.1 amu (e) 235.7 amu (f) 392.3 amu (g) 137.5 amu **3.23** (a) 16.8% (b) 16.1% (c) 21.1% (d) 28.8% (e) 27.2% (f) 26.5% **3.25** (a) 79.2% (b) 63.2% (c) 64.6% **3.27** (a) 6.022×10^{23} (b) The formula weight of a substance in amu has the same numerical value as the molar mass expressed in grams. **3.29** 23 g Na contains 1 mol of atoms; 0.5 mol H_2O contains 1.5 mol atoms; 6.0×10^{23} N_2 molecules contain 2 mol of atoms. **3.31** 4.37×10^{25} kg (assuming 160 lb has 3 significant figures). One mole of people weighs 7.31 times as much as Earth. **3.33** (a) 35.9 g $C_{12}H_{22}O_{11}$ (b) 0.75766 mol $Zn(NO_3)_2$ (c) 6.0×10^{17} CH_3CH_2OH molecules (d) 2.47×10^{23} N atoms **3.35** (a) 0.373 g $(NH_4)_3PO_4$ (b) 5.737×10^{-3} mol Cl^- (c) 0.248 g $C_8H_{10}N_4O_2$ (d) 387 g cholesterol/mol **3.37** (a) Molar mass = 162.3 g (b) 3.08×10^{-5} mol allicin (c) 1.86×10^{19} allicin molecules (d) 3.71×10^{19} S atoms **3.39** (a) 2.500×10^{21} H atoms (b) 2.083×10^{20} $C_6H_{12}O_6$ molecules (c) 3.460×10^{-4} mol $C_6H_{12}O_6$ (d) 0.06227 g $C_6H_{12}O_6$ **3.41** 3.2×10^{-8} mol C_2H_3Cl/L; 1.9×10^{16} molecules/L **3.43** (a) C_2H_6O (b) Fe_2O_3 (c) CH_2O **3.45** (a) $CSCl_2$ (b) C_3OF_6 (c) Na_3AlF_6 **3.47** 31 g/mol **3.49** (a) C_6H_{12} (b) NH_2Cl **3.51** (a) Empirical formula, CH; molecular formula, C_8H_8 (b) empirical formula, $C_4H_5N_2O$; molecular formula, $C_8H_{10}N_4O_2$ (c) empirical formula and molecular formula, $NaC_5H_8O_4N$ **3.53** (a) C_7H_8 (b) The empirical and molecular formulas are $C_{10}H_{20}O$. **3.55** The molecular formula from the model is $C_8H_{16}O_2$, which corresponds to an empirical formula of C_4H_8O. The results from combustion analysis are consistent with this empirical formula. **3.57** $x = 10$; $Na_2CO_3 \cdot 10\,H_2O$ **3.59** If the equation is not balanced, the mole ratios derived from the coefficients will be incorrect and lead to erroneous calculated amounts of products. **3.61** (a) 2.40 mol HF (b) 5.25 g NaF (c) 0.610 g Na_2SiO_3 **3.63** (a) $Al(OH)_3(s) + 3\,HCl(aq) \longrightarrow AlCl_3(aq) + 3\,H_2O(l)$ (b) 0.701 g HCl (c) 0.855 g $AlCl_3$; 0.347 g H_2O (d) Mass of reactants = 0.500 g + 0.701 g = 1.201 g; mass of products = 0.855 g + 0.347 g = 1.202 g. Mass is conserved, within the precision of the data. **3.65** (a) $Al_2S_3(s) + 6\,H_2O(l) \longrightarrow 2\,Al(OH)_3(s) + 3\,H_2S(g)$ (b) 14.7 g $Al(OH)_3$ **3.67** (a) 2.25 mol N_2 (b) 15.5 g NaN_3 (c) 548 g NaN_3 **3.69** (a) 5.50×10^{-3} mol Al (b) 1.47 g $AlBr_3$ **3.71** (a) The *limiting reactant* determines the maximum number of product moles resulting from a chemical reaction; any other reactant is an *excess reactant*. (b) The limiting reactant regulates the amount of products because it is completely used up during the reaction; no more product can be made when one of the reactants is unavailable. (c) Combining ratios are molecule and mole ratios. Since different molecules have different masses, comparing initial masses of reactants will not provide a comparison of numbers of molecules or moles. **3.73** (a) 2255 bicycles (b) 50 frames left over, 305 wheels left over (c) the handlebars **3.75** NaOH is the limiting reactant; 0.925 mol Na_2CO_3 can be produced; 0.075 mol CO_2 remains. **3.77** (a) $NaHCO_3$ is the limiting reactant. (b) 0.524 g CO_2 (c) 0.238 g citric acid remains **3.79** 0.00 g $AgNO_3$ (limiting reactant), 1.94 g Na_2CO_3, 4.06 g Ag_2CO_3, 2.50 g $NaNO_3$ **3.81** (a) The theoretical yield is 60.3 g C_6H_5Br. (b) 70.1% yield **3.83** 28 g S_8 actual yield **3.85** (a) $C_2H_4O_2(l) + 2\,O_2(g) \longrightarrow 2\,CO_2(g) + 2\,H_2O(l)$ (b) $Ca(OH)_2(s) \longrightarrow CaO(s) + H_2O(g)$ (c) $Ni(s) + Cl_2(g) \longrightarrow NiCl_2(s)$ **3.89** (a) 8×10^{-20} g Si (b) 2×10^3 Si atoms (with 2 significant figures, 1700 Si atoms) (c) 1×10^3 Ge atoms (with 2 significant figures, 1500 Ge atoms) **3.93** $C_8H_8O_3$ **3.97** (a) 1.19×10^{-5} mol NaI (b) 8.1×10^{-3} g NaI **3.101** 7.5 mol H_2 and 4.5 mol N_2 present initially **3.105** 6.46×10^{24} O atoms **3.107** (a) 88 kg CO_2 (b) 4×10^2 (400) kg CO_2 **3.109** (a) $S(s) + O_2(g) \longrightarrow SO_2(g)$; $SO_2(g) + CaO(s) \longrightarrow CaSO_3(s)$ (b) 7.9×10^7 g CaO (c) 1.7×10^8 g $CaSO_3$

CHAPTER 4

4.1 Diagram (c) represents Li_2SO_4 **4.3** (a) HCOOH is a weak electrolyte. (b) HNO_3 is a strong electrolyte. (c) CH_3CH_2OH is a nonelectrolyte. **4.5** $BaCl_2$ **4.7** (b) NO_3^- and (c) NH_4^+ will always be spectator ions. **4.9** In a redox reaction, electrons are transferred from the oxidized substance to the reduced substance. In an acid–base reaction, protons are transferred from an acid to a base. **4.11** No. Electrolyte solutions conduct electricity because the dissolved ions carry charge through the solution from one electrode to the other. **4.13** Although H_2O molecules are electrically neutral, there is an unequal distribution of electrons throughout the molecule. The partially

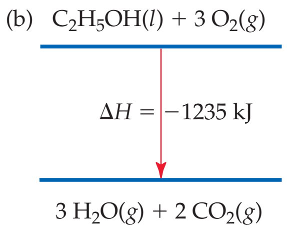
positive ends of H_2O molecules are attracted to anions in the solid, while the partially negative ends are attracted to cations. Thus, both cations and anions in an ionic solid are surrounded and separated (dissolved) by H_2O. We do not expect ionic compounds to be soluble in molecular liquids such as $Br_2(l)$ or $Hg(l)$. There is a symmetrical charge distribution in Hg atoms and Br_2 molecules, so there are no attractive forces to stabilize the separated ions of an ionic solid.
4.15 (a) $ZnCl_2(aq) \longrightarrow Zn^{2+}(aq) + 2\,Cl^-(aq)$ (b) $HNO_3(aq) \longrightarrow H^+(aq) + NO_3^-(aq)$ (c) $(NH_4)_2SO_4(aq) \longrightarrow 2\,NH_4^+(aq) + SO_4^{2-}(aq)$ (d) $Ca(OH)_2(aq) \longrightarrow Ca^{2+}(aq) + 2\,OH^-(aq)$
4.17 HCOOH molecules, H^+ ions, and $HCOO^-$ ions; $HCOOH(aq) \rightleftharpoons H^+(aq) + HCOO^-(aq)$ **4.19** (a) Soluble (b) insoluble (c) soluble (d) soluble (e) soluble **4.21** (a) $Na_2CO_3(aq) + 2\,AgNO_3(aq) \longrightarrow Ag_2CO_3(s) + 2\,NaNO_3(aq)$
(b) No precipitate (c) $FeSO_4(aq) + Pb(NO_3)_2(aq) \longrightarrow PbSO_4(s) + Fe(NO_3)_2(aq)$ **4.23** (a) Na^+, SO_4^{2-} (b) Na^+, NO_3^- (c) NH_4^+, Cl^-
4.25 The solution contains Pb^{2+} .
4.27

Compound	$Ba(NO_3)_2$ Result	NaCl Result
$AgNO_3(aq)$	No ppt	AgCl ppt
$CaCl_2(aq)$	No ppt	No ppt
$Al_2(SO_4)_3(aq)$	$BaSO_4$ ppt	No ppt

This sequence of tests would definitely identify the bottle contents. **4.29** LiOH is a strong base, HI is a strong acid, and CH_3OH is a molecular compound and nonelectrolyte. The strong acid HI will have the greatest concentration of solvated protons. **4.31** (a) A monoprotic acid has one ionizable (acidic) H, whereas a diprotic acid has two. (b) A strong acid is completely ionized in aqueous solution, whereas only a fraction of weak acid molecules are ionized. (c) An acid is an H^+ donor, and a base is an H^+ acceptor. **4.33** When each of the strong acids in Table 4.2 dissociates, the anions formed are the same ones that normally form soluble ionic compounds (Table 4.1). The one exception is acetate, CH_3COO^-, the anion of a weak acid. **4.35** (a) Acid, mixture of ions and molecules (weak electrolyte) (b) none of the above, entirely molecules (nonelectrolyte) (c) salt, entirely ions (strong electrolyte) (d) base, entirely ions (strong electrolyte) **4.37** (a) H_2SO_3, weak electrolyte (b) C_2H_5OH, nonelectrolyte (c) NH_3, weak electrolyte (d) $KClO_3$, strong electrolyte (e) $Cu(NO_3)_2$, strong electrolyte
4.39 (a) $2\,HBr(aq) + Ca(OH)_2(aq) \longrightarrow CaBr_2(aq) + 2\,H_2O(l)$; $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$ (b) $Cu(OH)_2(s) + 2\,HClO_4(aq) \longrightarrow Cu(ClO_4)_2(aq) + 2\,H_2O(l)$; $Cu(OH)_2(s) + 2\,H^+(aq) \longrightarrow 2\,H_2O(l) + Cu^{2+}(aq)$ (c) $Al(OH)_3(s) + 3\,HNO_3(aq) \longrightarrow Al(NO_3)_3(aq) + 3\,H_2O(l)$; $Al(OH)_3(s) + 3\,H^+(aq) \longrightarrow 3\,H_2O(l) + Al^{3+}(aq)$ **4.41** (a) $CdS(s) + H_2SO_4(aq) \longrightarrow CdSO_4(aq) + H_2S(g)$; $CdS(s) + 2H^+(aq) \longrightarrow H_2S(g) + Cd^{2+}(aq)$
(b) $MgCO_3(s) + 2HClO_4(aq) \longrightarrow Mg(ClO_4)_2(aq) + H_2O(l) + CO_2(g)$; $MgCO_3(s) + 2\,H^+(aq) \longrightarrow H_2O(l) + CO_2(g) + Mg^{2+}(aq)$
4.43 (a) $MgCO_3(s) + 2\,HCl(aq) \longrightarrow MgCl_2(aq) + H_2O(l) + CO_2(g)$; $MgCO_3(s) + 2\,H^+(aq) \longrightarrow Mg^{2+}(aq) + H_2O(l) + CO_2(g)$; $MgO(s) + 2\,HCl(aq) \longrightarrow MgCl_2(aq) + H_2O(l)$; $MgO(s) + 2\,H^+(aq) \longrightarrow Mg^{2+}(aq) + H_2O(l)$; $Mg(OH)_2(s) + 2\,HCl(aq) \longrightarrow MgCl_2(aq) + 2\,H_2O(l)$; $Mg(OH)_2(s) + 2\,H^+(aq) \longrightarrow Mg^{2+}(aq) + 2\,H_2O(l)$ (b) Yes. The reaction involving magnesium carbonate, $MgCO_3(s)$, produces $CO_2(g)$, which appears as bubbles. The other two reactions are calm. (c) If excess $HCl(aq)$ is added in each case, the identity of the ions in the clear product solution is the same. The ions are $Mg^{2+}(aq)$; $Cl^-(aq)$; and $H^+(aq)$. **4.45** (a) In terms of electron transfer, oxidation is the loss of electrons by a substance and reduction is the gain of electrons (LEO says GER). (b) Relative to oxidation numbers, when a substance is oxidized, its oxidation number increases. When a substance is reduced, its oxidation number decreases. **4.47** Metals in region A are most easily oxidized. Nonmetals in region D are least easily oxidized.
4.49 (a) +4 (b) +4 (c) +7 (d) +1 (e) 0 (f) −1
4.51 (a) $N_2 \longrightarrow 2\,NH_3$, N is reduced; $3\,H_2 \longrightarrow 2\,NH_3$, H is oxidized (b) $Fe^{2+} \longrightarrow Fe$, Fe is reduced; $Al \longrightarrow Al^{3+}$, Al is oxidized (c) $Cl_2 \longrightarrow 2\,Cl^-$, Cl is reduced; $2\,I^- \longrightarrow I_2$ I is oxidized (d) $S^{2-} \longrightarrow SO_4^{2-}$, S is oxidized; $H_2O_2 \longrightarrow H_2O$, O is reduced
4.53 (a) $Mn(s) + H_2SO_4(aq) \longrightarrow MnSO_4(aq) + H_2(g)$; $Mn(s) + 2\,H^+(aq) \longrightarrow Mn^{2+}(aq) + H_2(g)$
(b) $2\,Cr(s) + 6\,HBr(aq) \longrightarrow 2\,CrBr_3(aq) + 3\,H_2(g)$; $2\,Cr(s) + 6\,H^+(aq) \longrightarrow 2\,Cr^{3+}(aq) + 3\,H_2(g)$
(c) $Sn(s) + 2\,HCl(aq) \longrightarrow SnCl_2(aq) + H_2(g)$; $Sn(s) + 2\,H^+(aq) \longrightarrow Sn^{2+}(aq) + H_2(g)$
(d) $2\,Al(s) + 6\,HCOOH(aq) \longrightarrow 2\,Al(HCOO)_3(aq) + 3\,H_2(g)$; $2\,Al(s) + 6\,HCOOH(aq) \longrightarrow 2\,Al^{3+}(aq) + 6\,HCOO^-(aq) + 3\,H_2(g)$
4.55 (a) $Fe(s) + Cu(NO_3)_2(aq) \longrightarrow Fe(NO_3)_2(aq) + Cu(s)$
(b) NR (c) $Sn(s) + 2\,HBr(aq) \longrightarrow SnBr_2(aq) + H_2(g)$ (d) NR
(e) $2\,Al(s) + 3\,CoSO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 3\,Co(s)$
4.57 (a) i. $Zn(s) + Cd^{2+}(aq) \longrightarrow Cd(s) + Zn^{2+}(aq)$; ii. $Cd(s) + Ni^{2+}(aq) \longrightarrow Ni(s) + Cd^{2+}(aq)$ (b) Cd is between Zn and Ni on the activity series. (c) Place an iron strip in $CdCl_2(aq)$. If $Cd(s)$ is deposited, Cd is less active than Fe; if there is no reaction, Cd is more active than Fe. Do the same test with Co if Cd is less active than Fe or with Cr if Cd is more active than Fe. **4.59** (a) Intensive; the ratio of amount of solute to total amount of solution is the same, regardless of how much solution is present. (b) The term 0.50 mol HCl defines an amount (~18 g) of the pure substance HCl. The term 0.50 *M* HCl is a ratio; it indicates that there is 0.50 mol of HCl solute in 1.0 liter of solution. **4.61** (a) 1.17 *M* $ZnCl_2$ (b) 0.158 mol HNO_3 (c) 54.2 mL of 6.00 *M* NaOH **4.63** 16 g $Na^+(aq)$ **4.65** BAC of $0.08 = 0.02\,M$ CH_3CH_2OH (alcohol) **4.67** (a) 5.21 g KBr (b) 0.06537 *M* $Ca(NO_3)_2$ (c) 10.2 mL of 1.50 *M* Na_3PO_4 **4.69** (a) 0.15 *M* K_2CrO_4 has the highest K^+ concentration. (b) 30.0 mL of 0.15 *M* K_2CrO_4 has more K^+ ions. **4.71** (a) 0.25 *M* Na^+, 0.25 *M* NO_3^- (b) $1.3 \times 10^{-2}\,M\,Mg^{2+}$, $1.3 \times 10^{-2}\,M\,SO_4^{2-}$ (c) 0.0150 *M* $C_6H_{12}O_6$ (d) 0.111 *M* Na^+, 0.111 *M* Cl^-, 0.0292 *M* NH_4^+, 0.0146 *M* CO_3^{2-}
4.73 (a) 16.9 mL 14.8 *M* NH_3 (b) 0.296 *M* NH_3 **4.75** (a) Add 21.4 g $C_{12}H_{22}O_{11}$ to a 250-mL volumetric flask, dissolve in a small volume of water, and add water to the mark on the neck of the flask. Agitate thoroughly to ensure total mixing. (b) Thoroughly rinse, clean, and fill a 50-mL buret with the 1.50 *M* $C_{12}H_{22}O_{11}$. Dispense 23.3 mL of this solution into a 350-mL volumetric container, add water to the mark, and mix thoroughly. **4.77** 1.398 *M* CH_3COOH **4.79** 0.227 g KCl
4.81 (a) 38.0 mL of 0.115 *M* $HClO_4$ (b) 769 mL of 0.128 *M* HCl (c) 0.408 *M* $AgNO_3$ (d) 0.275 g KOH **4.83** 27 g $NaHCO_3$
4.85 (a) Molar mass of metal hydroxide is 103 g/mol. (b) Rb^+
4.87 (a) $NiSO_4(aq) + 2\,KOH(aq) \longrightarrow Ni(OH)_2(s) + K_2SO_4(aq)$ (b) $Ni(OH)_2$ (c) KOH is the limiting reactant. (d) 0.927 g $Ni(OH)_2$ (e) 0.0667 *M* $Ni^{2+}(aq)$, 0.0667 *M* $K^+(aq)$, 0.100 *M* $SO_4^{2-}(aq)$
4.89 91.40% $Mg(OH)_2$ **4.92** The precipitate is $CdS(s)$. $Na^+(aq)$ and $NO_3^-(aq)$ remain in solution, along with any excess reactant ions. The net ionic equation is $Cd^{2+}(aq) + S^{2-}(aq) \longrightarrow CdS(s)$. **4.94** (a, b) Expt. 1: NR; Expt. 2: $2\,Ag^+(aq) + CrO_4^{2-}(aq) \longrightarrow Ag_2CrO_4(s)$ red precipitate; Expt. 3: $2\,Ca^{2+}(aq) + CrO_4^{2-}(aq) \longrightarrow CaCrO_4(s)$ yellow precipitate; Expt. 4: $2\,Ag^+(aq) + C_2O_4^{2-}(aq) \longrightarrow Ag_2C_2O_4(s)$ white precipitate; Expt. 5: $Ca^{2+}(aq) + C_2O_4^{2-}(aq) \longrightarrow CaC_2O_4(s)$ white precipitate; Expt. 6: $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$ white precipitate. **4.96** $4\,NH_3(g) + 5\,O_2(g) \longrightarrow 4\,NO(g) + 6\,H_2O(g)$. (a) redox reaction (b) N is oxidized, O is reduced. $2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$. (a) redox reaction (b) N is oxidized, O is reduced. $3\,NO_2(g) + H_2O(l) \longrightarrow HNO_3(aq) + NO(g)$. (a) redox reaction (b) N is both oxidized and reduced. **4.99** 1.42 *M* KBr **4.100** (a) 2.2×10^{-9} *M* Na^+ (b) $1.3 \times 10^{12}\,Na^+$ ions
4.103 (a) 1.718 *M* $Sr(OH)_2$ (b) $2\,HNO_3(aq) + Sr(OH)_2(s) \longrightarrow Sr(NO_3)_2(aq) + 2\,H_2O(l)$ (c) 2.61 *M* HNO_3 **4.106** (a) The molar-mass of the acid is 136 g/mol. (b) The molecular formula is $C_8H_8O_2$.
4.109 (a) $Mg(OH)_2(s) + 2\,HNO_3(aq) \longrightarrow Mg\,(NO_3)_2(aq) + 2\,H_2O(l)$ (b) HNO_3 is the limiting reactant. (c) 0.0923 mol $Mg(OH)_2$, 0 mol HNO_3, and 0.00250 mol $Mg(NO_3)_2$ are present.
4.112 1.766% Cl^- by mass **4.114** 1.5×10^{-5} g Na_3AsO_4 in 1.00 L H_2O

CHAPTER 5

5.1 (a) As the book falls, potential energy decreases and kinetic energy increases. (b) 71 J, assuming no transfer of energy as heat (c) A heavier book falling from the same shelf has greater kinetic energy when it hits the floor. **5.5** (a) No. The distance traveled to the top of a mountain depends on the path taken by the hiker. Distance is a path function, not a state function. (b) Yes. Change in elevation depends only on the location of the base camp and the height of the mountain, not on the path to the top. Change in elevation is a state function, not a path function. **5.8** (a) The sign of w is (+). (b) The internal energy of the system increases during the change; the sign of ΔE is (+). **5.11** (a) $\Delta H_A = \Delta H_B + \Delta H_C$. The diagram and equation both show that the net enthalpy change for a process is independent of path, that ΔH is a state function. (b) $\Delta H_Z = \Delta H_X + \Delta H_Y$. (c) Hess's law states that the enthalpy change for net reaction Z is the sum of the enthalpy changes for steps X and Y, regardless of whether the reaction actually occurs via this path. The diagrams are a visual statement of Hess's law. **5.13** An object can possess energy by virtue of its motion or position. Kinetic energy depends on the mass of the object and its velocity. Potential energy depends on the position of the object relative to the body with which it interacts. **5.15** (a) 1.9×10^5 J (b) 4.6×10^4 cal (c) As the automobile brakes to a stop, its speed (and hence its kinetic energy) drops to zero. The kinetic energy of the automobile is primarily transferred to friction between brakes and wheels and somewhat to deformation of the tire and friction between the tire and road. **5.17** 1 Btu = 1054 J **5.19** (a) The *system* is the well-defined part of the universe whose energy changes are being studied. (b) A *closed system* can exchange heat but not mass with its surroundings. (c) Any part of the universe not part of the system is called the surroundings. **5.21** (a) Work is a force applied over a distance. (b) The amount of work done is the magnitude of the force times the distance over which it is applied. $w = F \times d$. **5.23** (a) Gravity; work is done because the force of gravity is opposed and the pencil is lifted. (b) Mechanical force; work is done because the force of the coiled spring is opposed as the spring is compressed over a distance. **5.25** (a) In any chemical or physical change, energy can be neither created nor destroyed; energy is conserved. (b) The *internal energy (E)* of a system is the sum of all the kinetic and potential energies of the system components. (c) Internal energy of a closed system increases when work is done on the system and when heat is transferred to the system. **5.27** (a) $\Delta E = -0.077$ kJ, endothermic (b) $\Delta E = -22.1$ kJ, exothermic (c) $\Delta E = 7.25$ kJ, endothermic **5.29** (a) Since no work is done by the system in case (2), the gas will absorb most of the energy as heat; the case (2) gas will have the higher temperature. (b) In case (2) $w = 0$ and $q = 100$ J. In case (1) energy will be used to do work on the surroundings $(-w)$, but some will be absorbed as heat $(+q)$. (c) ΔE is greater for case (2) because the entire 100 J increases the internal energy of the system rather than a part of the energy doing work on the surroundings. **5.31** (a) A *state function* is a property that depends only on the physical state (pressure, temperature, etc.) of the system, not on the route used to get to the current state. (b) Internal energy is a state function; heat is not a state function. (c) Volume is a state function. The volume of a system depends only on conditions (pressure, temperature, amount of substance), not the route or method used to establish that volume. **5.33** (a) ΔH is usually easier to measure than ΔE because at constant pressure, $\Delta H = q_p$. The heat flow associated with a process at constant pressure can easily be measured as a change in temperature, while measuring ΔE requires a means to measure both q and w. (b) H is a static quantity that depends only on the specific conditions of the system. q is an energy *change* that, in the general case, does depend on how the change occurs. We can equate change in enthalpy, ΔH, with heat, q_p, only for the specific conditions of constant pressure and exclusively P-V work. (c) The process is endothermic. **5.35** At constant pressure, $\Delta E = \Delta H - P\Delta V$. The values of either P and ΔV or T and Δn must be known to calculate ΔE from ΔH. **5.37** $\Delta E = 1.47$ kJ; $\Delta H = 0.824$ kJ **5.39** (a) $C_2H_5OH(l) + 3\,O_2(g) \longrightarrow 3\,H_2O + 2\,CO_2(g)$, $\Delta H = -1235$ kJ



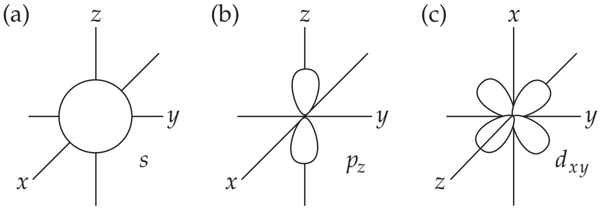
5.41 (a) $\Delta H = -142.3$ kJ/mol $O_3(g)$ (b) $2\,O_3(g)$ has the higher enthalpy. **5.43** (a) Exothermic (b) −87.9 kJ heat transferred (c) 15.7 g MgO produced (d) 602 kJ heat absorbed **5.45** (a) −29.5 kJ (b) −4.11 kJ (c) 60.6 J **5.47** (a) $\Delta H = 726.5$ kJ (b) $\Delta H = -1453$ kJ (c) The exothermic forward reaction is more likely to be thermodynamically favored. (d) Vaporization is endothermic. If the product were $H_2O(g)$, the reaction would be more endothermic and would have a less negative ΔH. **5.49** (a) J/mol-°C or J/mol-K (b) J/g-°C or J/g-K (c) To calculate heat capacity from specific heat, the mass of the particular piece of copper pipe must be known. **5.51** (a) 4.184 J/g-K (b) 75.40 J/mol-°C (c) 774 J/°C (d) 904 kJ **5.53** (a) 2.66×10^3 J (b) It will require more heat to increase the temperature of one mole of octane, $C_8H_{18}(l)$, by a certain amount than to increase the temperature of one mole of water, $H_2O(l)$, by the same amount. **5.55** $\Delta H = -44.4$ kJ/mol NaOH **5.57** $\Delta H_{rxn} = -25.5$ kJ/g $C_6H_4O_2$ or -2.75×10^3 kJ/mol $C_6H_4O_2$ **5.59** (a) Heat capacity of the complete calorimeter = 14.4 kJ/°C (b) 7.56 °C **5.61** Hess's law is a consequence of the fact that enthalpy is a state function. Since ΔH is independent of path, we can describe a process by any series of steps that adds up to the overall process. ΔH for the process is the sum of ΔH values for the steps. **5.63** $\Delta H = -1300.0$ kJ **5.65** $\Delta H = -2.49 \times 10^3$ kJ **5.67** (a) *Standard conditions* for enthalpy changes are $P = 1$ atm and some common temperature, usually 298 K. (b) *Enthalpy of formation* is the enthalpy change that occurs when a compound is formed from its component elements. (c) *Standard enthalpy of formation* ΔH_f° is the enthalpy change that accompanies formation of one mole of a substance from elements in their standard states. **5.69** (a) $\frac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g)$, $\Delta H_f^\circ = 33.84$ kJ (b) $S(s) + 3/2\,O_2(g) \longrightarrow SO_3(g)$, $\Delta H_f^\circ = -395.2$ kJ (c) $Na(s) + \frac{1}{2}Br_2(l) \longrightarrow NaBr(s)$, $\Delta H_f^\circ = -361.4$ kJ (d) $Pb(s) + N_2(g) + 3\,O_2(g) \longrightarrow Pb(NO_3)_2(s)$, $\Delta H_f^\circ = -451.9$ kJ **5.71** $\Delta H^\circ_{rxn} = -847.6$ kJ **5.73** (a) $\Delta H^\circ_{rxn} = -196.6$ kJ (b) $\Delta H^\circ_{rxn} = 37.1$ kJ (c) $\Delta H^\circ_{rxn} = -976.94$ kJ (d) $\Delta H^\circ_{rxn} = -68.3$ kJ **5.75** $\Delta H_f^\circ = -248$ kJ **5.77** (a) $C_8H_{18}(l) + \frac{25}{2}O_2(g) \longrightarrow 8\,CO_2(g) + 9\,H_2O(g)$, $\Delta H = -5064.9$ kJ (b) $8\,C(s, \text{graphite}) + 9\,H_2(g) \longrightarrow C_8H_{18}(l)$ (c) $\Delta H_f^\circ = -259.5$ kJ **5.79** (a) $C_2H_5OH(l) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 3\,H_2O(g)$ (b) $\Delta H^\circ_{rxn} = -1234.8$ kJ (c) 2.11×10^4 kJ/L heat produced (d) 0.071284 g CO_2/kJ heat emitted **5.81** (a) *Fuel value* is the amount of energy produced when 1 g of a substance (fuel) is combusted. (b) 5 g of fat (c) These products of metabolism are expelled as waste via the alimentary tract, $H_2O(l)$ primarily in urine and feces, and $CO_2(g)$ as gas. **5.83** 108 or 1×10^2 Cal/serving (b) Sodium does not contribute to the calorie content of the food because it is not metabolized by the body. **5.85** 59.7 Cal **5.87** (a) $\Delta H_{comb} = -1850$ kJ/mol C_3H_4, -1926 kJ/mol C_3H_6, -2044 kJ/mol C_3H_8 (b) $\Delta H_{comb} = -4.616 \times 10^4$ kJ/kg C_3H_4, -4.578×10^4 kJ/kg C_3H_6, -4.635×10^4 kJ/kg C_3H_8 (c) These three substances yield nearly identical quantities of heat per unit mass, but propane is marginally higher than the other two. **5.89** 1×10^{12} kg $C_6H_{12}O_6$/yr **5.91** (a) 469.4 m/s (b) 5.124×10^{-21} J (c) 3.086 kJ/mol **5.93** The spontaneous air bag reaction is probably exothermic, with $-\Delta H$ and thus $-q$. When the bag inflates, work is done by the system, so the sign of w is also negative. **5.97** $\Delta H = 38.95$ kJ; $\Delta E = 36.48$ kJ **5.102** (a) $\Delta H^\circ_{rxn} = -353.0$ kJ (b) 1.2 g Mg needed **5.106** (a) $\Delta H^\circ = -631.3$ kJ (b) 3 mol of acetylene gas has greater enthalpy. (c) Fuel values are 50 kJ/g $C_2H_2(g)$, 42 kJ/g $C_6H_6(l)$. **5.109** If all work is used to increase the man's potential energy, the stair climbing uses 58 Cal and will not compensate for the extra order of 245 Cal fries. (More than 58 Cal will be required to climb the stairs because some energy is used to move limbs and some will be lost as heat.)

5.112 (a) 1.479×10^{-18} J/molecule (b) 1×10^{-15} J/photon. The X-ray has approximately 1000 times more energy than is produced by the combustion of 1 molecule of $CH_4(g)$. **5.114** (a) $\Delta H°$ for neutralization of the acids is HNO_3, -55.8 kJ; HCl, -56.1 kJ; NH_4^+, -4.1 kJ. (b) $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$ is the net ionic equation for the first two reactions. $NH_4^+(aq) + OH^-(aq) \longrightarrow NH_3(aq) + H_2O(l)$ (c) The $\Delta H°$ values for the first two reactions are nearly identical, -55.8 kJ and -56.1 kJ. Since spectator ions do not change during a reaction and these two reactions have the same net ionic equation, it is not surprising that they have the same $\Delta H°$. (d) Strong acids are more likely than weak acids to donate H^+. Neutralization of the two strong acids is energetically favorable, while the third reaction is barely so. NH_4^+ is likely a weak acid. **5.116** (a) $\Delta H° = -65.7$ kJ (b) $\Delta H°$ for the complete molecular equation will be the same as $\Delta H°$ for the net ionic equation. Since the overall enthalpy change is the enthalpy of products minus the enthalpy of reactants, the contributions of spectator ions cancel. (c) $\Delta H_f°$ for $AgNO_3(aq)$ is -100.4 kJ/mol.

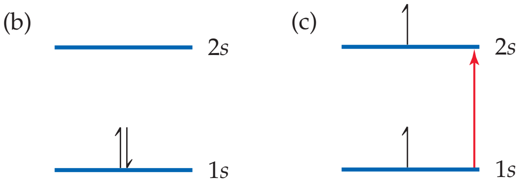
CHAPTER 6

6.2 (a) 0.1 m or 10 cm (b) No. Visible radiation has wavelengths much shorter than 0.1 m. (c) Energy and wavelength are inversely proportional. Photons of the longer 0.1-m radiation have less energy than visible photons. (d) Radiation with $\lambda = 0.1$ m is in the low-energy portion of the microwave region. The appliance is probably a microwave oven. **6.5** (a) Increase (b) decrease (c) the light from the hydrogen discharge tube is a line spectrum, so not all visible wavelengths will be in our "hydrogen discharge rainbow." Starting on the inside, the rainbow will be violet, then blue and blue-green. After a gap, the final band will be red. **6.8** (a) 1 (b) *p* (c) For the $n = 4$ shell, the lobes in the contour representation would extend farther along the *y*-axis. **6.11** (a) Meters (b) 1/second (c) meters/second **6.13** (a) True (b) False. Ultraviolet light has shorter wavelengths than visible light. (c) False. X-rays travel at the same speed as microwaves. (d) False. Electromagnetic radiation and sound waves travel at different speeds. **6.15** Wavelength of X-rays < ultraviolet < green light < red light < infrared < radio waves **6.17** (a) $3.0 \times 10^{13}\ s^{-1}$ (b) 5.45×10^{-7} m = 545 nm (c) The radiation in (b) is visible; the radiation in (a) is not. (d) 1.50×10^4 m **6.19** $5.64 \times 10^{14}\ s^{-1}$; green. **6.21** Quantization means that energy changes can happen only in certain allowed increments. If the human growth quantum is one foot, growth occurs instantaneously in one-foot increments. The child experiences growth spurts of one foot; her height can change only by one-foot increments. **6.23** (a) 4.47×10^{-21} J (b) 6.17×10^{-19} J (c) 69.2 nm **6.25** (a) $\lambda = 3.3\ \mu m$, $E = 6.0 \times 10^{-20}$ J; $\lambda = 0.154$ nm, $E = 1.29 \times 10^{-15}$ J (b) The 3.3-μm photon is in the infrared region and the 0.154-nm photon is in the X-ray region; the X-ray photon has the greater energy. **6.27** (a) 6.11×10^{-19} J/photon (b) 368 kJ/mol (c) 1.64×10^{15} photons (d) 368 kJ/mol **6.29** (a) The $\sim 1 \times 10^{-6}$ m radiation is in the infrared portion of the spectrum. (b) 8.1×10^{16} photons/s **6.31** (a) $E_{min} = 7.22 \times 10^{-19}$ J (b) $\lambda = 275$ nm (c) $E_{120} = 1.66 \times 10^{-18}$ J. The excess energy of the 120-nm photon is converted into the kinetic energy of the emitted electron. $E_k = 9.3 \times 10^{-19}$ J/electron. **6.33** When applied to atoms, the notion of quantized energies means that only certain values of ΔE are allowed. These are represented by the lines in the emission spectra of excited atoms. **6.35** (a) Emitted (b) absorbed (c) emitted **6.37** (a) $E_2 = -5.45 \times 10^{-19}$ J; $E_6 = -0.606 \times 10^{-19}$ J; $\Delta E = 4.84 \times 10^{-19}$ J; $\lambda = 410$ nm (b) visible, violet **6.39** (a) Only lines with $n_f = 2$ represent ΔE values and wavelengths that lie in the visible portion of the spectrum. Lines with $n_f = 1$ have shorter wavelengths and lines with $n_f > 2$ have longer wavelengths than visible radiation. (b) $n_i = 3$, $n_f = 2$; $\lambda = 6.56 \times 10^{-7}$ m; this is the red line at 656 nm. $n_i = 4$, $n_f = 2$; $\lambda = 4.86 \times 10^{-7}$ m; this is the blue-green line at 486 nm. $n_i = 5$, $n_f = 2$; $\lambda = 4.34 \times 10^{-7}$ m; this is the blue-violet line at 434 nm. **6.41** (a) Ultraviolet region (b) $n_i = 6$, $n_f = 1$ **6.43** (a) $\lambda = 5.6 \times 10^{-37}$ m (b) $\lambda = 2.65 \times 10^{-34}$ m (c) $\lambda = 2.3 \times 10^{-13}$ m (d) $\lambda = 1.51 \times 10^{-11}$ m **6.45** 4.14×10^3 m/s **6.47** (a) $\Delta x \geq 4 \times 10^{-27}$ m (b) $\Delta x \geq 3 \times 10^{-10}$ m **6.49** (a) The uncertainty principle states that there is a limit to how precisely we can simultaneously know the position and momentum (a quantity related to energy) of an electron. The Bohr model states that electrons move about the nucleus in precisely circular orbits of known radius and energy. This violates the uncertainty principle. (b) De Broglie stated that electrons demonstrate the properties of both particles and waves and that each moving particle has a wave associated with it. A wave function is the mathematical description of the matter wave of an electron. (c) Although we cannot predict the exact location of an electron in an allowed energy state, we can determine the probability of finding an electron at a particular position. This statistical knowledge of electron location is the *probability density* and is a function of Ψ^2, the square of the wave function Ψ. **6.51** (a) $n = 4$, $l = 3, 2, 1, 0$ (b) $l = 2$, $m_l = -2, -1, 0, 1, 2$ (c) $m_l = 2$, $l \geq 2$ or $l = 2, 3$ or 4 **6.53** (a) 3*p*: $n = 3$, $l = 1$ (b) 2*s*: $n = 2$, $l = 0$ (c) 4*f*: $n = 4$, $l = 3$ (d) 5*d*: $n = 5$, $l = 2$ **6.55** (a) impossible, 1*p* (b) possible (c) possible (d) impossible, 2*d*

6.57



6.59 (a) The hydrogen atom 1*s* and 2*s* orbitals have the same overall spherical shape, but the 2*s* orbital has a larger radial extension and one more node than the 1*s* orbital. (b) A single 2*p* orbital is directional in that its electron density is concentrated along one of the three Cartesian axes of the atom. The $d_{x^2-y^2}$ orbital has electron density along both the *x*- and *y*-axes, while the p_x orbital has density only along the *x*-axis. (c) The average distance of an electron from the nucleus in a 3*s* orbital is greater than for an electron in a 2*s* orbital. (d) 1*s* < 2*p* < 3*d* < 4*f* < 6*s* **6.61** (a) In the hydrogen atom, orbitals with the same principal quantum number, *n*, have the same energy. (b) In a many-electron atom, for a given *n* value, orbital energy increases with increasing *l* value: *s* < *p* < *d* < *f*. **6.63** (a) There are two main pieces of experimental evidence for electron "spin." The Stern-Gerlach experiment shows that atoms with a single unpaired electron interact differently with an inhomogeneous magnetic field. Examination of the fine details of emission line spectra of multi-electron atoms reveals that each line is really a close pair of lines. Both observations can be rationalized if electrons have the property of spin.



6.65 (a) 6 (b) 10 (c) 2 (d) 14 **6.67** (a) "Valence electrons" are those involved in chemical bonding. They are part or all of the outer-shell electrons listed after the core. (b) "Core electrons" are inner-shell electrons that have the electron configuration of the nearest noble-gas element. (c) Each box represents an orbital. (d) Each half-arrow in an orbital diagram represents an electron. The direction of the half-arrow represents electron spin. **6.69** (a) Cs, $[Xe]6s^1$ (b) Ni, $[Ar]4s^23d^8$ (c) Se, $[Ar]4s^23d^{10}4p^4$ (d) Cd, $[Kr]5s^24d^{10}$ (e) U, $[Rn]5f^36d^17s^2$ (f) Pb, $[Xe]6s^24f^{14}5d^{10}6p^2$ **6.71** (a) Be, 0 unpaired electrons (b) O, 2 unpaired electrons (c) Cr, 6 unpaired electrons (d) Te, 2 unpaired electrons **6.73** (a) The fifth electron would fill the 2*p* subshell before the 3*s*. (b) Either the core is [He], or the outer electron configuration should be $3s^23p^3$. (c) The 3*p* subshell would fill before the 3*d*. **6.75** (a) $\lambda_A = 3.6 \times 10^{-8}$ m, $\lambda_B = 8.0 \times 10^{-8}$ m (b) $\nu_A = 8.4 \times 10^{15}\ s^{-1}$, $\nu_B = 3.7 \times 10^{15}\ s^{-1}$ (c) A, ultraviolet; B, ultraviolet **6.78** 66.7 min **6.82** 1.6×10^7 photons/s, 5.1×10^{-12} J/s **6.85** (a) The Paschen series lies in the infrared. (b) $n_i = 4$, $\lambda = 1.87 \times 10^{-6}$ m; $n_i = 5$, $\lambda = 1.28 \times 10^{-6}$ m; $n_i = 6$, $\lambda = 1.09 \times 10^{-6}$ m **6.90** (a) *l* (b) *n* and *l* (c) m_s (d) m_l **6.92** (a) The nodal plane of the p_z orbital is the *xy*-plane. (b) The two nodal planes of the d_{xy} orbital are the ones where

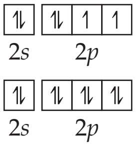
$x = 0$ and $y = 0$. These are the *yz*- and *xz*-planes. (c) The two nodal planes of the $d_{x^2-y^2}$ orbital are the ones that bisect the *x*- and *y*-axes and contain the *z*-axis. **6.94** If m_s had three allowed values instead of two, each orbital would hold three electrons instead of two. Assuming that there is no change in the *n*, *l*, and m_l values, the number of elements in each of the first four rows would be 1st row, 3 elements; 2nd row, 12 elements; 3rd row, 12 elements; 4th row, 27 elements **6.97** (a) 1.7×10^{28} photons (b) 34 s **6.101** (a) Bohr's theory was based on the Rutherford nuclear model of the atom: a dense positive charge at the center and a diffuse negative charge surrounding it. Bohr's theory then specified the nature of the diffuse negative charge. The prevailing theory before the nuclear model was Thomson's plum pudding model: discrete electrons scattered about a diffuse positive charge cloud. Bohr's theory could not have been based on the Thomson model of the atom. (b) De Broglie's hypothesis is that electrons exhibit both particle and wave properties. Thomson's conclusion that electrons have mass is a particle property, while the nature of cathode rays is a wave property. De Broglie's hypothesis actually rationalizes these two seemingly contradictory observations about the properties of electrons.

CHAPTER 7

7.3 (a) The bonding atomic radius of A, r_A, is $d_1/2$; $r_x = d_2 - (d_1/2)$. (b) The length of the X—X bond is $2r_x$ or $2d_2 - d_1$. **7.6** (a) $X + 2F_2 \rightarrow XF_4$ (b) X in the diagram has about the same bonding radius as F, so it is likely to be a nonmetal. **7.7** The number of columns in the various blocks of the periodic chart corresponds to the maximum number of electrons that can occupy the various kinds of atomic orbitals: 2 columns on the left for 2 electrons in *s* orbitals, 10 columns in the transition metals for 10 electrons in *d* orbitals, 6 columns on the right for 6 electrons in *p* orbitals, 14-member rows below for 14 electrons in *f* orbitals. The order of blocks corresponds to the filling order of atomic orbitals, and the row number corresponds to the principal quantum number of the valence electrons of elements in that row, *ns*, *np*, $(n-1)d$, $(n-2)f$. **7.9** In general, elements are discovered according to their ease of isolation in elemental form. **7.11** (a) *Effective nuclear charge*, Z_{eff}, is a representation of the average electrical field experienced by a single electron. It is the average environment created by the nucleus and the other electrons in the molecule, expressed as a net positive charge at the nucleus. (b) Going from left to right across a period, effective nuclear charge increases. **7.13** (a) For both Na and K, $Z_{\text{eff}} = 1$. (b) For both Na and K, $Z_{\text{eff}} = 2.2$. (c) Slater's rules give values closer to the detailed calculations: Na, 2.51; K, 3.49. (d) Both approximations give the same value of Z_{eff} for Na and K; neither accounts for the gradual increase in Z_{eff} moving down a group. (e) Following the trend from detailed calculations, we predict a Z_{eff} value of approximately 4.5. **7.15** The $n = 3$ electrons in Kr experience a greater effective nuclear charge and thus have a greater probability of being closer to the nucleus. **7.17** (a) Atomic radii are determined by measuring distances between atoms in various situations. (b) Bonding radii are calculated from the internuclear separation of two atoms joined by a covalent chemical bond. Nonbonding radii are calculated from the internuclear separation between two gaseous atoms that collide and move apart but do not bond. (c) For a given element, the nonbonding radius is always larger than the bonding radius. (d) If a free atom reacts to become part of a covalent molecule, its radius changes from nonbonding to bonding and the atom gets smaller. **7.19** (a) 1.37 Å (b) The distance between W atoms will decrease. **7.21** From the sum of the atomic radii, As—I = 2.52 Å. This is very close to the experimental value of 2.55 Å. **7.23** (a) Decrease (b) increase (c) O < Si < Ge < I **7.25** (a) Cs > K > Li (b) Pb > Sn > Si (c) N > O > F **7.27** (a) False (b) true (c) false **7.29** The red sphere is a metal; its size decreases on reaction, characteristic of the change in radius when a metal atom forms a cation. The blue sphere is a nonmetal; its size increases on reaction, characteristic of the change in radius when a nonmetal atom forms an anion. **7.31** (a) An isoelectronic series is a group of atoms or ions that have the same number of electrons and the same electron configuration. (b) Ga^{3+}: Ar; Zr^{4+}: Kr; Mn^{7+}: Ar; I^-: Xe; Pb^{2+}: Hg **7.33** (a) Ar (b) Ar (c) There is no neutral atom isoelectronic with Fe^{2+}. Because transition metals fill the *s* subshell first but also lose *s* electrons first when they form ions, many transition metal ions do not have isolectronic neutral atoms. (d) No isoelectronic neutral atom; same reason as part (c). (e) No isoelectronic neutral atom; same reason as part (c). **7.35** (a) K^+ is smaller. (b) Cl^-, $Z_{\text{eff}} = 7$; K^+, $Z_{\text{eff}} = 9$ (c) Cl^-: $Z_{\text{eff}} = 5.75$; K^+, $Z_{\text{eff}} = 7.75$ (d) For isoelectronic ions, as nuclear charge (*Z*) increases, effective nuclear charge (Z_{eff}) increases and ionic radius decreases. **7.37** (a) $Se < Se^{2-} < Te^{2-}$ (b) $Co^{3+} < Fe^{3+} < Fe^{2+}$ (c) $Ti^{4+} < Sc^{3+} < Ca$ (d) $Be^{2+} < Na^+ < Ne$ **7.39** $Al(g) \longrightarrow Al^+(g) + \text{le}^-$; $Al^+(g) \longrightarrow Al^{2+}(g) + \text{le}^-$; $Al^{2+}(g) \longrightarrow Al^{3+}(g) + \text{le}^-$. The process for the first ionization energy requires the least amount of energy. **7.41** (a) False. Ionization energies are always positive quantities. (b) False. F has a greater first ionization energy than O. (c) True. **7.43** (a) The smaller the atom, the larger its first ionization energy. (b) Of the nonradioactive elements, He has the largest and Cs the smallest first ionization energy. **7.45** (a) Cl (b) Ca (c) K (d) Ge (e) Sn **7.47** (a) Fe^{2+}, $[Ar]3d^6$ (b) Hg^{2+}, $[Xe]4f^{14}5d^{10}$ (c) Mn^{2+}, $[Ar]3d^5$ (d) Pt^{2+}, $[Xe]4f^{14}5d^8$ (e) P^{3-}, $[Ne]3s^23p^6$ **7.49** Ni^{2+}, $[Ar]3d^8$; Pd^{2+}, $[Kr]4d^8$; Pt^{2+}, $[Xe]4f^{14}5d^8$ **7.51** (a) Positive, endothermic, values for ionization energy and electron affinity mean that energy is required to either remove or add electrons. Valence electrons in Ar experience the largest Z_{eff} of any element in the third row, resulting in a large, positive ionization energy. When an electron is added to Ar, the $n = 3$ electrons become core electrons that screen the extra electron so effectively that Ar^- has a higher energy than an Ar atom and a free electron. This results in a large positive electron affinity. (b) kJ/mol **7.53** Electron affinity of Br: $Br(g) + 1\,e^- \longrightarrow Br^-(g)$; $[Ar]4s^23d^{10}4p^5 \longrightarrow [Ar]4s^23d^{10}4p^6$; electron affinity of Kr: $Kr(g) + 1\,e^- \longrightarrow Kr^-(g)$; $[Ar]4s^23d^{10}4p^6 \longrightarrow [Ar]4s^23d^{10}4p^65s^1$. Br^- adopts the stable electron configuration of Kr; the added electron experiences essentially the same Z_{eff} and stabilization as the other valence electrons and electron affinity is negative. In Kr^- ion, the added electron occupies the higher energy 5*s* orbital. A 5*s* electron is farther from the nucleus, effectively shielded by the spherical Kr core and not stabilized by the nucleus; electron affinity is positive. **7.55** (a) Ionization energy (I_1) of Ne: $Ne(g) \longrightarrow Ne^+(g) + 1\,e^-$; $[He]2s^22p^6 \longrightarrow [He]2s^22p^5$; electron affinity ($E_1$) of F: $F(g) + 1\,e^- \longrightarrow F^-(g)$; $[He]2s^22p^5 \longrightarrow [He]2s^22p^6$. (b) I_1 of Ne is positive; E_1 of F is negative. (c) One process is apparently the reverse of the other, with one important difference. Ne has a greater *Z* and Z_{eff}, so we expect I_1 for Ne to be somewhat greater in magnitude and opposite in sign to E_1 for F. **7.57** The smaller the first ionization energy of an element, the greater the metallic character of that element. **7.59** Agree. When forming ions, all metals form cations. The only nonmetallic element that forms cations is the metalloid Sb, which is likely to have significant metallic character. **7.61** Ionic: SnO_2, Al_2O_3, Li_2O, Fe_2O_3; molecular: CO_2, H_2O. Ionic compounds are formed by combining a metal and a nonmetal; molecular compounds are formed by two or more nonmetals. **7.63** (a) An *acidic oxide* dissolved in water produces an acidic solution; a *basic oxide* dissolved in water produces a basic solution. (b) Oxides of nonmetals, such as SO_3, are acidic; oxides of metals, such as CaO, are basic. **7.65** (a) Dichlorineheptoxide (b) $2\,Cl_2(g) + 7\,O_2(g) \longrightarrow 2\,Cl_2O_7(l)$ (c) While most nonmetal oxides we have seen, such as CO_2 or SO_2, are gases, a boiling point of 81 °C is expected for a large molecule like Cl_2O_7. (d) Cl_2O_7 is an acidic oxide, so it will be more reactive to base, OH^-. (e) The oxidation state of Cl in Cl_2O_7 is +7; the corresponding electron configuration for Cl is $[He]2s^22p^6$ or [Ne]. **7.67** (a) $BaO(s) + H_2O(l) \longrightarrow Ba(OH)_2(aq)$ (b) $FeO(s) + 2\,HClO_4(aq) \longrightarrow Fe(ClO_4)_2(aq) + H_2O(l)$ (c) $SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$ (d) $CO_2(g) + 2\,NaOH(aq) \longrightarrow Na_2CO_3(aq) + H_2O(l)$ **7.69** Yes, the reactivity of a metal correlates with its first ionization energy. Since metals lose electrons when they form ions, the less energy required for this process, the more reactive the metal. However, we usually observe reactivity of metals in the solid state and ionization energy is a gas phase property, so there are differences between the two properties. **7.71** (a) Ca is more reactive because it has a lower ionization energy than Mg. (b) K is more reactive because it has a lower ionization energy than Ca. **7.73** (a) $2\,K(s) + Cl_2(g) \longrightarrow 2\,KCl(s)$ (b) $SrO(s) + H_2O(l) \longrightarrow Sr(OH)_2(aq)$ (c) $4\,Li(s) + O_2(g) \longrightarrow 2\,Li_2O(s)$ (d) $2\,Na(s) + S(l) \longrightarrow Na_2S(s)$ **7.75** (a) Both classes of reaction are redox reactions where either hydrogen or the halogen gains electrons and is reduced. The product is an ionic solid, where either hydride ion, H^-, or a halide ion, X^-, is the anion. (b) $Ca(s) + F_2(g) \longrightarrow CaF_2(s)$; $Ca(s) + H_2(g) \longrightarrow CaH_2(s)$. Both products are ionic solids containing Ca^{2+} and the corresponding anion in a 1:2 ratio. **7.77** (a) Br, $[Ar]4s^24p^5$; Cl, $[Ne]3s^23p^5$ (b) Br and Cl are in the same group, and both adopt a 1− ionic charge. (c) The ionization energy of Br is smaller than that of Cl, because the 4*p* valence electrons in Br are farther from the nucleus and less tightly held than the 3*p* electrons of Cl. (d) Both react slowly with water to form HX + HOX. (e) The electron affinity of Br is less negative than that of Cl, because the electron added to the 4*p* orbital in Br is farther from the nucleus and less tightly held than the electron added to the 3*p* orbital of Cl. (f) The atomic radius of Br is larger than that of Cl, because the 4*p* valence electrons in Br are farther from the nucleus and less tightly held than the 3*p* electrons of Cl. **7.79** (a) The term *inert* was dropped because it no longer described all the Group 8A elements. (b) In the 1960s, scientists discovered that Xe would react with substances having a strong tendency to remove electrons, such as F_2. Thus, Xe could not be categorized as an "inert" gas. (c) The group is now called the noble gases. **7.81** (a) $2\,O_3(g) \longrightarrow 3\,O_2(g)$ (b) $Xe(g) + F_2(g) \longrightarrow XeF_2(g)$; $Xe(g) + 2\,F_2(g) \longrightarrow XeF_4(s)$; $Xe(g) + 3\,F_2(g) \longrightarrow XeF_6(s)$ (c) S(*s*) + (d) $2\,F_2(g) + 2\,H_2O(l) \longrightarrow 4\,HF(aq) + O_2(g)$ **7.83** Up to $Z = 82$, there are three instances where atomic weights are reversed relative to atomic numbers: Ar and K; Co and Ni; Te and I. In each case the most abundant isotope of the element with the larger atomic number has one more proton but fewer neutrons than the element with the smaller atomic number. The smaller number of neutrons causes the element with the larger *Z* to have a smaller than expected atomic weight. **7.85** (a) 5+ (b) 4.8+ (c) Shielding is greater for 3*p* electrons, owing to penetration by 3*s* electrons, so Z_{eff} for 3*p* electrons is less than that for 3*s* electrons. (d) The first electron lost is a 3*p* electron because it has a smaller Z_{eff} and experiences less attraction for the nucleus than a 3*s* electron does. **7.88** (a) The estimated distances are a bit longer than the measured distances. This probably shows a systematic bias in either the estimated radii or in the method of obtaining the measured values. (b) The principal quantum number of the outer electrons and thus the average distance of these electrons from the nucleus increase from P($n = 3$) to As($n = 4$) to Sb($n = 5$). This causes the systematic increase in M – H distance. **7.92** (a) $2\,Sr(s) + O_2(g) \longrightarrow 2\,SrO(s)$ (b) Based on ionic radii, the length of the side of the cube is 5.16 Å. (c) There are four SrO units in the cube.

7.95 (a) O, $[He]2s^22p^4$

O^{2-}, $[He]2s^22p^6 = [Ne]$



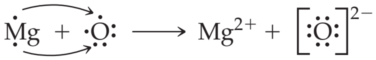
(b) O^{3-}, $[Ne]3s^1$. The third electron would be added to the 3*s* orbital, which is farther from the nucleus and more strongly shielded by the [Ne] core. The overall attraction of this 3*s* electron for the oxygen nucleus is not large enough for O^{3-} to be a stable particle. **7.98** (a) For both H and the alkali metals, the added electron will complete an *ns* subshell, so shielding and repulsion effects will be similar. For the halogens, the electron is added to an *np* subshell, so the energy change is likely to be quite different. (b) True. The electron configuration of H is $1s^1$. The single 1*s* electron experiences no repulsion from other electrons and feels the full unshielded nuclear charge. The outer electrons of all other elements that form compounds are shielded by a spherical inner core of electrons and are less strongly attracted to the nucleus, resulting in larger bonding atomic radii. (c) Both H and the halogens have large ionization energies. The relatively large effective nuclear charge experienced by *np* electrons of the halogens is similar to the unshielded nuclear charge experienced by the H 1*s* electron. For the alkali metals, the *ns* electron being removed is effectively shielded by the core electrons, so ionization energies are low. (d) ionization energy of hydride, $H^-(g) \longrightarrow H(g) + 1\,e^-$ (e) electron affinity of hydrogen, $H(g) + 1\,e^- \longrightarrow H^-(g)$. The value for the ionization energy of hydride is equal in magnitude but opposite in sign to the electron affinity of hydrogen. **7.103** Electron configuration, $[Rn]7s^25f^{14}6d^{10}7p^5$; first ionization energy, 805 kJ/mol; electron affinity, −235 kJ/mol; atomic size, 1.65 Å; common oxidation state, −1 **7.106** (a) Li, $[He]2s^1$; $Z_{eff} \approx 1+$ (b) $I_1 \approx 5.45 \times 10^{-19}$ J/mol ≈ 328 kJ/mol (c) The estimated value of 328 kJ/mol is less than the Table 7.4 value of 520 kJ/mol. Our estimate for Z_{eff} was a lower limit; the [He] core electrons do not perfectly shield the 2*s* electron from the nuclear charge. (d) Based on the experimental ionization energy, $Z_{eff} = 1.26$. This value is greater than the estimate from part (a) but agrees well with the "Slater" value of 1.3 and is consistent with the explanation in part (c). **7.108** (a) 9.8902 Å. (b) For Hg, the first ionization energy is 1007 kJ/mol, while the XPS energy of the 4*f* electron is 10,100 kJ/mol. The energy required to remove a 4*f* core electron is 10 times the energy required to remove a 6*s* valence electron. For O, the first ionization energy is 1314 kJ/mol, while the XPS energy of a 1*s* electron is 51,200 kJ/mol. The energy required to remove a 1*s* core electron is 40 times that required to remove a 2*p* valence electron. (c) Hg^{2+}, $[Xe]4f^{14}5d^{10}$; valence electrons are 5*d*. O^{2-}, $[He]2s^22p^6$ or [Ne]; valence electrons are 2*p* (d) $Hg^{2+}5d$, $Z_{eff} = 18.85$; $Hg^{2+}4f$, $Z_{eff} = 43.85$; $O^{2-}4f$, $Z_{eff} = 3.85$. **7.110** (a) Mg_3N_2 (b) $Mg_3N_2(s) + 3\,H_2O(l) \longrightarrow 3\,MgO(s) + 2\,NH_3(g)$; the driving force is the production of $NH_3(g)$. (c) 17% Mg_3N_2 (d) $3\,Mg(s) + 2\,NH_3(g) \longrightarrow Mg_3N_2(s) + 3\,H_2(g)$. NH_3 is the limiting reactant and 0.46 g H_2 is formed. (e) $\Delta H^\circ_{rxn} = -368.70$ kJ

CHAPTER 8

8.1 (a) Group 4A or 14 (b) Group 2A or 2 (c) Group 5A or 15 **8.4** (a) Ru (b) $[Kr]5s^24d^6$. **8.7** (a) Moving from left to right along the molecule, the first C needs 2 H atoms, the second needs 1, the third needs none, and the fourth needs 1. (b) In order of increasing bond length: $3 < 1 < 2$ (c) In order of increasing bond enthalpy: $2 < 1 < 3$ **8.9** (a) Valence electrons are those that take part in chemical bonding. This usually means the electrons beyond the core noble-gas configuration of the atom, although it is sometimes only the outer-shell electrons. (b) A nitrogen atom has 5 valence electrons. (c) The atom (Si) has 4 valence electrons. **8.11** Si, $1s^22s^22p^63s^23p^2$. The $n = 3$ electrons are valence electrons; the others are nonvalence electrons. Valence electrons participate in chemical bonding; the others do not.

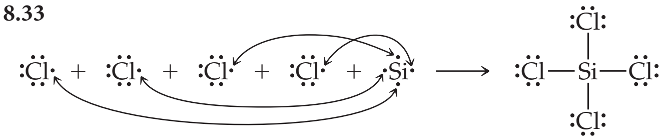
8.13

8.15



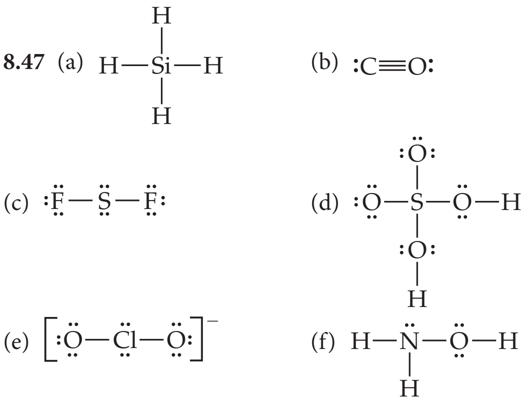
8.17 (a) AlF_3 (b) K_2S (c) Y_2O_3 (d) Mg_3N_2 **8.19** (a) Sr^{2+}, $[Ar]4s^23d^{10}4p^6 = [Kr]$, noble-gas configuration (b) Ti^{2+}, $[Ar]3d^2$ (c) Se^{2-}, $[Ar]4s^23d^{10}4p^6 = [Kr]$, noble-gas configuration (d) Ni^{2+}, $[Ar]3d^8$ (e) Br^-, $[Ar]4s^23d^{10}4p^6 = [Kr]$, noble-gas configuration (f) Mn^{3+}, $[Ar]3d^4$ **8.21** (a) *Lattice energy* is the energy required to totally separate one mole of solid ionic compound into its gaseous ions. (b) The magnitude of the lattice energy depends on the magnitudes of the charges of the two ions, their radii, and the arrangement of ions in the lattice. **8.23** KF, 808 kJ/mol; CaO, 3414 kJ/mol; ScN, 7547 kJ/mol. The interionic distances in the three compounds are similar. For compounds with similar ionic separations, the lattice energies should be related as the product of the charges of the ions. The lattice energies above are approximately related as 1 : 4 : 9. Slight variations are due to the small differences in ionic separations. **8.25** Since the ionic charges are the same in the two compounds, the K—Br and Cs—Cl separations must be approximately equal. **8.27** The large attractive energy between oppositely charged Ca^{2+} and O^{2-} more than compensates for the energy required to form Ca^{2+} and O^{2-} from the neutral atoms. **8.29** The lattice energy of RbCl(*s*) is +692 kJ/mol. This value is smaller than the lattice energy for NaCl because Rb^+ has a larger ionic radius than Na^+ and therefore cannot approach Cl^- as closely as Na^+ can. **8.31** (a) A *covalent bond* is the bond formed when two atoms share one or more pairs of electrons. (b) Any simple compound whose component atoms are nonmetals, such as H_2, SO_2, and CCl_4, are molecular and have covalent bonds between atoms. (c) Covalent, because it is a gas at room temperature and below.

8.33

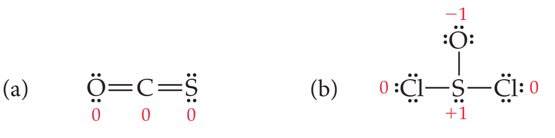


8.35 (a) $\ddot{O}=\ddot{O}$ (b) A double bond is required because there are not enough electrons to satisfy the octet rule with single bonds and unshared pairs. (c) The greater the number of shared electron pairs between two atoms, the shorter the distance between the atoms. An O═O double bond is shorter than an O—O single bond. **8.37** (a) *Electronegativity* is the ability of an atom in a molecule to attract electrons to itself. (b) The range of electronegativities on the Pauling scale is 0.7–4.0. (c) Fluorine is the most electronegative element. (d) Cesium is the least electronegative element that is not radioactive. **8.39** (a) Mg (b) S (c) C (d) As **8.41** The bonds in (a), (c), and (d) are polar. The more electronegative element in each polar bond is (a) F (c) O (d) I. **8.43** (a) The calculated charge on H and Br is 0.12*e*. (b) From Sample Exercise 8.5, the calculated charge on H and Cl in HCl is 0.178*e*. HBr has a smaller dipole moment and longer bond length than HCl; these properties both contribute to the smaller charge separation in HBr. **8.45** (a) $SiCl_4$, molecular, silicon tetrachloride; LaF_3, ionic, lanthanum(III) fluoride (b) $FeCl_2$, ionic, iron(II) chloride; $ReCl_6$, molecular (metal in high oxidation state), rhenium hexachloride. (c) $PbCl_4$, molecular (by contrast to the distinctly ionic RbCl), lead tetrachloride; RbCl, ionic, rubidium chloride

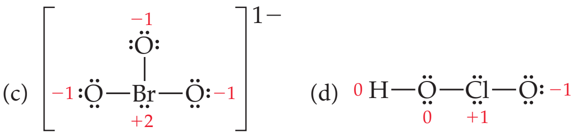
8.47



8.49 (a) *Formal charge* is the charge on each atom in a molecule, assuming all atoms have the same electronegativity. (b) Formal charges are not actual charges. They are a bookkeeping system that assumes perfect covalency, one extreme for the possible electron distribution in a molecule. (c) Oxidation numbers are a bookkeeping system that assumes the more electronegative element holds all electrons in a bond. The true electron distribution is some composite of the two extremes. **8.51** Formal charges are shown on the Lewis structures; oxidation numbers are listed below each structure.

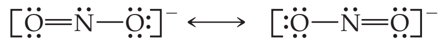


O, −2; C, +4; S, −2 S, +4; Cl, −1; O, −2

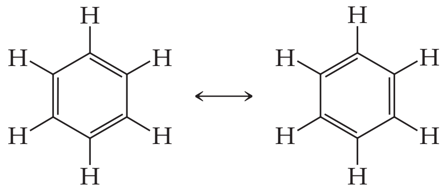


Br, +5; O, −2 Cl, +3; H, +1; O, −2

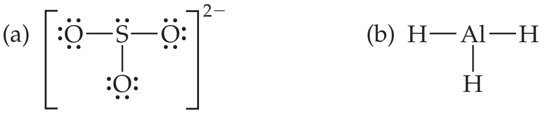
8.53 (a)



(b) O_3 is isoelectronic with NO_2^-; both have 18 valence electrons. (c) Since each N—O bond has partial double-bond character, the N—O bond length in NO_2^- should be shorter than an N—O single bond. **8.55** The more electron pairs shared by two atoms, the shorter the bond. Thus, the C—O bond lengths vary in the order $CO < CO_2 < CO_3^{2-}$. **8.57** (a) Two equally valid Lewis structures can be drawn for benzene.

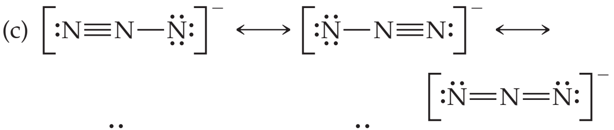


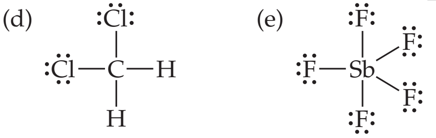
The concept of resonance dictates that the true description of bonding is some hybrid or blend of these two Lewis structures. The most obvious blend of these two resonance structures is a molecule with six equivalent C—C bonds with equal lengths. (b) This model predicts a uniform C—C bond length that is shorter than a single bond but longer than a double bond. **8.59** (a) The octet rule states that atoms will gain, lose, or share electrons until they are surrounded by eight valence electrons. (b) The octet rule applies to atoms in a covalent compound and the individual ions in an ionic compound. In the covalent compound CCl_4, the atoms share electrons in order to surround themselves with an octet. In the ionic compound $MgCl_2$, Mg loses 2 e^- to become Mg^{2+} with the electron configuration of Ne. Each Cl atom gains one electron to form Cl^- with the electron configuration of Ar. **8.61** No chlorine oxide will obey the octet rule. Chlorine has seven valence electrons, and oxygen has six. For neutral chlorine oxides, regardless of the number of oxygen atoms in the molecule, the total number of valence electrons will be an (odd + even) sum, which is always an odd number. **8.63**



Other resonance structures that minimize formal charges but violate the octet rule can be drawn. The octet rule versus formal charge debate is ongoing.

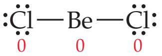
6 electrons around Al





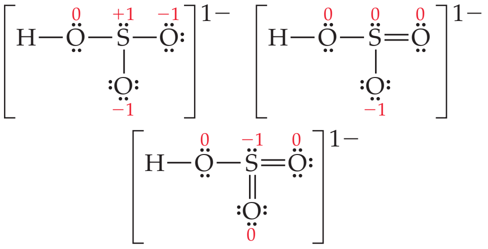
10 electrons around Sb

8.65 (a)

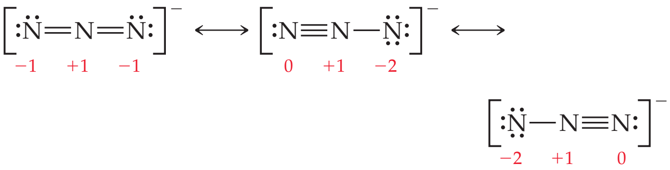


This structure violates the octet rule.

(c) Formal charges are minimized on the structure that violates the octet rule; this form is probably dominant. **8.67** Three resonance structures for HSO_3^- are shown here. Because the ion has a 1− charge, the sum of the formal charges of the atoms is −1.



The structure with no double bonds obeys the octet rule for all atoms, but does not lead to minimized formal charges. The structures with one and two double bonds both minimize formal charge but do not obey the octet rule. Of these two, the structure with one double bond is preferred because the formal charge is localized on the more electronegative oxygen atom. **8.69** (a) $\Delta H = -304$ kJ (b) $\Delta H = -82$ kJ (c) $\Delta H = -467$ kJ **8.71** (a) $\Delta H = -321$ kJ (b) $\Delta H = -103$ kJ (c) $\Delta H = -203$ kJ **8.73** (a) −97 kJ; exothermic (b) The ΔH calculated from bond enthalpies (−97 kJ) is slightly more exothermic (more negative) than that obtained using ΔH_f° values (−92.38 kJ). **8.75** The average Ti—Cl bond enthalpy is 430 kJ/mol. **8.77** (a) Six (nonradioactive) elements. Yes, they are in the same family, assuming H is placed with the alkali metals. The Lewis symbol represents the number of valence electrons of an element, and all elements in the same family have the same number of valence electrons. By definition of a family, all elements with the same Lewis symbol must be in the same family. **8.81** The charge on M is likely to be 3+. The range of lattice energies for ionic compounds with the general formula MX and a charge of 2+ on the metal is 3-4 $\times 10^3$ kJ/mol. The lattice energy of 6×10^3 kJ/mol indicates that the charge on M must be greater than 2+. **8.85** (a) B—O. The most polar bond will be formed by the two elements with the greatest difference in electronegativity. (b) Te—I. These elements have the two largest covalent radii among this group. (c) TeI_2. The octet rule is be satisfied for all three atoms. (d) P_2O_3. Each P atom needs to share $3e^-$ and each O atom $2e^-$ to achieve an octet. And B_2O_3. Although this is not a purely ionic compound, it can be understood in terms of gaining and losing electrons to achieve a noble-gas configuration. If each B atom were to lose $3e^-$ and each O atom were to gain $2e^-$, charge balance and the octet rule would be satisfied. **8.90** (a) +1 (b) −1 (c) +1 (assuming the odd electron is on N) (d) 0 (e) +3 **8.95** An experimentally determined molecular structure will reveal bond lengths and angles of the B—A═B molecule. If resonance structures are important, the two B—A bond lengths will be identical. If the molecule features one single and one double bond, the lengths will be significantly different. **8.98** (a) $\Delta H = 7.85$ kJ/g nitroglycerine (b) $4\,C_7H_5N_3O_6(s) \longrightarrow 6\,N_2(g) + 7\,CO_2(g) + 10\,H_2O(g) + 21\,C(s)$ **8.101** (a) Ti^{2+}, $[Ar]3d^2$; Ca, $[Ar]4s^2$. Yes. The 2 valence electrons in Ti^{2+} and Ca are in different principal quantum levels and different subshells. (b) In Ca the 4*s* is lower in energy than the 3*d*, while in Ti^{2+} the 3*d* is lower in energy than the 4*s*. (c) No. There is only one 4*s* orbital, so the 2 valence electrons in Ca are paired; there are 5 degenerate 3*d* orbitals, so the 2 valence electrons in Ti^{2+} are unpaired. **8.107** (a) Azide ion is N_3^-. (b) Resonance structures with formal charges are shown.

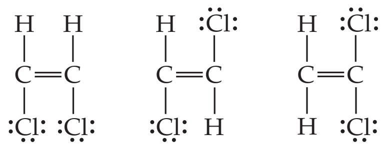


(c) The structure with two double bonds minimizes formal charges and is probably the main contributor. (d) The N—N distances will be equal and have the approximate length of a N—N double bond, 1.24 Å. **8.112** (a) D(Br—Br)(*l*) = 223.6 kJ; D(Br—Br)(*g*) = 193 kJ (b) D(C—Cl)(*l*) = 336.1 kJ; D(C—Cl)(*g*) = 328 kJ (c) D(O—O)(*l*) = 192.7 kJ; D(O—O)(*g*) = 146 kJ (d) Breaking bonds in the liquid requires more energy than breaking bonds in the gas phase. Bond dissociation in the liquid phase can be thought of in two steps, vaporization of the liquid followed by bond dissociation in the gas phase. The greater bond dissociation enthalpy in the liquid phase is due to the contribution from the enthalpy of vaporization.

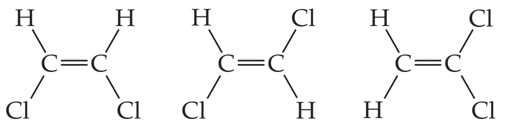
CHAPTER 9

9.1 Removing an atom from the equatorial plane of the trigonal bipyramid in Figure 9.3 creates a seesaw shape. **9.3** (a) 2 electron-domain geometries, linear and trigonal bipyramidal (b) 1 electron-domain geometry, trigonal bipyramidal (c) 1 electron-domain geometry, octahedral (c) 1 electron-domain geometry, octahedral (d) 1 electron domain geometry, octahedral (e) 1 electron domain geometry, octahedral (f) 1 electron-domain geometry, trigonal bipyramidal (This triangular pyramid is an unusual molecular geometry not listed in Table 9.3. It could occur if the equatorial substituents on the trigonal bipyramid were extremely bulky, causing the nonbonding electron pair to occupy an axial position.) **9.5** (a) Zero energy corresponds to two separate, noninteracting Cl atoms. This infinite Cl—Cl distance is beyond the right extreme of the horizontal axis on the diagram. (b) According to the valence bond model, valence orbitals on the approaching atoms overlap, allowing two electrons to mutually occupy space between the two nuclei and be stabilized by two nuclei rather than one. (c) The Cl—Cl distance at the energy minimum on the plot is the Cl—Cl bond length. (d) At interatomic separations shorter than the bond distance, the two nuclei begin to repel each other, increasing the overall energy of the system. (e) The *y*-coordinate of the minimum point on the plot is a good estimate of the Cl—Cl bond energy or bond strength. **9.6** $SiCl_4$, 109°; PF_3, 107°; SF_2, 105°. Each molecule has tetrahedral electron domain geometry, but the number of nonbonding electron pairs increases from 0 to 2, respectively. Because nonbonding electron pairs occupy more space than bonding pairs, we expect the bond angles to decrease in the series. **9.9** (a) i, Two *s* atomic orbitals; ii, two *p* atomic orbitals overlapping end to end; iii, two *p* atomic orbitals overlapping side to side (b) i, σ-type MO; ii, σ-type MO; iii, π-type MO (c) i, antibonding; ii, bonding; iii, antibonding (d) i, the nodal plane is between the atom centers, perpendicular to the interatomic axis and equidistant from each atom. ii, there are two nodal planes; both are perpendicular to the interatomic axis. One is left of the left atom and the second is right of the right atom. iii, there are two nodal planes; one is between the atom centers, perpendicular to the interatomic axis and equidistant from each atom. The second contains the interatomic axis and is perpendicular to the first. **9.11** (a) Yes. The stated shape defines the bond angle and the bond length tells the size. (b) No. Atom A could have 2, 3, or 4 nonbonding electron pairs. **9.13** A molecule with tetrahedral molecular geometry has an atom at each vertex of the tetrahedron. A trigonal-pyramidal molecule has one vertex of the tetrahedron occupied by a nonbonding electron pair rather than an atom. **9.15** (a) An *electron domain* is a region in a molecule where electrons are most likely to be found. (b) Like the balloons in Figure 9.5, each electron domain occupies a finite volume of space, so they also adopt an arrangement where repulsions are minimized. **9.17** (a) The number of electron domains in a molecule or ion is the number of bonds (double and triple bonds count as one domain) plus the number of nonbonding electron pairs. (b) A *bonding electron domain* is a region between two bonded atoms that contains one or more pairs of bonding electrons. A *nonbonding electron domain* is localized on a single atom and contains one pair of nonbonding electrons. **9.19** (a) No effect on molecular shape (b) 1 nonbonding pair on P influences molecular shape (c) no effect (d) no effect (e) 1 nonbonding pair on S influences molecular shape **9.21** (a) 2 (b) 1 (c) none (d) 3 **9.23** The electron-domain geometry indicated by VSEPR describes the arrangement of all bonding and nonbonding electron domains. The molecular geometry describes just the atomic positions. In H_2O there are 4 electron domains around oxygen, so the electron-domain geometry is tetrahedral. Because there are 2 bonding and 2 nonbonding domains, the molecular geometry is bent. We make this distinction because all electron domains must be considered when describing the atomic arrangement and bond angles in a molecule but the molecular geometry or shape is a description of just the atom positions. **9.25** (a) Tetrahedral, tetrahedral (b) trigonal bipyramidal, T-shaped (c) octahedral, square pyramidal (d) octahedral, square planar **9.27** (a) Linear, linear (b) tetrahedral, trigonal pyramidal (c) trigonal bipyramidal, seesaw (d) octahedral, octahedral (e) tetrahedral, tetrahedral (f) linear, linear **9.29** (a) i, trigonal planar; ii, tetrahedral; iii, trigonal bipyramidal (b) i, 0; ii, 1; iii, 2 (c) N and P (d) Cl (or Br or I). This T-shaped molecular geometry arises from a trigonal-bipyramidal electron-domain geometry with 2 nonbonding domains. Assuming each F atom has 3 nonbonding domains and forms only single bonds with A, A must have 7 valence electrons and be in or below the third row of the periodic table to produce these electron-domain and molecular geometries. **9.31** (a) 1–109°, 2–109° (b) 3–109°, 4–109° (c) 5–180° (d) 6–120°, 7–109°, 8–109° **9.33** The two molecules with trigonal-bipyramidal electron-domain geometry, PF_5 and SF_4, have more than one F—A—*F* bond angle. **9.35** (a) Although both ions have 4 bonding electron domains, the 6 total domains around Br require octahedral domain geometry and square-planar molecular geometry, while the 4 total domains about B lead to tetrahedral domain and molecular geometry. (b) The less electronegative the central atom, the larger the nonbonding electron domain, and the greater the effect of repulsive forces on adjacent bonding domains. The less electronegative the central atom, the greater the deviation from ideal tetrahedral angles. The angles will vary as $H_2O > H_2S > H_2Se$. **9.37** A bond dipole is the asymmetric charge distribution between two bonded atoms with unequal electronegativities. A molecular dipole moment is the three-dimensional sum of all the bond dipoles in a molecule. **9.39** (a) Yes. The net dipole moment vector points along the Cl—S—Cl angle bisector. (b) No, $BeCl_2$ does not have a dipole moment. **9.41** (a) In Exercise 9.29, molecules (ii) and (iii) will have nonzero dipole moments. Molecule (i) has no nonbonding electron pairs on A, and the 3 A—F bond dipoles are oriented so that they cancel. Molecules (ii) and (iii) have nonbonding electron pairs on A and their bond dipoles do not cancel. (b) In Exercise 9.30, molecules (i) and (ii) have a zero dipole moment. **9.43** (a) IF (d) PCl_3 and (f) IF_5 are polar.

9.45 (a) Lewis structures



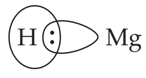
Molecular geometries



Polar Nonpolar Polar

(b) The middle isomer has a zero net dipole moment. (c) C_2H_3Cl has only one isomer, and it has a dipole moment. **9.47** (a) *Orbital overlap* occurs when valence atomic orbitals on two adjacent atoms share the same region of space. (b) A chemical bond is a concentration of electron density between the nuclei of two atoms. This concentration can take place because orbitals on the two atoms overlap. **9.49** (a) H—Mg—H, linear electron domain and molecular geometry (b) The linear electron-domain geometry in MgH_2 requires *sp* hybridization.

(c)

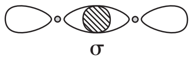


9.51

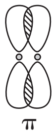
Molecule	Electron-Domain Geometry	Hybridization of Central Atom	Dipole Moment? Yes or No
CO_2	Linear	*sp*	No
NH_3	Tetrahedral	sp^3	Yes
CH_4	Tetrahedral	sp^3	No
BH_3	Trigonal planar	sp^2	No
SF_4	Trigonal bipyramidal	Not applicable	Yes
SF_6	Octahedral	Not applicable	No
H_2CO	Trigonal planar	sp^2	Yes
PF_5	Trigonal bipyramidal	Not applicable	No
XeF_2	Trigonal bipyramidal	Not applicable	No

9.53 (a) B, $[He]2s^22p^1$. One 2s electron is "promoted" to an empty 2*p* orbital. The 2*s* and two 2*p* orbitals that each contain one electron are hybridized to form three equivalent hybrid orbitals in a trigonal-planar arrangement. (b) sp^2 (d) A single 2*p* orbital is unhybridized. It lies perpendicular to the trigonal plane of the sp^2 hybrid orbitals. **9.55** (a) sp^2 (b) sp^3 (c) *sp* (d) sp^3 **9.57** No hybrid orbitals discussed in this chapter form angles of 90° with each other; *p* atomic orbitals are perpendicular to each other. 109.5°, sp^3; 120°, sp^2

9.59 (a)

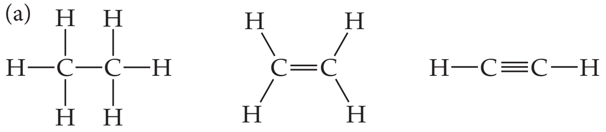


(b)



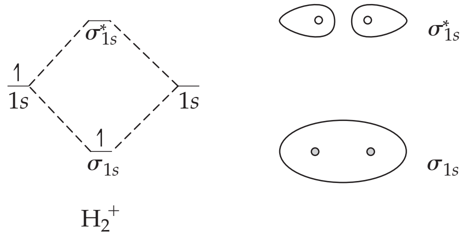
(c) A σ bond is generally stronger than a π bond because there is more extensive orbital overlap. (d) No. Overlap of two *s* orbitals results in electron density along the internuclear axis, while a π bond has none.

9.61 (a)



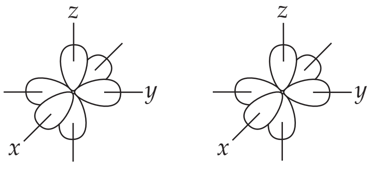
(b) sp^3, sp^2, *sp* (c) nonplanar, planar, planar (d) 7 σ, 0 π; 5 σ, 1 π; 3 σ, 2 π (e) The Si analogs would have the same hybridization as the C compounds given in part (b). That Si is in the row below C means it has a larger bonding atomic radius and atomic orbitals than C. The close approach of Si atoms required to form strong, stable π bonds in Si_2H_4 and Si_2H_2 is not possible and these Si analogs do not readily form. **9.63** (a) 18 valence electrons (b) 16 valence electrons form σ bonds. (c) 2 valence electrons form π bonds. (d) No valence electrons are nonbonding. (e) The left and central C atoms are sp^2 hybridized; the right C atom is sp^3 hybridized. **9.65** (a) ~109° about the leftmost C, sp^3; ~120° about the right-hand C, sp^2 (b) The doubly bonded O can be viewed as sp^2, and the other as sp^3; the nitrogen is sp^3 with approximately 109° bond angles. (c) nine σ bonds, one π bond **9.67** (a) In a localized π bond, the electron density is concentrated between the two atoms forming the bond. In a delocalized π bond, the electron density is spread over all the atoms that contribute *p* orbitals to the network. (b) The existence of more than one resonance form is a good indication that a molecule will have delocalized π bonding. (c) delocalized **9.69** (a) Linear (b) The two central C atoms each have trigonal planar geometry with ~120° bond angles about them. The C and O atoms lie in a plane with the H atoms free to rotate in and out of this plane. (c) The molecule is planar with ~120° bond angles about the two N atoms. **9.71** (a) Hybrid orbitals are mixtures of atomic orbitals from a single atom and remain localized on that atom. Molecular orbitals are combinations of atomic orbitals from two or more atoms and are delocalized over at least two atoms. (b) Each MO can hold a maximum of two electrons. (c) Antibonding molecular orbitals can have electrons in them.

9.73 (a)

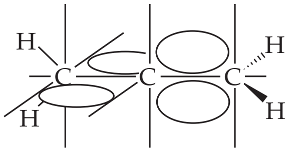


(b) There is one electron in H_2^+. (c) σ_{1s}^1 (d) BO $= \frac{1}{2}$ (e) Fall apart. If the single electron in H_2^+ is excited to the σ_{1s}^* orbital, its energy is higher than the energy of an H 1*s* atomic orbital and H_2^+ will decompose into a hydrogen atom and a hydrogen ion.

9.75

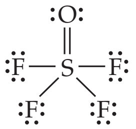


(a) 1 σ bond (b) 2 π bonds (c) 1 σ^* and 2 π^* **9.77** (a) When comparing the same two bonded atoms, bond order and bond energy are directly related, while bond order and bond length are inversely related. When comparing different bonded nuclei, there are no simple relationships. (b) Be_2 is not expected to exist; it has a bond order of zero and is not energetically favored over isolated Be atoms. Be_2^+ has a bond order of 0.5 and is slightly lower in energy than isolated Be atoms. It will probably exist under special experimental conditions. **9.79** (a, b) Substances with no unpaired electrons are weakly repelled by a magnetic field. This property is called *diamagnetism*. (c) O_2^{2-}, Be_2^{2+} **9.81** (a) B_2^+, $\sigma_{2s}^2\sigma_{2s}^{*2}\pi_{2p}^1$, increase (b) Li_2^+, $\sigma_{1s}^2\sigma_{1s}^{*2}\sigma_{2s}^1$, increase (c) N_2^+, $\sigma_{2s}^2\sigma_{2s}^{*2}\pi_{2p}^4\sigma_{2p}^1$, increase (d) Ne_2^{2+}, $\sigma_{2s}^2\sigma_{2s}^{*2}\sigma_{2p}^2\pi_{2p}^4\pi_{2p}^{*4}$, decrease **9.83** CN, $\sigma_{2s}^2\sigma_{2s}^{*2}\sigma_{2p}^2\pi_{2p}^3$, bond order = 2.5; CN^+, $\sigma_{2s}^2\sigma_{2s}^{*2}\sigma_{2p}^2\pi_{2p}^2$, bond order = 2.0; CN^-, $\sigma_{2s}^2\sigma_{2s}^{*2}\sigma_{2p}^2\pi_{2p}^4$, bond order = 3.0. (a) CN^- (b) CN, CN^+ **9.85** (a) 3*s*, $3p_x$, $3p_y$, $3p_z$ (b) π_{3p} (c) 2 (d) If the MO diagram for P_2 is similar to that of N_2, P_2 will have no unpaired electrons and be diamagnetic. **9.89** SiF_4 is tetrahedral, SF_4 is seesaw, XeF_4 is square planar. The shapes are different because the number of nonbonding electron domains is different in each molecule, even though all have four bonding electron domains. Bond angles and thus molecular shape are determined by the total number of electron domains. **9.92** (a) 2 σ bonds, 2 π bonds (b) 3 σ bonds, 4 π bonds (c) 3 σ bonds, 1 π bond (d) 4 σ bonds, 1 π bond **9.94** BF_3 is trigonal planar, the B—F bond dipoles cancel and the molecule is nonpolar. PF_3 has a tetrahedral electron-domain geometry with one position occupied by a nonbonding electron pair. The nonbonding electron pair ensures an asymmetrical electron distribution and the molecule is polar. **9.99**



(a) The molecule is nonplanar. (b) Allene has no dipole moment. (c) The bonding in allene would not be described as delocalized. The π electron clouds of the two adjacent C═C are mutually perpendicular, so there is no overlap and no delocalization of π electrons. **9.101** (a) All O atoms have sp^2 hybridization. (b) The two σ bonds are formed by overlap of sp^2 hybrid orbitals, the π bond is formed by overlap of atomic *p* orbitals, one nonbonded pair is in a *p* atomic orbital and the other five nonbonded pairs are in sp^2 hybrid orbitals. (c) unhybridized *p* atomic orbitals (d) four, two from the π bond and two from the nonbonded pair in the *p* atomic orbital **9.104** $\sigma_{2s}^2\sigma_{2s}^{*2}\pi_{2p}^4\sigma_{2p}^1\pi_{2p}^{*1}$ (a) Paramagnetic (b) The bond order of N_2 in the ground state is 3; in the first excited state it has a bond order of 2. Owing to the reduction in bond order, N_2 in the first excited state has a weaker N—N bond. **9.110** (a) $2\,SF_4(g) + O_2(g) \longrightarrow 2\,OSF_4(g)$

(b)



(c) $\Delta H = -551$ kJ, exothermic (d) The electron-domain geometry is trigonal bipyramidal. The O atom can be either equatorial or axial. (e) Since F is more electronegative than O, the structure that minimizes 90° F—S—F angles, the one with O axial, is preferred.

CHAPTER 10

10.1 It would be much easier to drink from a straw on Mars. When a straw is placed in a glass of liquid, the atmosphere exerts equal pressure inside and outside the straw. When we drink through a straw, we withdraw air, thereby reducing the pressure on the liquid inside. If only 0.007 atm is exerted on the liquid in the glass, a very small reduction in pressure inside the straw will cause the liquid to rise. **10.4** (a) As the reaction proceeds at constant temperature and pressure, the number of particles decreases and the container volume decreases. (b) As the reaction proceeds at constant volume and temperature, the number of particles decreases and pressure decreases. **10.7** (a) $P_{red} < P_{yellow} < P_{blue}$ (b) $P_{red} = 0.28$ atm; $P_{yellow} = 0.42$ atm; $P_{blue} = 0.70$ atm **10.10** (a) $P(ii) < P(i) = P(iii)$ (b) $P_{He}(iii) < P_{He}(ii) < P_{He}(i)$ (c) $d(ii) < d(i) < d(iii)$ (d) The average kinetic energies of the particles in the three containers are equal. **10.13** (a) A gas is much less dense than a liquid. (b) A gas is much more compressible than a liquid. (c) All mixtures of gases are homogenous. Similar liquid molecules form homogeneous mixtures, while very dissimilar molecules form heterogeneous mixtures. (d) Both gases and liquids conform to the shape of their container. A gas also adopts the volume of its container, while a liquid maintains its own volume. **10.15** (a) 1.8×10^3 kPa (b) 18 atm (c) 2.6×10^2 lb/in.^{2} **10.17** (a) 10.3 m (b) 2.1 atm **10.19** (a) The tube can have any cross-sectional area. (b) At equilibrium the force of gravity per unit area acting on the mercury column is not equal to the force of gravity per unit area acting on the atmosphere. (c) The column of mercury is held up by the pressure of the atmosphere applied to the exterior pool of mercury. (d) If you took the mercury barometer with you on a trip from the beach to high mountains, the height of the mercury column would decrease with elevation. **10.21** (a) 0.349 atm (b) 265 mm Hg (c) 3.53×10^4 Pa (d) 0.353 bar (e) 5.13 psi **10.23** (a) $P = 773.4$ torr (b) $P = 1.018$ atm (c) The pressure in Chicago is greater than standard atmospheric pressure, and so it makes sense to classify this weather system as a "high-pressure system." **10.25** (i) 0.31 atm (ii) 1.88 atm (iii) 0.136 atm **10.27** (a) If *V* decreases by a factor of 4, *P* increases by a factor of 4. (b) If *T* decreases by a factor of 2, *P* decreases by a factor of 2. (c) If *n* decreases by a factor of 4, *P* decreases by a factor of 4. **10.29** (a) If equal volumes of gases at the same temperature and pressure contain equal numbers of molecules and molecules react in the ratios of small whole numbers, it follows that the volumes of reacting gases are in the ratios of small whole numbers. (b) Since the two gases are at the same temperature and pressure, the ratio of the numbers of atoms is the same as the ratio of volumes. There are 1.5 times as many Xe atoms as Ne atoms. (c) Yes. By definition, one mole of an ideal gas contains Avogadro's number of particles. At a given temperature and pressure, equal numbers of particles occupy the same volume, so one mole of an ideal gas will always occupy the same volume at the given temperature and pressure. **10.31** (a) An ideal gas exhibits pressure, volume, and temperature relationships described by the equation $PV = nRT$. (b) Boyle's law, $V = \text{constant}/P$; Charles's law, $V = \text{constant} \times T$; Avogadro's law, $V = \text{constant} \times n$. Collect all the equalities: $V = (\text{constant} \times T \times n)/P$. Call the constant *R* and multiply both sides of the equation by *P*, $PV = nRT$. (c) $PV = nRT$; *P* in atmospheres, *V* in liters, *n* in moles, *T* in kelvins. (d) $R = 0.08315$ L-bar/mol-K. **10.33** Flask A contains the gas with $\mathcal{M} = 30$ g/mol, and flask B contains the gas with $\mathcal{M} = 60$ g/mol. **10.35**

P	*V*	*n*	*T*
2.00 atm	1.00 L	0.500 mol	48.7 K
0.300 atm	0.250 L	3.05×10^{-3} mol	27 °C
650 torr	11.2 L	0.333 mol	350 K
10.3 atm	585 mL	0.250 mol	295 K

10.37 8.2×10^2 kg He **10.39** (a) 5.15×10^{22} molecules (b) 6.5 kg air **10.41** (a) 91 atm (b) 2.3×10^2 L **10.43** (a) 29.8 g Cl_2 (b) 9.42 L (c) 501 K (d) 2.28 atm **10.45** (a) $n = 2 \times 10^{-4}$ mol O_2 (b) The roach needs 8×10^{-3} mol O_2 in 48 h, approximately 100% of the O_2 in the jar. **10.47** (a) 1.32×10^7 L (b) 5.1×10^8 mol Hg **10.49** For gas samples at the same conditions, molar mass determines density. Of the three gases listed, (c) Cl_2 has the largest molar mass. **10.51** (c) Because the helium atoms are of lower mass than the average air molecule, the helium gas is less dense than air. The balloon thus weighs less than the air displaced by its volume. **10.53** (a) $d = 1.77$ g/L (b) $\mathcal{M} = 80.1$ g/mol **10.55** $\mathcal{M} = 89.4$ g/mol **10.57** 4.1×10^{-9} g Mg **10.59** (a) 21.4 L CO_2 (b) 40.7 L O_2 **10.61** 0.402 g Zn **10.63** (a) When the stopcock is opened, the volume occupied by $N_2(g)$ increases from 2.0 L to 5.0 L. $P_{N_2} = 0.40$ atm (b) When the gases mix, the volume of $O_2(g)$ increases from 3.0 L to 5.0 L. $P_{O_2} = 1.2$ atm (c) $P_t = 1.6$ atm

10.65 (a) $P_{He} = 1.87\,atm$, $P_{Ne} = 0.807\,atm$, $P_{Ar} = 0.269\,atm$, (b) $P_t = 2.95\,atm$ **10.67** $\chi_{CO_2} = 0.00039$ **10.69** $P_{CO_2} = 0.305\,atm$, $P_t = 1.232$ atm **10.71** $P_{N_2} = 1.3\,atm$, $P_{O_2} = 0.54$ atm, $P_{CO_2} = 0.27\,atm$ **10.73** 2.5 mole % O_2 **10.75** $P_t = 2.47\,atm$ **10.77** (a) Increase in temperature at constant volume or decrease in volume or increase in pressure (b) decrease in temperature (c) increase in volume, decrease in pressure (d) increase in temperature **10.79** The fact that gases are readily compressible supports the assumption that most of the volume of a gas sample is empty space. **10.81** Average speed is the sum of the speeds of all particles divided by the total number of particles. The root mean square speed is the speed of a molecule with the same kinetic energy as the average kinetic energy of the sample. The root mean square speed is larger for a given gas sample at a fixed temperature, but the difference between the two is small. **10.83** (a) Average kinetic energy of the molecules increases. (b) Root mean square speed of the molecules increases. (c) Strength of an average impact with the container walls increases. (d) Total collisions of molecules with walls per second increases. **10.85** (a) In order of increasing speed and decreasing molar mass: $HBr < NF_3 < SO_2 < CO < Ne$ (b) $u_{NF_3} = 324\ m/s$ (c) The most probable speed of an ozone molecule in the stratosphere is 306 m/s. **10.87** Effusion is the escape of gas molecules through a tiny hole. Diffusion is the distribution of a gas throughout space or throughout another substance. **10.89** The order of increasing rate of effusion is $^2H^{37}Cl < {}^1H^{37}Cl < {}^2H^{35}Cl < {}^1H^{35}Cl$. **10.91** As_4S_6 **10.93** (a) Non-ideal-gas behavior is observed at very high pressures and low temperatures. (b) The real volumes of gas molecules and attractive intermolecular forces between molecules cause gases to behave nonideally. (c) According to the ideal-gas law, the ratio PV/RT should be constant for a given gas sample at all combinations of pressure, volume, and temperature. If this ratio changes with increasing pressure, the gas sample is not behaving ideally. **10.95** Ar ($a = 1.34$, $b = 0.0322$) will behave more like an ideal gas than CO_2 ($a = 3.59$, $b = 0.427$) at high pressures. **10.97** (a) $P = 4.89\,atm$ (b) $P = 4.69\,atm$ (c) Qualitatively, molecular attractions are more important as the amount of free space decreases and the number of molecular collisions increases. Molecular volume is a larger part of the total volume as the container volume decreases. **10.99** From the value of b for Xe, the nonbonding radius is 2.72 Å. From Figure 7.6, the bonding atomic radius of Xe is 1.30 Å. We expect the bonding radius of an atom to be smaller than its nonbonding radius, but this difference is quite large. **10.101** $V = 3.1\,mm^3$ **10.105** (a) 13.4 mol $C_3H_8(g)$ (b) 1.47×10^3 mol $C_3H_8(l)$ (c) The ratio of moles liquid to moles gas is 110. Many more molecules and moles of liquid fit in a container of fixed volume because there is much less space between molecules in the liquid phase. **10.108** $P_t = 5.3 \times 10^2$ torr **10.111** 42.2 g O_2 **10.115** $T_2 = 687\,°C$ **10.120** (a) $P(\text{ideal}) = 177\,atm$ (b) $P(\text{van der Waals}) = 187.4\,atm$ (c) Under the conditions of this problem (large number of moles of gas), the correction for the real volume of molecules dominates. **10.123** (a) 44.58% C, 6.596% H, 16.44% Cl, 32.38% N (b) $C_8H_{14}N_5Cl$ (c) Molar mass of the compound is required in order to determine molecular formula when the empirical formula is known. **10.128** (a) 5.02×10^8 L $CH_3OH(l)$ (b) $CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l)$, $\Delta H° = -890.4$ kJ; ΔH for combustion of the methane is -1.10×10^{13} kJ. $CH_3OH(l) + 3/2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l)$, $\Delta H° = -726.6$ kJ; ΔH for combustion of the methanol is -9.00×10^{12} kJ. (c) The enthalpy change upon combustion of 1.00 L of $CH_4(l)$ is -2.59×10^4 kJ and for 1.00 L of $CH_3OH(l)$, -1.79×10^4 kJ. Clearly $CH_4(l)$ has the higher enthalpy of combustion per unit volume.

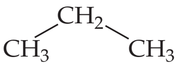
CHAPTER 11

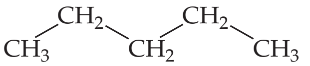
11.1 The diagram best describes a liquid. The particles are close together, mostly touching, but there is no regular arrangement or order. This rules out a gaseous sample, where the particles are far apart, and a crystalline solid, which has a regular repeating structure in all three directions. **11.4** (a) In its final state, methane is a gas at 185 °C. **11.5** (a) 385 mm Hg (b) 22 °C (c) 47 °C **11.6** The stronger the intermolecular forces, the higher the boiling point of a liquid. Propanol, $CH_3CH_2CH_2OH$, has hydrogen bonding and the higher boiling point. **11.7** (a) Normal boiling point, 360 K; normal freezing point, 260 K (b) (i) gas (ii) solid (iii) liquid (c) The triple point is approximately 185 K at 0.45 atm. **11.9** (a) Solid < liquid < gas (b) gas < liquid < solid (c) Matter in the gaseous state is most easily compressed because particles are far apart and there is much empty space. **11.11** $Ar < CCl_4 < Si$ **11.13** (a) The molar volumes of Cl_2 and NH_3 are nearly the same because they are both gases. (b) On cooling to 160 K, both compounds condense from the gas phase to the solid-state, so we expect a significant decrease in the molar volume. (c) The molar volumes are 0.0351 L/mol Cl_2 and 0.0203 L/mol NH_3 (d) Solid-state molar volumes are not as similar as those in the gaseous state, because most of the empty space is gone and molecular characteristics determine properties. $Cl_2(s)$ is heavier, has a longer bond distance and weaker intermolecular forces, so it has a significantly larger molar volume than $NH_3(s)$. (e) There is little empty space between molecules in the liquid state, so we expect their molar volumes to be closer to those in the solid state than those in the gaseous state. **11.15** (a) London dispersion forces (b) dipole–dipole and London dispersion forces (c) dipole–dipole forces and in certain cases hydrogen bonding **11.17** (a) SO_2, dipole–dipole and London dispersion forces (b) CH_3COOH, London dispersion, dipole–dipole, and hydrogen bonding (c) H_2Se, dipole–dipole and London dispersion forces (but not hydrogen bonding) **11.19** (a) *Polarizability* is the ease with which the charge distribution in a molecule can be distorted to produce a transient dipole. (b) Sb is most polarizable because its valence electrons are farthest from the nucleus and least tightly held. (c) in order of increasing polarizability: $CH_4 < SiH_4 < SiCl_4 < GeCl_4 < GeBr_4$ (d) The magnitudes of London dispersion forces and thus the boiling points of molecules increase as polarizability increases. The order of increasing boiling points is the order of increasing polarizability given in (c). **11.21** (a) H_2S (b) CO_2 (c) GeH_4 **11.23** Both rodlike butane molecules and spherical 2-methylpropane molecules experience dispersion forces. The larger contact surface between butane molecules facilitates stronger forces and produces a higher boiling point. **11.25** (a) A molecule must contain H atoms, bound to either N, O, or F atoms, in order to participate in hydrogen bonding with like molecules. (b) CH_3NH_2 and CH_3OH **11.27** (a) Replacing a hydroxyl hydrogen with a CH_3 group eliminates hydrogen bonding in that part of the molecule. This reduces the strength of intermolecular forces and leads to a lower boiling point. (b) $CH_3OCH_2CH_2OCH_3$ is a larger, more polarizable molecule with stronger London dispersion forces and thus a higher boiling point.

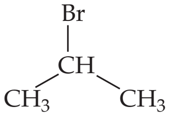
11.29

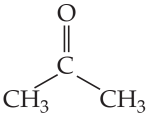
Physical Property	H_2O	H_2S
Normal boiling point, °C	100.00	−60.7
Normal melting point, °C	0.00	−85.5

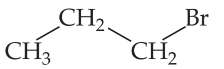
(a) Based on its much higher normal melting point and boiling point, H_2O has much stronger intermolecular forces. H_2O has hydrogen bonding, while H_2S has dipole–dipole forces. (b) H_2S is probably a typical compound with less empty space in the ordered solid than the liquid, so that the solid is denser than the liquid. For H_2O, maximizing the number of hydrogen bonds to each molecule in the solid requires more empty space than in the liquid, and the solid is less dense. (c) Specific heat is the energy required to raise the temperature of one gram of the substance one degree Celsius. Hydrogen bonding in water is such a strong attractive interaction that the energy required to disrupt it and increase molecular motion is large. **11.31** SO_4^{2-} has a greater negative charge than BF_4^-, so ion–ion electrostatic attractions are greater in sulfate salts and they are less likely to form liquids. **11.33** (a) As temperature increases, the number of molecules with sufficient kinetic energy to overcome intermolecular attractive forces increases, and viscosity and surface tension decrease. (b) The same attractive forces that cause surface molecules to be difficult to separate (high surface tension) cause molecules elsewhere in the sample to resist movement relative to each other (high viscosity). **11.35** (a) $CHBr_3$ has a higher molar mass, is more polarizable, and has stronger dispersion forces, so the surface tension is greater. (b) As temperature increases, the viscosity of the oil decreases because the average kinetic energy of the molecules increases. (c) Adhesive forces between polar water and nonpolar car wax are weak, so the large surface tension of water draws the liquid into the shape with the smallest surface area, a sphere. (d) Adhesive forces between nonpolar oil and nonpolar car wax are similar to cohesive forces in oil, so the oil drops spread out on the waxed car hood. **11.37** (a) The three molecules have similar structures and experience the same types of intermolecular forces. As molar mass increases, the strength of dispersion forces increases and the boiling points, surface tension, and viscosities all increase. (b) Ethylene glycol has an —OH group at both ends of the molecule. This greatly increases the possibilities for hydrogen bonding; the overall intermolecular attractive forces are greater and the viscosity of ethylene glycol is much greater. (c) Water has the highest surface tension but lowest viscosity because it is the smallest molecule in the series. There is no hydrocarbon chain to inhibit their strong attraction to molecules in the interior of the drop, resulting in high surface tension. The absence of an alkyl chain also means the molecules can move around each other easily, resulting in the low viscosity. **11.39** (a) Melting, endothermic (b) evaporation, endothermic (c) deposition, exothermic (d) condensation, exothermic **11.41** Melting does not require separation of molecules, so the energy requirement is smaller than for vaporization, where molecules must be separated. **11.43** 2.3×10^3 g H_2O **11.45** (a) 39.3 kJ (b) 60 kJ **11.47** (a) The critical pressure is the pressure required to cause liquefaction at the critical temperature. (b) As the force of attraction between molecules increases, the critical temperature of the compound increases. (c) All the gases in Table 11.5 can be liquefied at the temperature of liquid nitrogen, given sufficient pressure. **11.49** (a) No effect (b) no effect (c) Vapor pressure decreases with increasing intermolecular attractive forces because fewer molecules have sufficient kinetic energy to overcome attractive forces and escape to the vapor phase. (d) Vapor pressure increases with increasing temperature because average kinetic energies of molecules increase. (e) Vapor pressure decreases with increasing density because attractive intermolecular forces increase. **11.51** (a) $CBr_4 < CHBr_3 < CH_2Br_2 < CH_2Cl_2 < CH_3Cl < CH_4$. The trend is dominated by dispersion forces even though four of the molecules are polar. The order of increasing volatility is the order of increasing vapor pressure, decreasing molar mass, and decreasing strength of dispersion forces. (b) Boiling point increases as the strength of intermolecular forces increases; this is the order of decreasing volatility and the reverse of the order in part (a). $CH_4 < CH_3Cl < CH_2Cl_2 < CH_2Br_2 < CHBr_3 < CBr_4$ **11.53** (a) The temperature of the water in the two pans is the same. (b) Vapor pressure does not depend on either volume or surface area of the liquid. At the same temperature, the vapor pressures of water in the two containers are the same. **11.55** (a) Approximately 48 °C (b) approximately 340 torr (c) approximately 17 °C (d) approximately 1000 torr **11.57** (a) The critical point is the temperature and pressure beyond which the gas and liquid phases are indistinguishable. (b) The line that separates the gas and liquid phases ends at the critical point because at conditions beyond the critical temperature and pressure, there is no distinction between gas and liquid. In experimental terms a gas cannot be liquefied at temperatures higher than the critical temperature, regardless of pressure. **11.59** (a) $H_2O(g)$ will condense to $H_2O(s)$ at approximately 4 torr; at a higher pressure, perhaps 5 atm or so, $H_2O(s)$ will melt to form $H_2O(l)$. (b) At 100 °C and 0.50 atm, water is in the vapor phase. As it cools, water vapor condenses to the liquid at approximately 82 °C, the temperature where the vapor pressure of liquid water is 0.50 atm. Further cooling results in freezing at approximately 0 °C. The freezing point of water increases with decreasing pressure, so at 0.50 atm the freezing temperature is very slightly above 0 °C. **11.61** (a) 24 K (b) Neon sublimes at pressures less than the triple point pressure, 0.43 atm. (c) No **11.63** (a) Methane on the surface of Titan is likely to exist in both solid and liquid forms. (b) As pressure decreases upon moving away from the surface of Titan, $CH_4(l)$ (at −178 °C) will vaporize to $CH_4(g)$, and $CH_4(s)$ (at temperatures below −180 °C) will sublime to $CH_4(g)$. **11.65** In a nematic liquid crystalline phase, molecules are aligned along their long axes, but the molecular ends are not aligned. Molecules are free to translate in all dimensions, but they cannot tumble or rotate out of the molecular plane, or the order of the nematic phase is lost and the sample becomes an ordinary liquid. In an ordinary liquid, molecules are randomly oriented and free to move in any direction. **11.67** The presence of polar groups or nonbonded electron pairs leads to relatively strong dipole–dipole interactions between molecules. These are a significant part of the orienting forces necessary for liquid crystal formation. **11.69** Because order is maintained in at least one dimension, the molecules in a liquid-crystalline phase are not totally free to change orientation. This makes the liquid-crystalline phase more resistant to flow, more viscous, than the isotropic liquid. **11.71** Melting provides kinetic energy sufficient to disrupt molecular alignment in one dimension in the solid, producing a smectic phase with ordering in two dimensions. Additional heating of the smectic phase provides kinetic energy sufficient to disrupt alignment in another dimension, producing a nematic phase with one-dimensional order. **11.73** (a) Decrease (b) increase (c) increase (d) increase (e) increase (f) increase (g) increase **11.77** When a halogen is substituted for H in benzene, molar mass, polarizability and strength of dispersion forces increase; the order of increasing molar mass is the order of increasing boiling points for the first three compounds. C_6H_5OH experiences hydrogen bonding, the strongest force between neutral molecules, so it has the highest boiling point. **11.82** (a) Evaporation is an endothermic process. The heat required to vaporize sweat is absorbed from your body, helping to keep it cool. (b) The vacuum pump reduces the pressure of the atmosphere above the water until atmospheric pressure equals the vapor pressure of water and the water boils. Boiling is an endothermic process, and the temperature drops if the system is not able to absorb heat from the surroundings fast enough. As the temperature of the water decreases, the water freezes. **11.86** At low Antarctic temperatures, molecules in the liquid crystalline phase have less kinetic energy due to temperature, and the applied voltage may not be sufficient to overcome orienting forces among the ends of molecules. If some or all of the molecules do not rotate when the voltage is applied, the display will not function properly. **11.90**

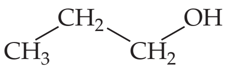

(i) $\mathcal{M} = 44$


(ii) $\mathcal{M} = 72$


(iii) $\mathcal{M} = 123$


(iv) $\mathcal{M} = 58$

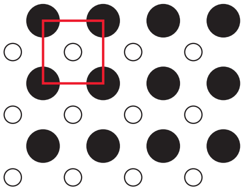
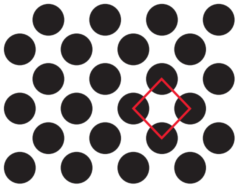

(v) $\mathcal{M} = 123$


(vi) $\mathcal{M} = 60$

(a) Molar mass: Compounds (i) and (ii) have similar rodlike structures. The longer chain in (ii) leads to greater molar mass, stronger London dispersion forces, and higher heat of vaporization. (b) Molecular shape: Compounds (iii) and (v) have the same chemical formula and molar mass but different molecular shapes. The more rodlike shape of (v) leads to more contact between molecules, stronger dispersion forces, and higher heat of vaporization. (c) Molecular polarity: Compound (iv) has a smaller molar mass than (ii) but a larger heat of vaporization, which must be due to the presence of dipole–dipole forces. (d) Hydrogen bonding interactions: Molecules (v) and (vi) have similar structures. Even though (v) has larger molar mass and dispersion forces, hydrogen bonding causes (vi) to have the higher heat of vaporization. **11.93** $P(\text{benzene vapor}) = 98.7$ torr

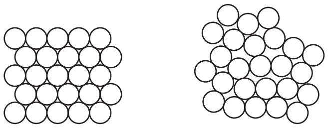
CHAPTER 12

12.1

Two-dimensional structure	**(i)**	**(ii)**
(a) unit cell		
(b) lattice	square	square
(c) cell contents	one black, one white	one black

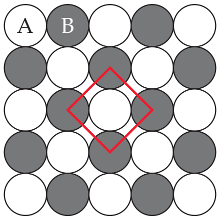
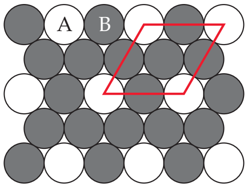
12.3 (a) 1 Re and 3 O atoms per unit cell (b) 3.92 Å (c) 6.46 g/cm^3 **12.5** We expect linear polymer (a), with ordered regions, to be denser and have a higher melting point than branched polymer (b). **12.7** In molecular solids, relatively weak intermolecular forces bind the molecules in the lattice, so relatively little energy is required to disrupt these forces. In covalent-network solids, covalent bonds join atoms into an extended network. Melting or deforming a covalent-network solid means breaking covalent bonds, which requires a large amount of energy. **12.9** (a) Hydrogen bonding, dipole-dipole forces, London dispersion forces (b) covalent chemical bonds (c) ionic bonds (d) metallic bonds **12.11** (a) Ionic (b) metallic (c) covalent-network (It could also be characterized as ionic with some covalent character to the bonds.) (d) molecular (e) molecular (f) molecular **12.13** Because of its relatively high melting point and properties as a conducting solution, the solid must be ionic.

12.15



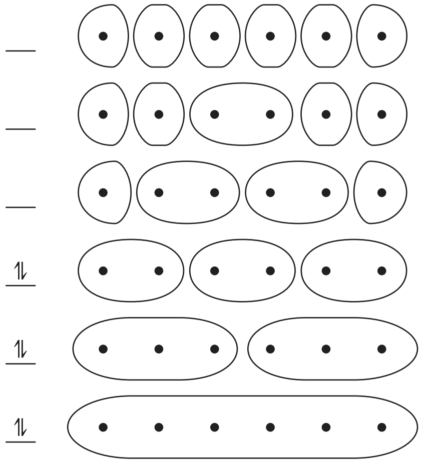
Crystalline Amorphous

12.17

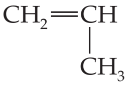
Two-dimensional structure	**(i)**	**(ii)**
(a) unit cell		
(b) γ, a, b	$\lambda = 90°$, $a = b$	$\lambda = 120°$, $a = b$
(c) lattice type	square	hexagonal

12.19 (a) Orthorhombic (d) tetragonal **12.21** Triclinic, rhombohedral **12.23** There is a minimum of two (metal) atoms in a body-centered cubic unit cell. **12.25** (a) Primitive hexagonal unit cell (b) NiAs **12.27** Moving left to right in the period, atomic mass and Z_{eff} increase. The increase in Z_{eff} leads to smaller bonding atomic radii and atomic volume. Mass increases, volume decreases, and density increases in the series. The variation in densities reflects shorter metal–metal bond distances and an increase in the extent of metal–metal bonding. The strength of metal–metal bonds in the series is probably the most important factor influencing the increase in density. **12.29** (a) Structure types A and C have equally dense packing and are more densely packed than structure type B. (b) Structure type B is least densely packed. **12.31** (a) The radius of an Ir atom is 1.355 Å. (b) The density of Ir is 22.67 g/cm^3 **12.33** (a) 4 Al atoms per unit cell (b) coordination number = 12 (c) a = 4.04 Å or 4.04 $\times 10^{-8}$ cm (d) density = 2.71 g/cm^3 **12.35** An *alloy* contains atoms of more than one element and has the properties of a metal. In a *solution alloy* the components are randomly dispersed. In a *heterogeneous alloy* the components are not evenly dispersed and can be distinguished at a macroscopic level. In an *intermetallic compound* the components have interacted to form a compound substance, as in Cu$_3$As. **12.37** (a) Interstitial alloy (b) substitutional alloy (c) intermetallic compound **12.39** (a) True (b) false (c) false **12.41** (a) Nickel or palladium, substitutional alloy (b) copper, substitutional alloy (c) indium, intermetallic compound (d) silver, substitutional alloy **12.43** In the electron-sea model, valence electrons move about the metallic lattice, while metal atoms remain more or less fixed in position. Under the influence of an applied potential, the electrons are free to move throughout the structure, giving rise to thermal and electrical conductivity.

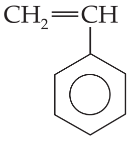
12.45



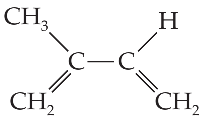
(a) Six AOs require six MOs (b) zero nodes in the lowest energy orbital (c) five nodes in highest energy orbital (d) two nodes in the HOMO (e) three nodes in the LUMO. **12.47** (a) Ag (b) Zn. Ductility decreases as the strength of metal–metal bonding increases, producing a stiffer lattice, less susceptible to distortion. **12.49** Moving from Y to Mo, the number of valence electrons, occupancy of the bonding band, and strength of metallic bonding increase. Stronger metallic bonding requires more energy to break bonds and mobilize atoms, resulting in higher melting points. **12.51** (a) SrTiO$_3$ (b) Each Sr atom is coordinated to twelve O atoms in eight unit cells that contain the Sr atom. **12.53** (a) a = 4.70 Å (b) 2.69 g/cm^3 **12.55** (a) 7.711 g/cm^3 (b) We expect Se^{2-} to have a larger ionic radius than S^{2-}, so HgSe will occupy a larger volume and the unit cell edge will be longer. (c) The density of HgSe is 8.241 g/cm^3. The greater mass of Se accounts for the greater density of HgSe. **12.57** (a) Cs$^+$ and I$^-$ have the most similar radii and will adopt the CsCl-type structure. The radii of Na$^+$ and I$^-$ are somewhat different; NaI will adopt the NaCl-type structure. The radii of Cu$^+$ and I$^-$ are very different; CuI has the ZnS-type structure. (b) CsI, 8; NaI, 6; CuI, 4 **12.59** (a) 6 (b) 3 (c) 6 **12.61** (a) False (b) true **12.63** (a) Ionic solids are much more likely to dissolve in water. (b) Covalent-network solids can become electrical conductors via chemical substitution. **12.65** (a) CdS (b) GaN (c) GaAs **12.67** Ge or Si (Ge is closer to Ga in bonding atomic radius.) **12.69** (a) A 1.1 eV photon corresponds to a wavelength of 1.1×10^{-6} m. (b) According to the figure, Si can absorb a portion of the visible light that comes from the sun. **12.71** λ = 560 nm **12.73** The band gap is approximately 1.85 eV, which corresponds to a wavelength of 672 nm. **12.75** Monomers are small molecules with low molecular mass that are joined together to form polymers. Three monomers mentioned in this chapter are



Propylene
(propene)

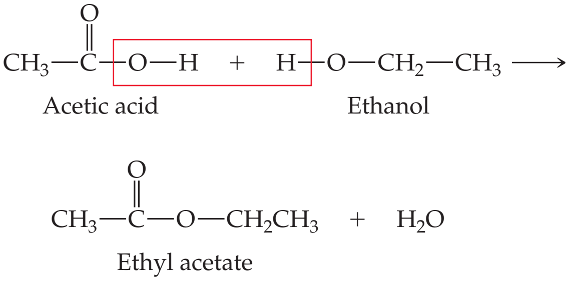


Styrene
(phenyl ethene)



Isoprene
(2-methyl-1,3-butadiene)

12.77



$$\mathrm{CH_3{-}\overset{O}{\overset{\|}{C}}{-}\boxed{O{-}H \;+\; H}{-}O{-}CH_2{-}CH_3 \longrightarrow}$$

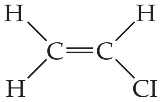
Acetic acid Ethanol

$$\mathrm{CH_3{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2CH_3 \;+\; H_2O}$$

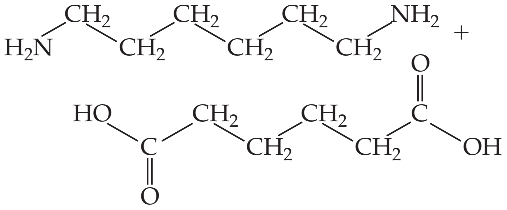
Ethyl acetate

If a dicarboxylic acid and a dialcohol are combined, there is the potential for propagation of the polymer chain at both ends of both monomers.

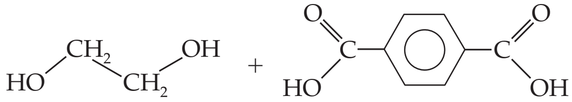
12.79 (a)



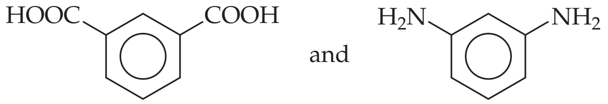
(b)



(c)

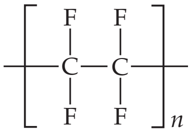


12.81

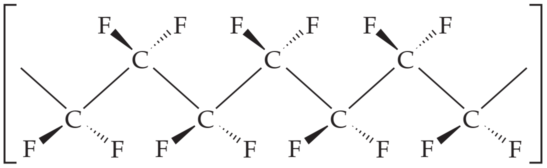


12.83 Flexibility of molecular chains causes flexibility of the bulk polymer. Flexibility is enhanced by molecular features that inhibit order, such as branching, and diminished by features that encourage order, such as cross-linking or delocalized π electron density. Cross-linking, the formation of chemical bonds between polymer chains, reduces flexibility of the molecular chains, increases the hardness of the material, and decreases the chemical reactivity of the polymer. **12.85** No. The function of the polymer determines whether high molecular mass and high degree of crystallinity are desirable properties. If the polymer will be used as a flexible wrapping or fiber, rigidity that is due to high molecular mass is an undesirable property. **12.87** If a solid has nanoscale dimensions of 1–10 nm, there may not be enough atoms contributing atomic orbitals to produce continuous energy bands of molecular orbitals. **12.89** (a) False. As particle size decreases, the band gap increases. (b) False. As particle size decreases, wavelength decreases. **12.91** 2.47×10^5 Au atoms **12.94** The face-centered structure will have the greater density. **12.98** (a) CsCl, primitive cubic lattice (b) Au, face-centered cubic lattice (c) NaCl, face-centered cubic lattice (d) Po, primitive cubic lattice, rare for metals (e) ZnS, face-centered cubic lattice **12.99** White tin has a structure characteristic of a metal, while gray tin has the diamond structure characteristic of group 4A semiconductors. Metallic white tin has the longer bond distance because the valence electrons are shared with twelve nearest neighbors rather than being localized in four bonds as in gray tin.

12.103



or



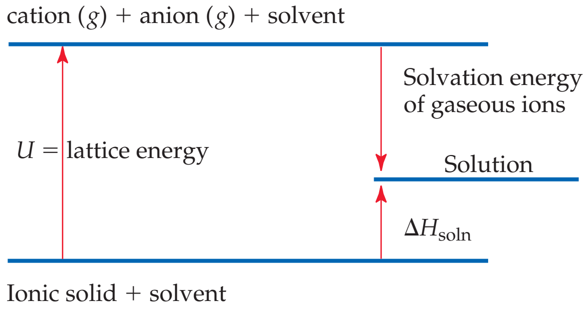
Teflon™ is formed by addition polymerization. **12.105** Diffraction, the phenomenon that enables us to measure interatomic distances in crystals, is most efficient when the wavelength of light is similar to or smaller than the size of the object doing the diffracting. Atom sizes are on the order of 1–10 Å, and the wavelengths of X-rays are also in this range. Visible light, 400–700 nm or 4000–7000 Å, is too long to be diffracted effectively by atoms (electrons) in crystals. **12.107** In a diffraction experiment, we expect a Ge crystal to diffract X-rays at a smaller θ angle than a Si crystal, assuming the X-rays have the same wavelength. **12.109** (a) The bonds in a semiconductor will be weakened by *n*-type doping. (b) The bonds in a semiconductor will also be weakened by *p*-type doping. **12.112** (a) 109° (b) 120° **12.113** (a) $\Delta H = -82$ kJ/mol (b) $\Delta H = -14$ kJ/mol (of either reactant) (c) $\Delta H = 0$ kJ

CHAPTER 13

13.1 (a) $<$ (b) $<$ (c) **13.3** The greater the lattice energy of an ionic solid, the more endothermic the dissolving process and the less soluble the salt in water. **13.7** Vitamin B_6 is largely water soluble because of its small size and capacity for extensive hydrogen-bonding interactions. Vitamin E is largely fat soluble. The long, rodlike hydrocarbon chain will lead to strong dispersion forces among vitamin E and mostly nonpolar fats. **13.9** (a) Yes, the *molarity* changes with a change in temperature. Molarity is defined as moles solute per unit volume of solution. A change of temperature changes solution volume and molarity. (b) No, *molality* does not change with change in temperature. Molality is defined as moles solute per kilogram of solvent. Temperature affects neither mass nor moles. **13.13** If the magnitude of ΔH_{mix} is small relative to the magnitude of ΔH_{solute}, ΔH_{soln} will be large and endothermic (energetically unfavorable) and not much solute will dissolve. **13.15** (a) Dispersion (b) hydrogen bonding (c) ion–dipole (d) dipole–dipole **13.17** Very soluble. In order for ΔH_{soln} to be negative, ΔH_{mix} must have a greater magnitude than $(\Delta H_{solute} + \Delta H_{solvent})$. The entropy of mixing always encourages solubility. In this case, the enthalpy of the system decreases and the entropy increases, so the ionic compound dissolves. **13.19** (a) ΔH_{solute} (b) ΔH_{mix} **13.21** (a) Since the solute and solvent experience very similar London dispersion forces, the energy required to separate them individually and the energy released when they are mixed are approximately equal. $\Delta H_{solute} + \Delta H_{solvent} \approx -\Delta H_{mix}$. Thus, ΔH_{soln} is nearly zero. (b) Since no strong intermolecular forces prevent the molecules from mixing, they do so spontaneously because of the increase in randomness. **13.23** (a) Supersaturated (b) Add a seed crystal. A seed crystal provides a nucleus of prealigned molecules, so that ordering of the dissolved particles (crystallization) is more facile. **13.25** (a) Unsaturated (b) saturated (c) saturated (d) unsaturated **13.27** The liquids water and glycerol form homogenous mixtures (solutions) regardless of the relative amounts of the two components. The $-OH$ groups of glycerol facilitate strong hydrogen bonding similar to that in water; like dissolves like. **13.29** Toluene, $C_6H_5CH_3$, is the best solvent for nonpolar solutes. Without polar groups or nonbonding electron pairs, it forms only dispersion interactions with itself and other molecules. **13.31** (a) Dispersion interactions among nonpolar $CH_3(CH_2)_{16}-$ chains dominate the properties of stearic acid, causing it to be more soluble in nonpolar CCl_4. (b) Dioxane can act as a hydrogen bond acceptor, so it will be more soluble than cyclohexane in water. **13.33** (a) CCl_4 is more soluble because dispersion forces among nonpolar CCl_4 molecules are similar to dispersion forces in hexane. (b) C_6H_6 is a nonpolar hydrocarbon and will be more soluble in the similarly nonpolar hexane. (c) The long, rodlike hydrocarbon chain of octanoic acid forms strong dispersion interactions and causes it to be more soluble in hexane. **13.35** (a) A sealed container is required to maintain a partial pressure of $CO_2(g)$ greater than 1 atm above the beverage. (b) Since the solubility of gases increases with decreasing temperature, more $CO_2(g)$ will remain dissolved in the beverage if it is kept cool. **13.37** $S_{He} = 5.6 \times 10^{-4}\,M$, $S_{N_2} = 9.0 \times 10^{-4}\,M$ **13.39** (a) 2.15% Na_2SO_4 by mass (b) 3.15 ppm Ag **13.41** (a) $X_{CH_3OH} = 0.0427$ (b) 7.35% CH_3OH by mass (c) 2.48 m CH_3OH **13.43** (a) $1.46 \times 10^{-2}\,M$ $Mg(NO_3)_2$ (b) 1.12 M $LiClO_4 \cdot 3\,H_2O$ (c) 0.350 M HNO_3 **13.45** (a) 4.70 m C_6H_6 (b) 0.235 m NaCl **13.47** (a) 43.01% H_2SO_4 by mass (b) $X_{H_2SO_4} = 0.122$ (c) 7.69 m H_2SO_4 (d) 5.827 M H_2SO_4 **13.49** (a) $X_{CH_3OH} = 0.227$ (b) 7.16 m CH_3OH (c) 4.58 M CH_3OH **13.51** (a) 0.150 mol $SrBr_2$ (b) 1.56×10^{-2} mol KCl (c) 4.44×10^{-2} mol $C_6H_{12}O_6$ **13.53** (a) Weigh out 1.3 g KBr, dissolve in water, dilute with stirring to 0.75 L. (b) Weigh out 2.62 g KBr, dissolve it in 122.38 g H_2O to make exactly 125 g of 0.180 m solution. (c) Dissolve 244 g KBr in water, dilute with stirring to 1.85 L. (d) Weigh 10.1 g KBr, dissolve it in a small amount of water, and dilute to 0.568 L. **13.55** 71% HNO_3 by mass **13.57** (a) 3.82 m Zn (b) 26.8 M Zn **13.59** $1.8 \times 10^{-3}\,M$ CO_2 **13.61** Freezing point depression, $\Delta T_f = K_f(m)$; boiling-point elevation, $\Delta T_b = K_b(m)$; osmotic pressure, $\Pi = MRT$; vapor pressure lowering, $P_A = X_A P_A^\circ$ **13.63** (a) Sucrose has a greater molar mass than glucose, so the sucrose solution will contain fewer particles and have a higher vapor pressure. **13.65** (a) $P_{H_2O} = 186.4$ torr (b) 78.9 g $C_3H_8O_2$ **13.67** (a) $X_{Eth} = 0.2812$ (b) $P_{soln} = 238$ torr (c) X_{Eth} in vapor $= 0.472$ **13.69** (a) Because NaCl is a strong electrolyte, one mole of NaCl produces twice as many dissolved particles as one mole of the molecular solute $C_6H_{12}O_6$. Boiling-point elevation is directly related to total moles of dissolved particles, so 0.10 m NaCl has the higher boiling point. (b) 0.10 m NaCl: $\Delta T_b = 0.101\,°C$, $T_b = 100.1\,°C$; 0.10 m $C_6H_{12}O_6$: $\Delta T_b = 0.051\,°C$, $T_b = 100.1\,°C$ (c) Interactions between ions in solution result in nonideal behavior. **13.71** 0.050 m LiBr $<$ 0.120 m glucose $<$ 0.050 m $Zn(NO_3)_2$ **13.73** (a) $T_f = -115.0\,°C$, $T_b = 78.7\,°C$ (b) $T_f = -67.3\,°C$, $T_b = 64.2\,°C$ (c) $T_f = -0.4\,°C$, $T_b = 100.1\,°C$ (c) $T_f = -0.6\,°C$, $T_b = 100.2\,°C$ **13.75** 167 g $C_2H_6O_2$ **13.77** $\Pi = 0.0168$ atm $= 12.7$ torr **13.79** Experimental molar mass of adrenaline is 1.8×10^2 g. The structure shows a molecular formula of $C_9H_{13}NO_3$, with a molar mass of 183 g. The two values agree to two significant figures, the precision of the experiment. **13.81** Molar mass of lysozyme $= 1.39 \times 10^4$ g **13.83** (a) $i = 2.8$ (b) The more concentrated the solution, the greater the ion pairing and the smaller the measured value of i. **13.85** (a) In the gaseous state, particles are far apart and intermolecular attractive forces are small. When two gases combine, all terms in Equation 13.1 are essentially zero and the mixture is always homogeneous. (b) To determine whether Faraday's dispersion is a true solution or a colloid, shine a beam of light on it. If light is scattered, the dispersion is a colloid. **13.87** (a) Hydrophobic (b) hydrophilic (c) hydrophobic (d) hydrophobic (but stabilized by adsorbed charges). **13.89** When electrolytes are added to a suspension of proteins, dissolved ions form ion pairs with the protein surface charges, effectively neutralizing them. The protein's capacity for ion–dipole interactions with water is diminished and the colloid separates into a protein layer and a water layer. **13.91** The periphery of the BHT molecule is mostly hydrocarbon-like groups, such as $-CH_3$. The one $-OH$ group is rather buried inside and probably does little to enhance solubility in water. Thus, BHT is more likely to be soluble in the nonpolar hydrocarbon hexane, C_6H_{14}, than in polar water. **13.94** (a) $k_{Rn} = 7.27 \times 10^{-3}$ mol/L-atm (b) $P_{Rn} = 1.1 \times 10^{-4}$ atm; $S_{Rn} = 8.1 \times 10^{-7}\,M$ **13.98** (a) 2.69 m LiBr (b) $X_{LiBr} = 0.0994$ (c) 81.1% LiBr by mass **13.100** $X_{H_2O} = 0.808$; 0.0273 mol ions; 0.0136 mol NaCl **13.103** (a) $-0.6\,°C$ (b) $-0.4\,°C$ **13.106** (a) CF_4, $1.7 \times 10^{-4}\,m$; $CClF_3$, $9 \times 10^{-4}\,m$; CCl_2F_2, $2.3 \times 10^{-2}\,m$; $CHClF_2$, $3.5 \times 10^{-2}\,m$ (b) Molality and molarity are numerically similar when kilograms solvent and liters solution are nearly equal. This is true when solutions are dilute and when the density of the solvent is nearly 1 g/mL, as in this exercise. (c) Water is a polar solvent; the solubility of solutes increases as their polarity increases. Nonpolar CF_4 has the lowest solubility and the most polar fluorocarbon, $CHClF_2$, has the greatest solubility in H_2O. (d) The Henry's law constant for $CHClF_2$ is 3.5×10^{-2} mol/L-atm. This value is greater than the Henry's law constant for $N_2(g)$ because $N_2(g)$ is nonpolar and of lower molecular mass than $CHClF_2$.

13.109

(a)

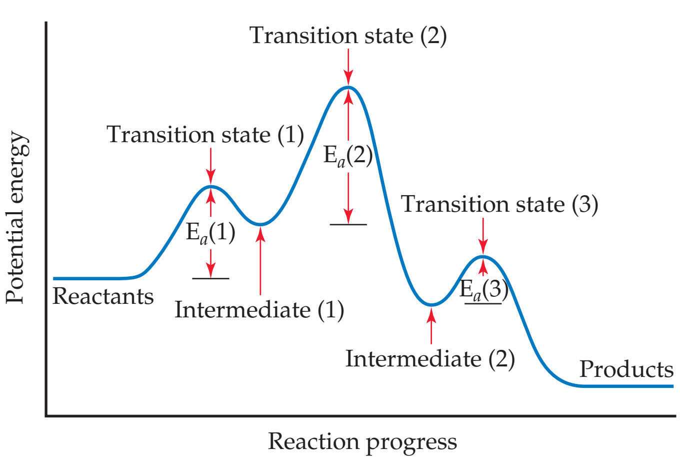


(b) Lattice energy (U) is inversely related to the distance between ions, so salts with large cations like $(CH_3)_4N^+$ have smaller lattice energies than salts with simple cations like Na^+. Also the $-CH_3$ groups in the large cation are capable of dispersion interactions with nonpolar groups of the solvent molecules, resulting in a more negative solvation energy of the gaseous ions. Overall, for salts with larger cations, lattice energy is smaller (less positive), the solvation energy of the gaseous ions is more negative, and ΔH_{soln} is less endothermic. These salts are more soluble in polar nonaqueous solvents. **13.112** The freezing point of the LiOH(*aq*) solution is essentially zero, $T_f = -0.00058\,°C$.

CHAPTER 14

14.1 Vessel 2 **14.3** Equation (d) **14.9** (1) Total potential energy of the reactants (2) E_a, activation energy of the reaction (3) ΔE, net energy change for the reaction (4) total potential energy of the products **14.12** (a) $NO_2 + F_2 \longrightarrow NO_2F + F$; $NO_2 + F \longrightarrow NO_2F$ (b) $2\,NO_2 + F_2 \longrightarrow 2\,NO_2F$ (c) F (atomic fluorine) is the intermediate (d) rate $= k[NO_2][F_2]$)

14.16



14.17 (a) *Reaction rate* is the change in the amount of products or reactants in a given amount of time. (b) Rates depend on concentration of reactants, surface area of reactants, temperature, and presence of catalyst. (c) The stoichiometry of the reaction (mole ratios of reactants and products) must be known to relate rate of disappearance of reactants to rate of appearance of products.

14.19

Time (min)	Mol A	(a) Mol B	[A] (mol/L)	Δ[A] (mol/L)	(b) Rate (M/s)
0	0.065	0.000	0.65		
10	0.051	0.014	0.51	−0.14	2.3×10^{-4}
20	0.042	0.023	0.42	−0.09	1.5×10^{-4}
30	0.036	0.029	0.36	−0.06	1.0×10^{-4}
40	0.031	0.034	0.31	−0.05	0.8×10^{-4}

(c) $\Delta[\mathrm{B}]_{\mathrm{avg}}/\Delta t = 1.3 \times 10^{-4}\,M/\mathrm{s}$

14.21 (a)

Time (s)	Time Interval (s)	Concentration (*M*)	ΔM	Rate (M/s)
0		0.0165		
2,000	2,000	0.0110	−0.0055	28×10^{-7}
5,000	3,000	0.00591	−0.0051	17×10^{-7}
8,000	3,000	0.00314	−0.00277	9.23×10^{-7}
12,000	4,000	0.00137	−0.00177	4.43×10^{-7}
15,000	3,000	0.00074	−0.00063	2.1×10^{-7}

(b) The average rate of reaction is $1.05 \times 10^{-6} M/\mathrm{s}$. (c) From the slopes of the tangents to the graph, the rates are $12 \times 10^{-7} M/\mathrm{s}$ at 5000 s, $5.8 \times 10^{-7} M/\mathrm{s}$ at 8000 s.

14.23

(a) $-\Delta[\mathrm{H_2O_2}]/\Delta t = \Delta[\mathrm{H_2}]/\Delta t = \Delta[\mathrm{O_2}]/\Delta t$

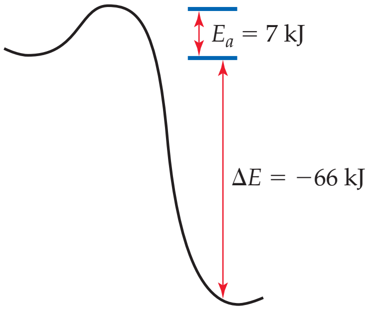
(b) $-\frac{1}{2}\Delta[\mathrm{N_2O}]/\Delta t = \frac{1}{2}\Delta[\mathrm{N_2}]/\Delta t = \Delta[\mathrm{O_2}]/\Delta t$

(c) $-\Delta[\mathrm{N_2}]/\Delta t = -1/3\Delta[\mathrm{H_2}]/\Delta t = -1/2\Delta[\mathrm{NH_3}]/2\Delta t$

(d) $-\Delta[\mathrm{C_2H_5NH_2}]/\Delta t = \Delta[\mathrm{C_2H_4}]/\Delta t = \Delta[\mathrm{NH_3}]/\Delta t$

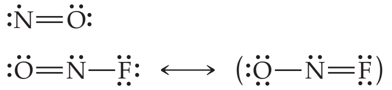
14.25 (a) $-\Delta[\mathrm{O_2}]/\Delta t = 0.24\ \mathrm{mol/s}$; $\Delta[\mathrm{H_2O}]/\Delta t = 0.48\ \mathrm{mol/s}$ (b) P_{total} decreases by 28 torr/min. **14.27** (a) If [A] doubles, there is no change in the rate or the rate constant. The overall rate is unchanged because [A] does not appear in the rate law; the rate constant changes only with a change in temperature. (b) The reaction is zero order in A, second order in B, and second order overall. (c) units of $k = M^{-1}\,\mathrm{s}^{-1}$ **14.29** (a) Rate $= k[\mathrm{N_2O_5}]$ (b) Rate $= 1.16 \times 10^{-4}\,M/\mathrm{s}$ (c) When the concentration of $\mathrm{N_2O_5}$ doubles, the rate doubles. (d) When the concentration of $\mathrm{N_2O_5}$ is halved, the rate doubles. **14.31** (a, b) $k = 1.7 \times 10^{2}\,M^{-1}\mathrm{s}^{-1}$ (c) If $[\mathrm{OH^-}]$ is tripled, the rate triples. (d) If $[\mathrm{OH^-}]$ and $[\mathrm{CH_3Br}]$ both triple, the rate increases by a factor of 9. **14.33** (a) Rate $= k[\mathrm{OCl^-}][\mathrm{I^-}]$ (b) $k = 60\,M^{-1}\,\mathrm{s}^{-1}$ (c) Rate $= 6.0 \times 10^{-5}\,M/\mathrm{s}$ **14.35** (a) Rate $= k[\mathrm{BF_3}][\mathrm{NH_3}]$ (b) The reaction is second order overall. (c) $k_{\mathrm{avg}} = 3.41\,M^{-1}\,\mathrm{s}^{-1}$ (d) $0.170\,M/\mathrm{s}$ **14.37** (a) Rate $= k[\mathrm{NO}]^2[\mathrm{Br_2}]$ (b) $k_{\mathrm{avg}} = 1.2 \times 10^{4}\,M^{-2}\,\mathrm{s}^{-1}$ (c) $\frac{1}{2}\Delta[\mathrm{NOBr}]/\Delta t = -\Delta[\mathrm{Br_2}]/\Delta t$ (d) $-\Delta[\mathrm{Br_2}]/\Delta t = 8.4\,M/\mathrm{s}$ **14.39** (a) $[\mathrm{A}]_0$ is the molar concentration of reactant A at time zero. $[\mathrm{A}]_t$ is the molar concentration of reactant A at time t. $t_{1/2}$ is the time required to reduce $[\mathrm{A}]_0$ by a factor of 2. k is the rate constant for a particular reaction. (b) A graph of ln[A] versus time yields a straight line for a first-order reaction. (c) On a graph of ln[A] versus time, the rate constant is the (–slope) of the straight line. **14.41** Plot [A] versus time. **14.43** (a) $k = 3.0 \times 10^{-6}\,\mathrm{s}^{-1}$ (b) $t_{1/2} = 3.2 \times 10^{4}\,\mathrm{s}$ **14.45** (a) $P = 30$ torr (b) $t = 51$ s **14.47** Plot ($\ln P_{\mathrm{SO_2Cl_2}}$) versus time, $k = -\text{slope} = 2.19 \times 10^{-5}\,\mathrm{s}^{-1}$ **14.49** (a) The plot of $1/[\mathrm{A}]$ versus time is linear, so the reaction is second order in [A]. (b) $k = 0.040\,M^{-1}\,\mathrm{min}^{-1}$ (c) $t_{1/2} = 38$ min **14.51** (a) The plot of $1/[\mathrm{NO_2}]$ versus time is linear, so the reaction is second order in $\mathrm{NO_2}$. (b) $k = \text{slope} = 10\,M^{-1}\,\mathrm{s}^{-1}$ (c) rate at $0.200\,M = 0.400\,M/\mathrm{s}$; rate at $0.100\,M = 0.100\,M/\mathrm{s}$; rate at $0.050\,M = 0.025\,M/\mathrm{s}$ **14.53** (a) The energy of the collision and the orientation of the molecules when they collide determine whether a reaction will occur. (b) At a higher temperature, there are more total collisions and each collision is more energetic. (c) The rate constant usually increases with an increase in reaction temperature. **14.55** $f = 4.94 \times 10^{-2}$. At 400 K approximately 1 out of 20 molecules has this kinetic energy.

14.57 (a)



(b) E_a (reverse) $= 73$ kJ **14.59** (a) False. If you compare two reactions with similar collision factors, the one with the larger activation energy will be slower. (b) False. A reaction that has a small rate constant will have either a small frequency factor, a large activation energy, or both. (c) True. **14.61** Reaction (b) is fastest and reaction (c) is slowest. **14.63** (a) $k = 1.1\,\mathrm{s}^{-1}$ (b) $k = 13\,\mathrm{s}^{-1}$ (c) The method in parts (a) and (b) assumes that the collision model and thus the Arrhenious equation describe the kinetics of the reactions. That is, activation energy is constant over the temperature range under consideration. **14.65** A plot of ln k versus $1/T$ has a slope of -5.71×10^{3}; $E_a = -R(\text{slope}) = 47.5$ kJ/mol. **14.67** The reaction will occur 88 times faster at 50 °C, assuming equal initial concentrations. **14.69** (a) An *elementary reaction* is a process that occurs in a single event; the order is given by the coefficients in the balanced equation for the reaction. (b) A *unimolecular* elementary reaction involves only one reactant molecule; a *bimolecular* elementary reaction involves two reactant molecules. (c) A *reaction mechanism* is a series of elementary reactions that describes how an overall reaction occurs and explains the experimentally determined rate law. **14.71** A transition state is a high-energy complex formed when one or more reactants collide and distort in a way that can lead to formation of product(s). An intermediate is the product of an early elementary reaction in a multistep reaction mechanism. **14.73** (a) Unimolecular, rate $= k[\mathrm{Cl_2}]$ (b) bimo- lecular, rate $= k[\mathrm{OCl^-}][\mathrm{H_2O}]$ (c) bimolecular, rate $= k[\mathrm{NO}][\mathrm{Cl_2}]$ **14.75** (a) Two intermediates, B and C. (b) three transition states (c) C $\longrightarrow$ D is fastest. (d) endothermic **14.77** (a) $\mathrm{H_2}(g) + 2\,\mathrm{ICl}(g) \longrightarrow \mathrm{I_2}(g) + 2\,\mathrm{HCl}(g)$ (b) HI is the intermediate. (c) If the first step is slow, the observed rate law is rate $= k[\mathrm{H_2}][\mathrm{ICl}]$. **14.79** The graph of 1/[NO] versus time is linear with positive slope, indicating that the reaction is second order in [NO]. The rate law obtained by assuming the second step is rate determining is rate $= [\mathrm{NO}]^2[\mathrm{Cl_2}]$. The two-step mechanism is consistent with the data. **14.81** (a) A catalyst is a substance that changes (usually increases) the speed of a chemical reaction without undergoing a permanent chemical change itself. (b) A homogeneous catalyst is in the same phase as the reactants, while a hetereogeneous catalyst is in a different phase. (c) A catalyst has no effect on the overall enthalpy change for a reaction, but it does affect activation energy. It can also affect the frequency factor. **14.83** (a) 270 Pt atoms in a 2.0-nm sphere (b) 200 Pt atoms on the surface of a 2.0-nm sphere (c) 74% Pt atoms on the surface (d) 4300 Pt atoms in a 5.0-nm sphere; 1300 Pt atoms on the surface; 30% Pt atoms on the surface (e) The 2-nm sphere will definitely be more catalytically active because it has a much greater percentage of its atoms on the surface where they can participate in the chemical reaction. **14.85** (a) Multiply the coefficients in the first reaction by 2 and sum. (b) $\mathrm{NO_2}(g)$ is a catalyst because it is consumed and then reproduced in the reaction sequence. (c) This is a homogeneous catalysis. **14.87** (a) Use of chemically stable supports makes it possible to obtain very large surface areas per unit mass of the precious metal catalyst because the metal can be deposited in a very thin, even monomolecular, layer on the surface of the support. (b) The greater the surface area of the catalyst, the more reaction sites, the greater the rate of the catalyzed reaction. **14.89** To put two D atoms on a single carbon, it is necessary that one of the already existing C—H bonds in ethylene be broken while the molecule is adsorbed, so that the H atom moves off as an adsorbed atom and is replaced by a D atom. This requires a larger activation energy than simply adsorbing C_2H_4 and adding one D atom to each carbon. **14.91** (a) Living organisms operate efficiently in a very narrow temperature range; the role of enzymes as homogeneous catalysts that speed up desirable reactions, without heating and undesirable side effects, is crucial for biological systems. (b) catalase: $2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$; nitrogenase: $N_2 \longrightarrow 2\,NH_3$ (nitrogen fixation) (c) This model assumes that the rate of the bound substrate being chemically transformed into bound product is slow and rate determining. **14.93** Carbonic anyhdrase lowers the activation energy of the reaction by 42 kJ. **14.95** (a) The catalyzed reaction is approximately 10,000,000 times faster at 25 °C. (b) The catalyzed reaction is 180,000 times faster at 125 °C. **14.99** (a) Rate $= 4.7 \times 10^{-5}\,M/s$ (b, c) $k = 0.84\,M^{-2}\,s^{-1}$ (d) If the [NO] is increased by a factor of 1.8, the rate would increase by a factor of 3.2. **14.101** The reaction is second order in NO_2. If $[NO_2]_0 = 0.100\,M$ and $[NO_2]_t = 0.025\,M$, use the integrated form of the second-order rate equation to solve for t. $t = 48\,s$ **14.105** (a) The half-life of ^{241}Am is 4.3×10^2 yr, that of ^{125}I is 63 days (b) ^{125}I decays at a much faster rate. (c) 0.13 mg of each isotope remains after 3 half-lives. (d) The amount of ^{241}Am remaining after 4 days is 1.00 mg. The amount of ^{125}I remaining after 4 days is 0.957 grams. **14.109** The plot of $1/[C_5H_6]$ versus time is linear and the reaction is second order. $k = 0.167\,M^{-1}\,s^{-1}$ **14.112** (a) When the two elementary reactions are added, $N_2O_2(g)$ appears on both sides and cancels, resulting in the overall reaction. $2NO(g) + H_2(g) \longrightarrow N_2O(g) + H_2O(g)$ (b) First reaction, $-[NO]/\Delta t = k[NO]^2$; second reaction, $-[H_2]/\Delta t = k[H_2][N_2O_2]$ (c) N_2O_2 is the intermediate. (d) Since $[H_2]$ appears in the rate law, the second step must be slow relative to the first. **14.115** (a) $Cl_2(g) + CHCl_3(g) \longrightarrow HCl(g) + CCl_4(g)$ (b) $Cl(g)$, $CCl_3(g)$ (c) reaction 1, unimolecular; reaction 2, bimolecular; reaction 3, bimolecular (d) Reaction 2 is rate determining. (e) Rate $= k[CHCl_3][Cl_2]^{1/2}$. **14.122** (a) $k = 8 \times 10^7\,M^{-1}\,s^{-1}$

(b)

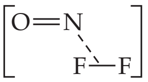


$:\dot{N}=\ddot{O}:$

$:\ddot{O}=\ddot{N}-\ddot{\underset{..}{F}}: \longleftrightarrow (:\underset{..}{\ddot{O}}-\ddot{N}=\underset{..}{\ddot{F}})$

(c) NOF is bent with a bond angle of approximately 120°.

(d)



(e) The electron-deficient NO molecule is attracted to electron-rich F_2, so the driving force for formation of the transition state is greater than simple random collisions.

CHAPTER 15

15.1 $k_f > k_r$ (b) The equilibrium constant is greater than 1. **15.7** From the smallest to the largest equilibrium constant, (c) < (b) < (a). **15.11** K_c decreases as T increases, so the reaction is exothermic. **15.13** (a) $K_p = K_c = 8.1 \times 10^{-3}$. (b) Since $k_f < k_r$, in order for the two rates to be equal, [A] must be greater than [B], and the partial pressure of A is greater than the partial pressure of B. **15.15** (a) $K_c = [N_2O][NO_2]/[NO]^3$; homogeneous (b) $K_c = [CS_2][H_2]^4/[CH_4][H_2S]^2$; homogeneous (c) $K_c = [CO]^4/[Ni(CO)_4]$; heterogeneous (d) $K_c = [H^+][F^-]/[HF]$; homogeneous (e) $K_c = [Ag^+]^2/[Zn^{2+}]$; heterogeneous (f) $K_c = [H^+][OH^-]$; homogeneous (g) $K_c = [H^+][OH^-]$; homogeneous **15.17** (a) Mostly reactants (b) mostly products **15.19** No, the equilibrium constant can never be a negative number. The equilibrium constant is a ratio of rate constants (or a ratio of concentrations), which are never negative. **15.21** $K_p = 1.0 \times 10^{-3}$ **15.23** (a) The equilibrium favors NO and Br_2 at this temperature. (b) $K_c = 77$ (c) $K_c = 8.8$ **15.25** (a) $K_p = 0.541$ (b) $K_p = 3.42$ (c) $K_c = 281$ **15.27** $K_c = 0.14$ **15.29** Pure solids and liquids are normally excluded from equilibrium-constant expressions because their concentrations, the ratio of moles of a substance to volume occupied by the substance, are constant. **15.31** (a) $K_p = P_{O_2}$ (b) $K_c = [Hg(solv)]^4[O_2(solv)]$ **15.33** $K_c = 10.5$ **15.35** (a) $K_p = 51$ (b) $K_c = 2.1 \times 10^3$ **15.37** (a) $[H_2] = 0.012\,M$, $[N_2] = 0.019\,M$, $[H_2O] = 0.138\,M$ (b) $K_c = 653.7 = 7 \times 10^2$ **15.39** (a) $P_{CO_2} = 4.10$ atm, $P_{H_2} = 2.05$ atm, $P_{H_2O} = 3.28$ atm (b) $P_{CO_2} = 3.87$ atm, $P_{H_2} = 1.82$ atm, $P_{CO} = 0.23$ atm (c) $K_p = 0.11$ **15.41** $K_c = 2.0 \times 10^4$ **15.43** (a) A reaction quotient is the result of a general set of concentrations whereas the equilibrium constant requires equilibrium concentrations. (b) to the right (c) The concentrations used to calculate Q must be equilibrium concentrations. **15.45** (a) $Q = 1.1 \times 10^{-8}$, the reaction will proceed to the left. (b) $Q = 5.5 \times 10^{-12}$, the reaction will proceed to the right. (c) $Q = 2.19 \times 10^{-10}$, the mixture is at equilibrium. **15.47** $P_{Cl_2} = 5.0$ atm **15.49** (a) $[Br_2] = 0.00767\,M$, $[Br] = 0.00282\,M$, 0.0451 g $Br(g)$ (b) $[H_2] = 0.014\,M$, $[I_2] = 0.00859\,M$, $[HI] = 0.081\,M$, 21 g HI **15.51** $[NO] = 0.002\,M$, $[N_2] = [O_2] = 0.087\,M$ **15.53** The equilibrium pressure of $Br_2(g)$ is 0.416 atm. **15.55** (a) $[Ca^{2+}] = [SO_4^{\ 2-}] = 4.9 \times 10^{-3}\,M$ (b) A bit more than 1.0 g $CaSO_4$ is needed in order to have some undissolved $CaSO_4(s)$ in equilibrium with 1.4 L of saturated solution. **15.57** $[IBr] = 0.223\,M$, $[I_2] = [Br_2] = 0.0133\,M$ **15.59** (a) $P_{CH_3I} = P_{HI} = 0.422$ torr, $P_{CH_4} = 104.7$ torr, $P_{I_2} = 7.54$ torr **15.61** (a) Shift equilibrium to the right (b) decrease the value of K (c) shift equilibrium to the left (d) no effect (e) no effect (f) shift equilibrium to the right **15.63** (a) No effect (b) no effect (c) no effect (d) increase equilibrium constant (e) no effect **15.65** (a) $\Delta H° = -155.7$ kJ (b) The reaction is exothermic, so the equilibrium constant will decrease with increasing temperature. (c) Δn does not equal zero, so a change in volume at constant temperature will affect the fraction of products in the equilibrium mixture. **15.67** An increase in pressure favors formation of ozone. **15.71** $K_p = 24.7$; $K_c = 3.67 \times 10^{-3}$ **15.74** (a) $P_{Br_2} = 1.61$ atm, $P_{NO} = 0.628$ atm, $P_{NOBr} = 0.179$ atm; $K_c = 0.0643$ (b) $P_t = 0.968$ atm (c) 10.49 g NOBr **15.77** At equilibrium, $P_{IBr} = 0.21$ atm, $P_{I_2} = P_{Br_2} = 1.9 \times 10^{-3}$ atm **15.80** $K_p = 4.33$, $K_c = 0.0480$ **15.83** $[CO_2] = [H_2] = 0.264\,M$, $[CO] = [H_2O] = 0.236\,M$ **15.87** (a) 26% of the CCl_4 is converted to C and Cl_2. (b) $P_{CCl_4} = 1.47$ atm, $P_{Cl_2} = 1.06$ atm **15.91** $Q = 8 \times 10^{-6}$. $Q > K_p$, so the system is not at equilibrium; it will shift left to attain equilibrium. A catalyst that speeds up the reaction and thereby promotes the attainment of equilibrium would decrease the CO concentration in the exhaust. **15.93** At equilibrium, $[H_6IO_4^{\ -}] = 0.0015\,M$ **15.97** At 850 °C, $K_p = 14.1$; at 950 °C, $K_p = 73.8$; at 1050 °C, $K_p = 2.7 \times 10^2$; at 1200 °C, $K_p = 1.7 \times 10^3$. Because K increases with increasing temperature, the reaction is endothermic.

CHAPTER 16

16.1 (a) HX, the H^+ donor, is the Brønsted–Lowry acid. NH_3, the H^+ acceptor, is the Brønsted–Lowry base. (b) HX, the electron pair acceptor, is the Lewis acid. NH_3, the electron pair donor, is the Lewis base. **16.3** (a) HY is a strong acid. There are no neutral HY molecules in solution, only H^+ cations and Y^- anions. (b) HX has the smallest K_a value. It has most neutral acid molecules and fewest ions. (c) HX has fewest H^+ and highest pH. **16.5** (a) True. (b) False. Methyl orange turns yellow at a pH slightly greater than 4, so solution B could be at any pH greater than 4. (c) True. **16.7** (a) Molecule A, NH_2OH (hydroxyl amine), acts as a base. Molecule A is an H^+ acceptor because of the nonbonded electron pair on the N atom of the amine ($-NH_2$) group, not because it contains an —OH group. (b) Molecule B, HCOOH (formic acid), acts as an acid. The molecule contains a —COOH group where the H atom bonded to O is ionizable and HCOOH is an H^+ donor. (c) Molecule C, CH_3OH (methanol), is an organic alcohol. The H atom bonded to O is not ionizable, and the —OH group does not dissociate in aqueous solution; it is neither an acid nor a base. **16.9** (a) Molecule (b) is more acidic because its conjugate base is resonance-stabilized and the ionization equilibrium favors the more stable products. (b) Increasing the electronegativity of X increases the strength of both acids. As X becomes more electronegative and attracts more electron density, the O—H bond becomes weaker, more polar, and more likely to be ionized. An electronegative X group also stabilizes the anionic conjugate base, causing the ionization equilibrium to favor products and the value of K_a to increase. **16.11** Solutions of HCl and H_2SO_4 conduct electricity, taste sour, turn litmus paper red (are acidic), neutralize solutions of bases, and react with active metals to form $H_2(g)$. HCl and H_2SO_4 solutions have these properties in common because both compounds are strong acids. That is, they both ionize completely in H_2O to form $H^+(aq)$ and an anion. (HSO_4^- is not completely ionized, but the first ionization step for H_2SO_4 is complete.) The presence of ions enables the solutions to conduct electricity; the presence of $H^+(aq)$ in excess of $1 \times 10^{-7}\,M$ accounts for all other properties listed. **16.13** (a) The Arrhenius definition of an acid is confined to aqueous solution; the Brønsted–Lowry definition applies to any physical state. (b) HCl is the Brønsted–Lowry acid; NH_3 is the Brønsted–Lowry base. **16.15** (a) (i) IO_3^- (ii) NH_3 (b) (i) OH^- (ii) H_3PO_4

16.17

Acid +	Base $\rightleftharpoons$	Conjugate Acid +	Conjugate Base
(a) $NH_4^+(aq)$	$CN^-(aq)$	$HCN(aq)$	$NH_3(aq)$
(b) $H_2O(l)$	$(CH_3)_3N(aq)$	$(CH_3)_3NH^+(aq)$	$OH^-(aq)$
(c) $HCOOH(aq)$	$PO_4^{3-}(aq)$	$HPO_4^{2-}(aq)$	$HCOO^-(aq)$

16.19 (a) Acid:
$HC_2O_4^-(aq) + H_2O(l) \rightleftharpoons C_2O_4^{2-}(aq) + H_3O^+(aq)$;
Base: $HC_2O_4^-(aq) + H_2O(l) \rightleftharpoons H_2C_2O_4(aq) + OH^-(aq)$.
(b) $H_2C_2O_4$ is the conjugate acid of $HC_2O_4^-$. $C_2O_4^{2-}$ is the conjugate base of $HC_2O_4^-$. **16.21** (a) CH_3COO^-, weak base; CH_3COOH, weak acid (b) HCO_3^-, weak base; H_2CO_3, weak acid (c) O_2^-, strong base; OH^-, strong base (d) Cl^-, negligible base; HCl, strong acid (e) NH_3, weak base; NH_4^+, weak acid **16.23** (a) HBr. It is one of the seven strong acids. (b) F^-. HCl is a stronger acid than HF, so F^- is the stronger conjugate base. **16.25** (a) $OH^-(aq) + OH^-(aq)$, the equilibrium lies to the right. (b) $H_2S(aq) + CH_3COO^-(aq)$, the equilibrium lies to the right. (c) $HNO_3(aq) + OH^-(aq)$, the equilibrium lies to the left. **16.27** (a) No. In pure water, the only source of H^+ is the autoionization reaction, which produces equal concentrations of H^+ and OH^-. As the temperature of water changes, the value of K_w changes, and the pH at which $[H^+] = [OH^-]$ changes. **16.29** (a) $[H^+] = 2.2 \times 10^{-11}\,M$, basic (b) $[H^+] = 1.1 \times 10^{-6}\,M$, acidic (c) $[H^+] = 1.0 \times 10^{-8}\,M$, basic **16.31** $[H^+] = [OH^-] = 3.5 \times 10^{-8}\,M$ **16.33** (a) $[H^+]$ changes by a factor of 100. (b) $[H^+]$ changes by afactor of 3.2 **16.35** (a) $[H^+]$ decreases, pH increases (b) The pH is between 3 and 4. By calculation, pH = 3.2; the solution is acidic. (c) pH = 5.2 is between pH 5 and pH 6, closer to pH = 5. A good estimate is $7 \times 10^{-6}\,M$ H^+ and $3 \times 10^{-9}\,M$ OH^-. By calculation, $[H^+] = 6 \times 10^{-6}\,M$ and $[OH^-] = 2 \times 10^{-9}\,M$.

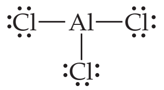
16.37

$[H^+]$	$[OH^-]$	pH	pOH	Acidic or Basic
$7.5 \times 10^{-3}\,M$	$1.3 \times 10^{-12}\,M$	2.12	11.88	acidic
$2.8 \times 10^{-5}\,M$	$3.6 \times 10^{-10}\,M$	4.56	9.44	acidic
$5.6 \times 10^{-9}\,M$	$1.8 \times 10^{-6}\,M$	8.25	5.75	basic
$5.0 \times 10^{-9}\,M$	$2.0 \times 10^{-6}\,M$	8.30	5.70	basic

16.39 $[H^+] = 4.0 \times 10^{-8}\,M$, $[OH^-] = 6.0 \times 10^{-7}\,M$, pOH = 6.22 **16.41** (a) A strong acid is completely ionized in aqueous solution. (b) $[H^+] = 0.500\,M$ (c) HCl, HBr, HI **16.43** (a) $[H^+] = 8.5 \times 10^{-3}\,M$, pH = 2.07 (b) $[H^+] = 0.0419\,M$, pH = 1.377 (c) $[H^+] = 0.0250\,M$, pH = 1.602 (d) $[H^+] = 0.167\,M$, pH = 0.778 **16.45** (a) $[OH^-] = 3.0 \times 10^{-3}\,M$, pH = 11.48 (b) $[OH^-] = 0.3758\,M$, pH = 13.5750 (c) $[OH^-] = 8.75 \times 10^{-5}\,M$, pH = 9.942 (d) $[OH^-] = 0.17\,M$, pH = 13.23 **16.47** $3.2 \times 10^{-3}\,M$ NaOH **16.49** (a) $HBrO_2(aq) \rightleftharpoons H^+(aq) + BrO_2^-(aq)$, $K_a = [H^+][BrO_2^-]/[HBrO_2]$; $HBrO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + BrO_2^-(aq)$, $K_a = [H_3O^+][BrO_2^-]/[HBrO_2]$ (b) $C_2H_5COOH(aq) \rightleftharpoons H^+(aq) + C_2H_5COO^-(aq)$, $K_a = [H^+][C_2H_5COO^-]/[C_2H_5COOH]$; $C_2H_5COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_5COO^-(aq)$, $K_a = [H_3O^+][C_2H_5COO^-]/[C_2H_5COOH]$ **16.51** $K_a = 1.4 \times 10^{-4}$ **16.53** $[H^+] = [ClCH_2COO^-] = 0.0110\,M$, $[ClCH_2COOH] = 0.089\,M$, $K_a = 1.4 \times 10^{-3}$ **16.55** $0.089\,M$ CH_3COOH **16.57** $[H^+] = [C_6H_5COO^-] = 1.8 \times 10^{-3}\,M$, $[C_6H_5COOH] = 0.048\,M$
16.59 (a) $[H^+] = 1.1 \times 10^{-3}\,M$, pH = 2.95
(b) $[H^+] = 1.7 \times 10^{-4}\,M$, pH = 3.76 (c) $[OH^-] = 1.4 \times 10^{-5}\,M$, pH = 9.15 **16.61** $[H^+] = 2.0 \times 10^{-2}\,M$, pH = 1.71 **16.63** (a) $[H^+] = 2.8 \times 10^{-3}\,M$, 0.69% ionization (b) $[H^+] = 1.4 \times 10^{-3}\,M$, 1.4% ionization (c) $[H^+] = 8.7 \times 10^{-4}\,M$, 2.2% ionization **16.65** $HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)$; $K_a = [H^+][X^-]/[HX]$. Assume that the percent of acid that ionizes is small. Let $[H^+] = [X^-] = y$, $K_a = y^2/[HX]$; $y = K_a^{1/2}[HX]^{1/2}$. Percent ionization = $y/[HX] \times 100$. Substituting for y, percent ionization = $100\,K_a^{1/2}[HX]^{1/2}/[HX]$ or $100\,K_a^{1/2}/[HX]^{1/2}$. That is, percent ionization varies inversely as the square root of the concentration of HX. **16.67** $[H^+] = 5.1 \times 10^{-3}M$, pH = 2.29, $[C_6H_5O_7^{3-}] = 1.3 \times 10^{-9}\,M$. The approximation that the first ionization is less than 5% of the total acid concentration is not valid; the quadratic equation must be solved. The $[H^+]$ produced from the second and third ionizations is small with respect to that present from the first step; the second and third ionizations can be neglected when calculating the $[H^+]$ and pH. $[C_6H_5O_7^{3-}]$ is much less than $[H^+]$. **16.69** (a) $HONH_3^+$ (b) When hydroxylamine acts as a base, the nitrogen atom accepts a proton. (c) In hydroxylamine, O and N are the atoms with nonbonding electron pairs; in the neutral molecule both have zero formal charges. Nitrogen is less electronegative than oxygen and more likely to share a lone pair of electrons with an incoming (and electron-deficient) H^+. The resulting cation with the +1 formal charge on N is more stable than the one with the +1 formal charge on O. **16.71** (a) $(CH_3)_2NH(aq) + H_2O(l) \rightleftharpoons (CH_3)_2NH_2^+(aq) + OH^-(aq)$; $K_b = [(CH_3)_2NH_2^+][OH^-]/[(CH_3)_2NH]$
(b) $CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$;
$K_b = [HCO_3^-][OH^-]/[(CO_3^{2-})]$ (c) $HCOO^-(aq) + H_2O(l) \rightleftharpoons HCOOH(aq) + OH^-(aq)$ $K_b = [HCOOH][OH^-]/[HCOO^-]$
16.73 From the quadratic formula, $[OH^-] = 6.6 \times 10^{-3}\,M$,
pH = 11.82. **16.75** (a) $[C_{10}H_{15}ON] = 0.033\,M$, $[C_{10}H_{15}ONH^+] = [OH^-] = 2.1 \times 10^{-3}\,M$ (b) $K_b = 1.4 \times 10^{-4}$ **16.77** (a) For a conjugate acid/conjugate base pair such as $C_6H_5OH/C_6H_5O^-$, K_b for the conjugate base can always be calculated from K_a for the conjugate acid, so a separate list of K_b values is not necessary. (b) $K_b = 7.7 \times 10^{-5}$ (c) Phenolate is a stronger base than NH_3. **16.79** (a) Acetic acid is stronger. (b) Hypochlorite ion is the stronger base. (c) For CH_3COO^-, $K_b = 5.6 \times 10^{-10}$; for ClO^-, $K_b = 3.3 \times 10^{-7}$. **16.81** (a) $[OH^-] = 6.3 \times 10^{-4}\,M$, pH = 10.80 (b) $[OH^-] = 9.2 \times 10^{-5}\,M$, pH = 9.96 (c) $[OH^-] = 3.3 \times 10^{-6}\,M$, pH = 8.52 **16.83** (a) Acidic (b) acidic (c) basic (d) neutral (e) acidic **16.85** K_b for the anion of the unknown salt is 1.4×10^{-11}; K_a for the conjugate acid is 7.1×10^{-4}. The conju-

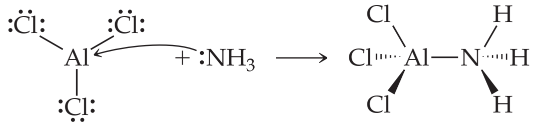
gate acid is HF and the salt is NaF. **16.87** (a) As the electronegativity of the central atom (X) increases, the strength of the oxyacid increases. (b) As the number of nonprotonated oxygen atoms in the molecule increases, the strength of the oxyacid increases. **16.89** (a) HNO_3 is a stronger acid because it has one more nonprotonated oxygen atom and thus a higher oxidation number on N. (b) For binary hydrides, acid strength increases going down a family, so H_2S is a stronger acid than H_2O. (c) H_2SO_4 is a stronger acid because H^+ is much more tightly held by the anion HSO_4^-. (d) For oxyacids, the greater the electronegativity of the central atom, the stronger the acid, so H_2SO_4 is the stronger acid. (e) CCl_3COOH is stronger because the electronegative Cl atoms withdraw electron density from other parts of the molecule, which weakens the O—H bond and stabilizes the anionic conjugate base. Both effects favor increased ionization and acid strength. **16.91** (a) BrO^- (b) BrO^- (c) HPO_4^{2-} **16.93** (a) True (b) False. In a series of acids that have the same central atom, acid strength increases with the number of nonprotonated oxygen atoms bonded to the central atom. (c) False. H_2Te is a stronger acid than H_2S because the H—Te bond is longer, weaker, and more easily ionized than the H—S bond. **16.95** Yes. The Arrhenius definition of a base, an $OH^-(aq)$ donor, is most restrictive; the Brønsted definition, an H^+ acceptor, is more general; and the Lewis definition, an electron-pair donor, is most general. Any substance that fits the narrow Arrhenius definition will fit the broader Brønsted and Lewis definitions. **16.97** (a) Acid, $Fe(ClO_4)_3$ or Fe^{3+}; base, H_2O (b) Acid, H_2O; base, CN^- (c) Acid, BF_3; base, $(CH_3)_3N$ (d) Acid, HIO; base, NH_2^- **16.99** (a) Cu^{2+}, higher cation charge (b) Fe^{3+}, higher cation charge (c) Al^{3+}, smaller cation radius, same charge **16.101** $(C_2H_5)_3N$ is a stronger base than NH_3 by virture of its smaller pK_b. **16.104** $K = 3.3 \times 10^7$ **16.107** (a) For solutions with equal concentrations, the weaker acid will have a lower $[H^+]$ and higher pH. (b) The acid with $K_a = 8 \times 10^{-5}$ is the weaker acid, so it has the higher pH. (c) The base with $pK_b = 4.5$ is the stronger base, has the greater $[OH^-]$ and smaller $[H^+]$, so higher pH. **16.109** $K_a = 1.4 \times 10^{-5}$ **16.115** 6.0×10^{13} H^+ ions **16.118** (a) To the precision of the reported data, the pH of rainwater 40 years ago was 5.4, no different from the pH today. With extra significant figures, $[H^+] = 3.61 \times 10^{-6}\,M$, pH $= 5.443$ (b) A 20.0-L bucket of today's rainwater contains 0.02 L (with extra significant figures, 0.0200 L) of dissolved CO_2.

16.119 (a)



The electron-domain geometry and molecular structure are trigonal planar. (b) The Al atom is electron deficient. It acts like a Lewis acid in order to complete its octet.

(c)



(d) The Lewis theory is most appropriate. H^+ and $AlCl_3$ are both electron pair acceptors. **16.121** Rx 1, $\Delta H = 104\,kJ$; Rx 2, $\Delta H = -32\,kJ$. Reaction 2 is exothermic while reaction 1 is endothesmic. For binary acids with heavy atoms (X) in the same family, the longer and weaker the H—X bond, the stronger the acid (and the more exothermic the ionization reaction). **16.124** (a) $K(i) = 5.6 \times 10^3$, $K(ii) = 10$ (b) Both (i) and (ii) have $K > 1$, so both could be written with a single arrow.

CHAPTER 17

17.1 The middle box has the highest pH. For equal amounts of acid HX, the greater the amount of conjugate base X^-, the smaller the amount of H^+ and the higher the pH. **17.4** (a) Drawing 3 (b) Drawing 1 (c) Drawing 2 **17.7** (a) The red curve corresponds to the more concentrated acid solution. (b) On the titration curve of a weak acid, pH $= pK_a$ at the volume halfway to the equivalence point. At this volume, the red curve has the smaller pK_a and the larger K_a. **17.10** (a) $Q = 4.67 \times 10^{-6}$; $Q < K_{sp}$ and the solution is not saturated. (b) $Ca(OH)_2$ precipitate forms in beaker (iii). **17.13** (a) The extent of ionization of a weak electrolyte is decreased when a strong electrolyte containing an ion in common with the weak electrolyte is added to it. (b) $NaNO_2$ **17.15** (a) $[H^+] = 1.8 \times 10^{-5}\,M$, pH $= 4.73$ (b) $[OH^-] = 4.8 \times 10^{-5}\,M$, pH $= 9.68$ (c) $[H^+] = 1.4 \times 10^{-5}\,M$, pH $= 4.87$ **17.17** (a) 4.5% ionization (b) 0.018% ionization **17.19** In a mixture of CH_3COOH and CH_3COONa, CH_3COOH reacts with added base and CH_3COO^- combines with added acid, leaving $[H^+]$ relatively unchanged. Although HCl and Cl^- are a conjugate acid–base pair, Cl^- has no tendency to combine with added acid to form undissociated HCl. Any added acid simply increases $[H^+]$ in an HCl—NaCl mixture. **17.21** (a) pH $= 3.82$ (b) pH $= 3.96$ **17.23** (a) pH $= 5.26$ (b)

$$Na^+(aq) + CH_3COO^-(aq) + H^+(aq) + Cl^-(aq) \longrightarrow CH_3COOH(aq) + Na^+(aq) + Cl^-(aq)$$

(c)

$$CH_3COOH(aq) + Na^+(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + H_2O(l) + Na^+(aq)$$

17.25 (a) pH $= 1.58$ (b) 36 g NaF **17.27** (a) pH $= 4.86$ (b) pH $= 5.0$ (c) pH $= 4.71$ **17.29** (a) $[HCO_3^-]/[H_2CO_3] = 11$ (b) $[HCO_3^-]/[H_2CO_3] = 5.4$ **17.31** 360 mL of 0.10 M HCOONa, 640 mL of 0.10 M HCOOH **17.33** (a) Curve B (b) pH at the approximate equivalence point of curve A $= 8.0$, pH at the approximate equivalence point of curve B $= 7.0$ (c) For equal volumes of A and B, the concentration of acid B is greater, since it requires a larger volume of base to reach the equivalence point. **17.35** (a) False (b) true (c) true **17.37** (a) Above pH 7 (b) below pH 7 (c) at pH 7 **17.39** The second color change of Thymol blue is in the correct pH range to show the equivalence point of the titration of a weak acid with a strong base. **17.41** (a) 42.4 mL NaOH soln (b) 35.0 mL NaOH soln (c) 29.8 mL NaOH soln **17.43** (a) pH $= 1.54$ (b) pH $= 3.30$ (c) pH $= 7.00$ (d) pH $= 10.69$ (e) pH $= 12.74$ **17.45** (a) pH $= 2.78$ (b) pH $= 4.74$ (c) pH $= 6.58$ (d) pH $= 8.81$ (e) pH $= 11.03$ (f) pH $= 12.42$ **17.47** (a) pH $= 7.00$ (b) $[HONH_3^+] = 0.100\,M$, pH $= 3.52$ (c) $[C_6H_5NH_3^+] = 0.100\,M$, pH $= 2.82$ **17.49** (a) The concentration of undissolved solid does not appear in the solubility product expression because it is constant. (b) $K_{sp} = [Ag^+][I^-]$; $K_{sp} = [Sr^{2+}][SO_4^{2-}]$; $K_{sp} = [Fe^{2+}][OH^-]^2$; $K_{sp} = [Hg_2^{2+}][Br^-]^2$ **17.51** (a) $K_{sp} = 7.63 \times 10^{-9}$ (b) $K_{sp} = 2.7 \times 10^{-9}$ (c) 5.3×10^{-4} mol $Ba(IO_3)_2$/L **17.53** $K_{sp} = 2.3 \times 10^{-9}$ **17.55** (a) 7.1×10^{-7} mol AgBr/L (b) 1.7×10^{-11} mol AgBr/L (c) 5.0×10^{-12} mol AgBr/L **17.57** (a) The amount of $CaF_2(s)$ on the bottom of the beaker increases. (b) The $[Ca^{2+}]$ in solution increases. (c) The $[F^-]$ in solution decreases. **17.59** (a) 1.4×10^3 g $Mn(OH)_2$/L (b) 0.014 g/L (c) 3.6×10^{-7} g/L **17.61** More soluble in acid: (a) $ZnCO_3$ (b) ZnS (d) AgCN (e) $Ba_3(PO_4)_2$ **17.63** $[Ni^{2+}] = 1 \times 10^{-8}\,M$ **17.65** (a) 9.1×10^{-9} mol AgI/L pure water (b) $K = K_{sp} \times K_f = 8 \times 10^4$ (c) 0.0500 mol AgI/L 0.100 M NaCN **17.67** (a) $Q < K_{sp}$; no $Ca(OH)_2$ precipitates (b) $Q < K_{sp}$; no Ag_2SO_4 precipitates **17.69** pH $= 11.5$ **17.71** AgI will precipitate first, at $[I^-] = 4.2 \times 10^{-13}\,M$. **17.73** AgCl will precipitate first. **17.75** The first two experiments eliminate group 1 and 2 ions (Figure 17.23). The absence of insoluble phosphate precipitates in the filtrate from the third experiment rules out group 4 ions. The ions that might be in the sample are those from group 3, Al^{3+}, Fe^{3+}, Cr^{3+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, or Co^{2+}, and from group 5, NH_4^+, Na^+, or K^+. **17.77** (a) Make the solution acidic with 0.2 M HCl; saturate with H_2S. CdS will precipitate; ZnS will not. (b) Add excess base; $Fe(OH_3)(s)$ precipitates, but Cr^{3+} forms the soluble complex $Cr(OH)_4^-$. (c) Add $(NH_4)_2HPO_4$; Mg^{2+} precipitates as $MgNH_4PO_4$; K^+ remains soluble. (d) Add 6 M HCl; precipitate Ag^+ as $AgCl(s)$; Mn^{2+} remains soluble. **17.79** (a) Base is required to increase $[PO_4^{3-}]$ so that the solubility product of the metal phosphates of interest is exceeded and the phosphate salts precipitate. (b) K_{sp} for the cations in group 3 is much larger, and so to exceed K_{sp}, a higher $[S^{2-}]$ is required. (c) They should all redissolve in strongly acidic solution.

17.81 $\mathrm{pOH} = \mathrm{p}K_b + \log\{|\mathrm{BH}^-|/|\mathrm{B}|\}$ **17.83** (a) $\mathrm{pH} = 3.171$ (b) $\mathrm{pH} = 2.938$ (c) $\mathrm{pH} = 12.862$ **17.86** (a) pH of buffer A = pH of buffer B = 3.74. For buffers containing the same conjugate acid and base components, the pH is determined by the ratio of concentrations of conjugate acid and base. Buffers A and B have the same ratio of concentrations, so their pH values are equal. (b) Buffer capacity is determined by the absolute amount of buffer components available to absorb strong acid or strong base. Buffer A has the greater capacity because it contains the greater absolute concentrations of HCOOH and $\mathrm{HCOO^-}$. (c) Buffer A: $\mathrm{pH} = 3.74$, $\Delta\mathrm{pH} = 0.00$; buffer B: $\mathrm{pH} = 3.66$, $\Delta\mathrm{pH} = -0.12$ (d) Buffer A: $\mathrm{pH} = 3.74$, $\Delta\mathrm{pH} = 0.00$; buffer B: $\mathrm{pH} = 2.74$, $\Delta\mathrm{pH} = -1.00$ (e) The results of parts (c) and (d) are quantitative confirmation that buffer A has a significantly greater capacity than buffer B. **17.88** (a) molar mass = 82.2 g/mol (b) $K_a = 3.8 \times 10^{-7}$ **17.90** At the halfway point, mol HA = mol $\mathrm{A^-}$ and $[\mathrm{HA}] = [\mathrm{A^-}]$.

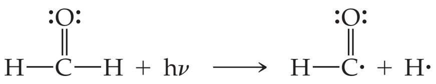
$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\text{conj. base}]}{[\text{conj. acid}]} = \mathrm{p}K_a + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA^-}]}.\ \text{If } [\mathrm{A^-}]/[\mathrm{HA}] = 1,$$

$\log(1) = 0$ and $\mathrm{pH} = \mathrm{p}K_a$ of the weak acid being titrated. **17.92** $\mathrm{pH} = 7.75$ **17.93** 1.6 L of 1.0 M NaOH **17.96** (a) CdS (b) $\mathrm{BaCrO_4}$ (c) $\mathrm{NiCO_3}$ (d) $\mathrm{Ag_2SO_4}$ **17.100** The solubility of $\mathrm{Mg(OH)_2}$ in 0.50 M $\mathrm{NH_4Cl}$ is 0.11 mol/L **17.101** $[\mathrm{KMnO_4}] = [\mathrm{MnO_4^-}] = 0.11\,M$ **17.104** $[\mathrm{OH^-}] = 1.7 \times 10^{-11}\,M$, pH of the buffer = 3.22 **17.107** (a) The molar solubility of $\mathrm{Cd(OH)_2}$ is 1.8×10^{-5} mol/L. (b) The initial concentration of NaBr required to increase the molar solubility of $\mathrm{Cd(OH)_2}$ to 1.0×10^{-3} mol/L is 2 M. **17.108** (a) $\mathrm{H^+}(aq) + \mathrm{HCOO^-}(aq) \longrightarrow \mathrm{HCOOH}(aq)$ (b) $K = 5.6 \times 10^3$ (c) $[\mathrm{Na^+}] = [\mathrm{Cl^-}] = 0.075\,M$, $[\mathrm{H^+}] = [\mathrm{HCOO^-}] = 3.7 \times 10^{-3}\,M$, $[\mathrm{HCOOH}] = 0.071\,M$ **17.114** $[\mathrm{Sr^{2+}}] = [\mathrm{SO_4^{2-}}] = 5.7 \times 10^{-4}\,M$, $K_{sp} = 3.2 \times 10^{-7}$

CHAPTER 18

18.1 (a) A greater volume than 22.4 L (b) The gas will occupy more volume at 85 km than at 50 km. (c) We expect gases to behave most ideally in the thermosphere, around the stratopause and in the troposphere at low altitude. **18.6** *Salt water* contains high concentrations of dissolved salts and solids. It includes the world ocean (97.2% of all water, approximately 35,000 ppm of dissolved salts) and brackish or salty water (0.1% of all water). *Freshwater* (0.6% of all water on earth) refers to natural waters that have low concentrations (less than 500 ppm) of dissolved salts and solids. It includes the waters of lakes, rivers, ponds, and streams. *Groundwater* is freshwater that is under the soil. It resides in aquifers, porous rock that holds water, and composes 20% of the world's freshwater. **18.9** The basic goals of green chemistry are to minimize or eliminate solvents and waste, generate nontoxic waste, be energy efficient, employ renewable starting materials, and take advantage of catalysts that enable the use of safe and common reagents. **18.11** (a) Its temperature profile (b) troposphere, 0 to 12 km; stratosphere, 12 to 50 km; mesosphere, 50 to 85 km; thermosphere, 85 to 110 km **18.13** (a) The partial pressure of $\mathrm{O_3}$ is 3.0×10^{-7} atm (2.2×10^{-4} torr). (b) 7.3×10^{15} $\mathrm{O_3}$ molecules/1.0 L air **18.15** 8.6×10^{16} CO molecules/1.0 L air **18.17** (a) 570 nm (b) visible electromagnetic radiation **18.19** (a) *Photodissociation* is cleavage of a bond such that two neutral species are produced. *Photoionization* is absorption of a photon with sufficient energy to eject an electron, producing an ion and the ejected electron. (b) Photoionization of $\mathrm{O_2}$ requires 1205 kJ/mol. Photodissociation requires only 495 kJ/mol. At lower elevations, high-energy short-wavelength solar radiation has already been absorbed. Below 90 km, the increased concentration of $\mathrm{O_2}$ and the availability of longer-wavelength radiation cause the photodissociation process to dominate. **18.21** Ozone depletion reactions, which involve only $\mathrm{O_3}$, $\mathrm{O_2}$, or O (oxidation state = 0), do not involve a change in oxidation state for oxygen atoms. Reactions involving ClO and one of the oxygen species with a zero oxidation state do involve a change in the oxidation state of oxygen atoms. **18.23** (a) A chlorofluorocarbon is a compound that contains chlorine, fluorine, and carbon, while a hydrofluorocarbon is a compound that contains hydrogen, fluorine, and carbon. An HFC contains hydrogen in place of the chlorine present in a CFC. (b) HFCs are potentially less harmful than CFCs because their photodissociation does not produce Cl atoms, which catalyze the destruction of ozone. **18.25** (a) The C—F bond requires more energy for dissociation than the C—Cl bond and is not readily cleaved by the available wavelengths of UV light. (b) Chlorine is present as chlorine atoms and chlorine oxide molecules, Cl and ClO, respectively. **18.27** (a) Methane, $\mathrm{CH_4}$, arises from decomposition of organic matter by certain microorganisms; it also escapes from underground gas deposits. (b) $\mathrm{SO_2}$ is released in volcanic gases and also is produced by bacterial action on decomposing vegetable and animal matter. (c) Nitric oxide, NO, results from oxidation of decomposing organic matter and is formed in lightning flashes. **18.29** (a) $\mathrm{H_2SO_4}(aq) + \mathrm{CaCO_3}(s) \longrightarrow \mathrm{CaSO_4}(s) + \mathrm{H_2O}(l) + \mathrm{CO_2}(g)$ (b) The $\mathrm{CaSO_4}(s)$ would be much less reactive with acidic solution, since it would require a strongly acidic solution to shift the relevant equilibrium to the right: $\mathrm{CaSO_4}(s) + 2\,\mathrm{H^+}(aq) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + 2\,\mathrm{HSO_4^-}(aq)$. $\mathrm{CaSO_4}$ would protect $\mathrm{CaCO_3}$ from attack by acid rain, but it would not provide the structural strength of limestone. **18.31** (a) Ultraviolet (b) 357 kJ/mol (c) The average C—H bond energy from Table 8.4 is 413 kJ/mol. The C—H bond energy in $\mathrm{CH_2O}$, 357 kJ/mol, is less than the "average" C—H bond energy.

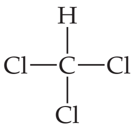
(d)

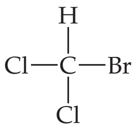


$$\mathrm{H{-}C({=}\ddot{O}{:}){-}H} + h\nu \longrightarrow \mathrm{H{-}\dot{C}({=}\ddot{O}{:})} + \mathrm{H}\cdot$$

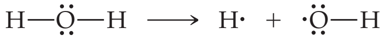
18.33 Incoming and outgoing energies are in different regions of the electromagnetic spectrum. $\mathrm{CO_2}$ is transparent to incoming visible radiation but absorbs outgoing infrared radiation. **18.35** 0.099 M $\mathrm{Na^+}$ **18.37** (a) 3.22×10^3 g $\mathrm{H_2O}$ (b) The final temperature is 43.4°C. **18.39** 4.361×10^5 g CaO **18.41** (a) *Groundwater* is freshwater (less than 500 ppm total salt content) that is under the soil; it composes 20% of the world's freshwater. (b) An *aquifer* is a layer of porous rock that holds groundwater. **18.43** The minimum pressure required to initiate reverse osmosis is greater than 5.1 atm. **18.45** (a) $\mathrm{CO_2}(g)$, $\mathrm{HCO_3^-}$, $\mathrm{H_2O}(l)$, $\mathrm{SO_4^{2-}}$, $\mathrm{NO_3^-}$, $\mathrm{HPO_4^{2-}}$, $\mathrm{H_2PO_4^-}$ (b) $\mathrm{CH_4}(g)$, $\mathrm{H_2S}(g)$, $\mathrm{NH_3}(g)$, $\mathrm{PH_3}(g)$ **18.47** 25.1 g $\mathrm{O_2}$ **18.49** $\mathrm{Mg^{2+}}(aq) + \mathrm{Ca(OH)_2}(s) \longrightarrow \mathrm{Mg(OH)_2}(s) + \mathrm{Ca^{2+}}(aq)$ **18.51** 0.42 mol $\mathrm{Ca(OH)_2}$, 0.18 mol $\mathrm{Na_2CO_3}$ **18.53** $4\,\mathrm{FeSO_4}(aq) + \mathrm{O_2}(aq) + 2\,\mathrm{H_2O}(l) \longrightarrow 4\,\mathrm{Fe^{3+}}(aq) + 4\,\mathrm{OH^-}(aq) + 4\,\mathrm{SO_4^{2-}}(aq)$; $\mathrm{Fe^{3+}}(aq) + 3\,\mathrm{HCO_3^-}(aq) \longrightarrow \mathrm{Fe(OH)_3}(s) + 3\,\mathrm{CO_2}(g)$ **18.55** (a) *Trihalomethanes* are the by-products of water chlorination; they contain one central carbon atom bound to one hydrogen and three halogen atoms.

(b)





18.57 The fewer steps in a process, the less waste is generated. Processes with fewer steps require less energy at the site of the process and for subsequent cleanup or disposal of waste. **18.59** (a) $\mathrm{H_2O}$ (b) It is better to prevent waste than to treat it. Atom economy. Less hazardous chemical synthesis and inherently safer for accident prevention. Catalysis and design for energy efficiency. Raw materials should be renewable. **18.61** (a) Water as a solvent, by criteria 5, 7, and 12. (b) Reaction temperature of 500 K, by criteria 6, 12, and 1. (c) Sodium chloride as a by-product, according to criteria 1, 3, and 12. **18.66** Multiply Equation 18.7 by a factor of 2; then add it to Equation 18.9. 2 Cl(g) and 2 ClO(g) cancel from each side of the resulting equation to produce Equation 18.10. **18.69** Although HFCs have long lifetimes in the stratosphere, it is infrequent that light with energy sufficient to dissociate a C−F bond will reach an HFC molecule. F atoms, the bad actors in ozone destruction, are much less likely than Cl atoms to be produced by photodissociation in the stratosphere. **18.71** The formation of NO(g) is endothermic, so K increases with increasing temperature. The oxidation of NO(g) to $NO_2(g)$ is exothermic, so the value of K decreases with increasing temperature. **18.75** $7.1 \times 10^8\ m^2$ **18.77** (a)CO_3^{2-} is a relatively strong Brønsted–Lowry base and produces OH^- in aqueous solution. If $[OH^-(aq)]$ is sufficient for the reaction quotient to exceed K_{sp} for $Mg(OH)_2$, the solid will precipitate. (b) At these ion concentrations, $Q > K_{sp}$ and $Mg(OH)_2$ will precipitate. **18.81** (a) 2.5×10^7 ton CO_2, 4.2×10^5 ton SO_2 (b) 4.3×10^5 ton $CaSO_3$ **18.84** (a)



$$H-\underset{..}{\ddot{O}}-H \longrightarrow H\cdot + \cdot\underset{..}{\ddot{O}}-H$$

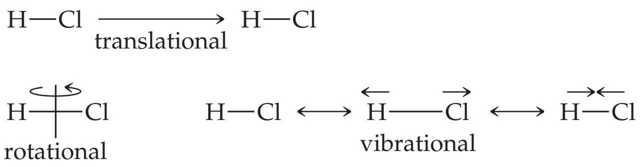
(b) 258 nm (c) The overall reaction is $O_3(g) + O(g) \longrightarrow 2\,O_2(g)$. OH($g$) is the catalyst in the overall reaction because it is consumed and then reproduced. **18.86** The enthalpy change for the first step is −141 kJ, for the second step, −249 kJ, for the overall reaction, −390 kJ. **18.90** (a) Rate $= k[O_3][H]$ (b) $k_{avg} = 1.13 \times 10^{44}\ M^{-1}\ s^{-1}$ **18.95** (a) Process (i) is greener because it involves neither the toxic reactant phosgene nor the by-product HCl. (b) Reaction (i): C in CO_2 is linear with sp hybridization; C in R—N=C=O is linear with sp hybridization; C in the urethane monomer is trigonal planar with sp^2 hybridization. Reaction (ii): C in $COCl_2$ is linear with sp^2 hybridization; C in R—N=C=O is linear with sp hybridization; C in the urethane monomer is trigonal planar with sp^2 hybridization. (c) The greenest way to promote formation of the isocyanate is to remove by-product, either water or HCl, from the reaction mixture.

CHAPTER 19

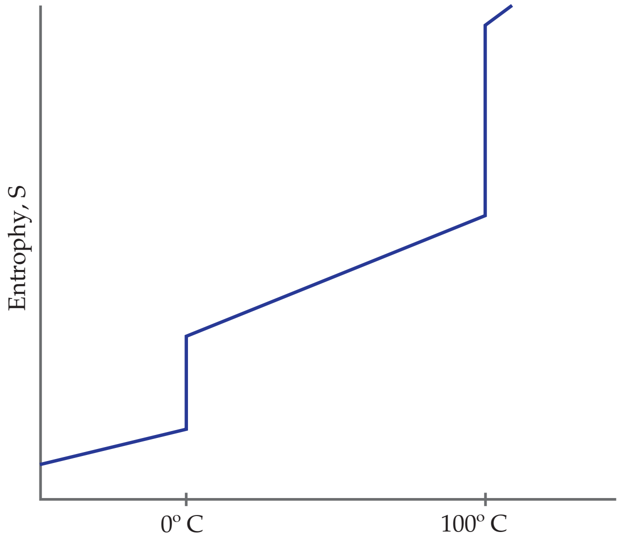
19.1 (a)

(b) $\Delta H = 0$ for mixing ideal gases. ΔS is positive because the disorder of the system increases. (c) The process is spontaneous and therefore irreversible. (d) Since $\Delta H = 0$, the process does not affect the entropy of the surroundings. **19.4** ΔS is positive. **19.7** (a) At 300 K, $\Delta G = 0$, and the system is at equilibrium. (b) The reaction is spontaneous at temperatures above 300 K. **19.10** (a) The minimum in the plot is the equilibrium position of the reaction. (b) The quantity x is $\Delta G°$. **19.11** Spontaneous: a, b, c, d; nonspontaneous: e **19.13** (a) $NH_4NO_3(s)$ dissolves in water, as in a chemical cold pack. Naphthalene (moth balls) sublimes at room temperature. (b) Melting of a solid is spontaneous above its melting point but nonspontaneous below its melting point. **19.15** (a) Endothermic (b) above 100 °C (c) below 100 °C (d) at 100 °C **19.17** (a) For a *reversible* process, the forward and reverse changes occur by the same path. In a reversible process, both the system and the surroundings are restored to their original condition by exactly reversing the change. A reversible change produces the maximum amount of work. (b) There is no net change in the surroundings. (c) The vaporization of water to steam is reversible if it occurs at the boiling temperature of water for a specified external (atmospheric) pressure and if the required heat is added infinitely slowly. (d) No. Natural processes are spontaneous in the direction they occur and nonspontaneous in the opposite direction. By definition they are irreversible. **19.19** (a) If the ideal gas is contained in a closed system at constant volume, a decrease in external temperature leads to a decrease in both temperature and pressure of the gas. (b) If the ideal gas is contained in a closed system at constant pressure, a decrease in external temperature leads to a decrease in both temperature and volume of the gas. (c) No. ΔE is a state function. $\Delta E = q + w$; q and w are not state functions. Their values do depend on path, but their sum, ΔE, does not. **19.21** (a) An ice cube can melt reversibly at the conditions of temperature and pressure where the solid and liquid are in equilibrium. (b) We know that melting is a process that increases the energy of the system even though there is no change in temperature. ΔE is not zero for the process. **19.23** (a) At constant temperature, $\Delta S = q_{rev}/T$, where q_{rev} is the heat that would be transferred if the process were reversible. (b) No. ΔS is a state function, so it is independent of path. **19.25** (a) Entropy increases. (b) 89.2 J/K **19.27** (a) For a spontaneous process, the entropy of the universe increases; for a reversible process, the entropy of the universe does not change. (b) For a reversible process, if the entropy of the system increases, the entropy of the surroundings must decrease by the same amount. (c) For a spontaneous process, the entropy of the universe must increase, so the entropy of the surroundings must decrease by less than 42 J/K. **19.29** (a) Positive ΔS (b) $\Delta S = 1.02$ J/K (c) Temperature need not be specified to calculate ΔS, as long as the expansion is isothermal. **19.31** (a) Yes, the expansion is spontaneous. (b) As the ideal gas expands into the vacuum, there is nothing for it to "push back," so no work is done. Mathematically, $w = -P_{ext}\Delta V$. Since the gas expands into a vacuum, $P_{ext} = 0$ and $w = 0$. (c) The "driving force" for the expansion of the gas is the increase in entropy. **19.33** (a) An increase in temperature produces more available microstates for a system. (b) A decrease in volume produces fewer available microstates for a system. (c) Going from liquid to gas, the number of available microstates increases. **19.35** (a) ΔS is positive. (b) S of the system clearly increases in 19.11 (b) and (e); it clearly decreases in 19.9 (c). The entropy change is difficult to judge in 19.9 (a) and definition of the system in (d) is problematic. **19.37** S increases in (a) and (c); S decreases in (b). **19.39** (a) The entropy of a pure crystalline substance at absolute zero is zero. (b) In translational motion the entire molecule moves in a single direction; in rotational motion the molecule rotates or spins around a fixed axis. In vibrational motion the bonds within a molecule stretch and bend, but the average position of the atoms does not change.

(c)



19.41 (a) Ar(g) (b) He(g) at 1.5 atm (c) 1 mol of Ne(g) in 15.0 L (d) $CO_2(g)$ **19.43** (a) $\Delta S < 0$ (b) $\Delta S > 0$ (c) $\Delta S < 0$ (d) $\Delta S \approx 0$ **19.45** (a)



(b) Boiling water, at 100 °C, has a much larger entropy change than melting ice at 0 °C. **19.47** (a) $C_2H_6(g)$ (b) $CO_2(g)$ **19.49** (a) Sc(s), 34.6 J/mol-K; Sc(g), 174.7 J/mol-K. In general, the gas phase of a substance has a larger $S°$ than the solid phase because of the greater volume and motional freedom of the molecules. (b) $NH_3(g)$, 192.5 J/mol-K; $NH_3(aq)$, 111.3 J/mol-K. Molecules in the gas phase have more motional freedom than molecules in solution. (c) 1 mol of

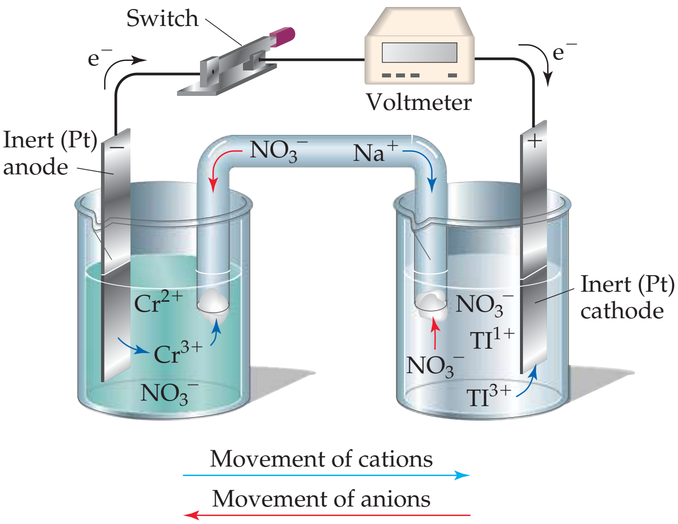
$P_4(g)$, 280 J/K; 2 mol of $P_2(g)$, $2(218.1) = 436.2$ J/K. More particles have a greater motional energy (more available microstates). (d) C (diamond), 2.43 J/mol-K; C (graphite), 5.69 J/mol-K. The internal entropy in graphite is greater because there is translational freedom among planar sheets of C atoms, while there is very little freedom within the covalent-network diamond lattice. **19.51** For elements with similar structures, the heavier the atoms, the lower the vibrational frequencies at a given temperature. This means that more vibrations can be accessed at a particular temperature, resulting in greater absolute entropy for the heavier elements. **19.53** (a) $\Delta S° = -120.5$ J/K. $\Delta S°$ is negative because there are fewer moles of gas in the products. (b) $\Delta S° = +176.6$ J/K. $\Delta S°$ is positive because there are more moles of gas in the products. (c) $\Delta S° = +152.39$ J/K. $\Delta S°$ is positive because the product contains more total particles and more moles of gas. (d) $\Delta S° = +92.3$ J/K. $\Delta S°$ is positive because there are more moles of gas in the products. **19.55** (a) $\Delta G = \Delta H - T\Delta S$ (b) If ΔG is positive, the process is nonspontaneous, but the reverse process is spontaneous. (c) There is no relationship between ΔG and rate of reaction. **19.57** (a) Exothermic (b) $\Delta S°$ is negative; the reaction leads to a decrease in disorder. (c) $\Delta G° = -9.9$ kJ (d) If all reactants and products are present in their standard states, the reaction is spontaneous in the forward direction at this temperature. **19.59** (a) $\Delta H° = -537.22$ kJ, $\Delta S° = 13.7$ J/K, $\Delta G° = -541.40$ kJ, $\Delta G° = \Delta H° - T\Delta S° = -541.31$ kJ (b) $\Delta H° = -106.7$ kJ, $\Delta S° = -142.2$ kJ, $\Delta G° = -64.0$ kJ, $\Delta G° = \Delta H° - T\Delta S° = -64.3$ kJ (c) $\Delta H° = -508.3$ kJ, $\Delta S° = -178$ kJ, $\Delta G° = -465.8$ kJ, $\Delta G° = \Delta H° - T\Delta S° = -455.1$ kJ. The discrepancy in $\Delta G°$ values is due to experimental uncertainties in the tabulated thermodynamic data. (d) $\Delta H° = -165.9$ kJ, $\Delta S° = 1.4$ kJ, $\Delta G° = -166.2$ kJ, $\Delta G° = \Delta H° - T\Delta S° = -166.3$ kJ **19.61** (a) $\Delta G° = -140.0$ kJ, spontaneous (b) $\Delta G° = +104.70$ kJ, nonspontaneous (c) $\Delta G° = +146$ kJ, nonspontaneous (d) $\Delta G° = -156.7$ kJ, spontaneous **19.63** (a) $2\,C_8H_{18}(l) + 25\,O_2(g) \longrightarrow 16\,CO_2(g) + 18\,H_2O(l)$ (b) Because $\Delta S°$ is positive, $\Delta G°$ is more negative than $\Delta H°$. **19.65** (a) The forward reaction is spontaneous at low temperatures but becomes nonspontaneous at higher temperatures. (b) The reaction is nonspontaneous in the forward direction at all temperatures. (c) The forward reaction is nonspontaneous at low temperatures but becomes spontaneous at higher temperatures. **19.67** $\Delta S > 60.8$ J/K **19.69** (a) $T = 330$ K (b) nonspontaneous **19.71** (a) $\Delta H° = 155.7$ kJ, $\Delta S° = 171.4$ kJ. Since $\Delta S°$ is positive, $\Delta G°$ becomes more negative with increasing temperature. (b) $\Delta G° = 19$ kJ. The reaction is not spontaneous under standard conditions at 800 K (c) $\Delta G° = -15.7$ kJ. The reaction is spontaneous under standard conditions at 1000 K. **19.73** (a) $T_b = 79$ °C (b) From the *Handbook of Chemistry and Physics*, 74th Edition, $T_b = 80.1$ °C. The values are remarkably close; the small difference is due to deviation from ideal behavior by $C_6H_6(g)$ and experimental uncertainty in the boiling point measurement and the thermodynamic data. **19.75** (a) $C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2\,CO_2(g) + H_2O(l)$ (b) -1299.5 kJ of heat produced/mol C_2H_2 burned (c) $w_{max} = -1235.1$ kJ/mol C_2H_2 **19.77** (a) ΔG becomes more negative. (b) ΔG becomes more positive. (c) ΔG becomes more positive. **19.79** (a) $\Delta G° = -5.40$ kJ (b) $\Delta G = 0.30$ kJ **19.81** (a) $\Delta G° = -16.77$ kJ, $K = 870$ (b) $\Delta G° = 8.0$ kJ, $K = 0.039$ (c) $\Delta G° = -497.9$ kJ, $K = 2 \times 10^{87}$ **19.83** $\Delta H° = 269.3$ kJ, $\Delta S° = 0.1719$ kJ/K (a) $P_{CO_2} = 6.0 \times 10^{-39}$ atm (b) $P_{CO_2} = 1.6 \times 10^{-4}$ atm **19.85** (a) $HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq)$ (b) $\Delta G° = 19.1$ kJ (c) $\Delta G = 0$ at equilibrium (d) $\Delta G = -2.7$ kJ **19.87** (a) The thermodynamic quantities T, E, and S are state functions. (b) The quantities q and w depend on the path taken. (c) There is only one *reversible* path between states. (d) $\Delta E = q_{rev} + w_{max}$, $\Delta S = q_{rev} / T$. **19.91** (a) 16 arrangements (b) 1 arrangement (c) The gas will spontaneously adopt the state with the most possible arrangements for the molecules, the state with maximum disorder. **19.96** (a) For all three compounds listed, there are fewer moles of gaseous products than reactants in the formation reaction, so we expect $\Delta S_f°$ to be negative. If $\Delta G_f° = \Delta H_f° - T\Delta S_f°$ and $\Delta S_f°$ is negative, $-T\Delta S_f°$ is positive and $\Delta G_f°$ is more positive than $\Delta H_f°$. (b) In this reaction, there are more moles of gas in products, $\Delta S_f°$ is positive, $-T\Delta S_f°$ is negative and $\Delta G_f°$ is more negative than $\Delta H_f°$. **19.100** (a) $K = 4 \times 10^{15}$ (b) An increase in temperature will decrease the mole fraction of CH_3COOH at equilibrium. Elevated temperatures must be used to increase the speed of the reaction. (c) $K = 1$ at 836 K or 563 °C. **19.104** (a) $\Delta G = 8.77$ kJ (b) $w_{min} = 8.77$ kJ. In practice, a larger than minimum amount of work is required. **19.108** (a) Acetone, $\Delta S°_{vap} = 88.4$ J/mol-K; dimethyl ether, $\Delta S°_{vap} = 86.6$ J/mol-K; ethanol, $\Delta S°_{vap} = 110$ J/mol-K; octane, $\Delta S°_{vap} = 86.3$ J/mol-K; pyridine, $\Delta S°_{vap} = 90.4$ J/mol-K. Ethanol does not obey Trouton's rule. (b) Hydrogen bonding (in ethanol and other liquids) leads to more ordering in the liquid state and a greater than usual increase in entropy upon vaporization. Liquids that experience hydrogen bonding are probably exceptions to Trouton's rule. (c) Owing to strong hydrogen bonding interactions, water probably does not obey Trouton's rule. $\Delta S°_{vap} = 109.0$ J/mol-K. (d) ΔH_{vap} for $C_6H_5Cl \approx 36$ kJ/mol **19.113** (a) For any given total pressure, the condition of equal moles of the two gases can be achieved at some temperature. For individual gas pressures of 1 atm and a total pressure of 2 atm, the mixture is at equilibrium at 328.5 K or 55.5 °C. (b) 333.0 K or 60 °C (c) 374.2 K or 101.2 °C (d) The reaction is endothermic, so an increase in the value of K as calculated in parts (a)–(c) should be accompanied by an increase in T.

CHAPTER 20

20.1 In a Brønsted–Lowry acid–base reaction, H^+ is transferred from the acid to the base. In a redox reaction, one or more electrons are transferred from the reductant to the oxidant. The greater the tendency of an acid to donate H^+, the lesser the tendency of its conjugate base to accept H^+. The stronger the acid, the weaker its conjugate base. Similarly, the greater the tendency of a reduced species to donate electrons, the lesser the tendency of the corresponding oxidized species to accept electrons. The stronger the reducing agent, the weaker the corresponding oxidizing agent. **20.4** (a) Add 1 M $A^{2+}(aq)$ to the beaker with the $A(s)$ electrode. Add 1 M $B^{2+}(aq)$ to the beaker with the $B(s)$ electrode. Add a salt bridge to enable the flow of ions from one compartment to the other. (b) The A electrode functions as the cathode. (c) Electrons flow through the external circuit from the anode to the cathode, from B to A in this cell. (d) $E°_{cell} = 1.00$ V. **20.7** (a) The sign of $\Delta G°$ is positive. (b) The equilibrium constant is less than one. (c) No. An electrochemical cell based on this reaction cannot accomplish work on its surroundings. **20.9** (a) Line 1 (b) $E_{red} = E°_{red} = 0.799$ V. **20.13** (a) *Oxidation* is the loss of electrons. (b) Electrons appear on the products' side (right side). (c) The *oxidant* is the reactant that is reduced. (d) An *oxidizing agent* is the substance that promotes oxidation; it is the oxidant. **20.15** (a) True (b) false (c) true **20.17** (a) I, +5 to 0; C, +2 to +4 (b) Hg, +2 to 0; N, −2 to 0 (c) N, +5 to +2; S, −2 to 0 (d) Cl, +4 to +3; O, −1 to 0 **20.19** (a) $TiCl_4(g) + 2\,Mg(l) \longrightarrow Ti(s) + 2\,MgCl_2(l)$ (b) $Mg(l)$ is oxidized; $TiCl_4(g)$ is reduced. (c) $Mg(l)$ is the reductant; $TiCl_4(g)$ is the oxidant. **20.21** (a) $Sn^{2+}(aq) \longrightarrow Sn^{4+}(aq) + 2e^-$, oxidation (b) $TiO_2(s) + 4\,H^+(aq) + 2e^- \longrightarrow Ti^{2+}(aq) + 2\,H_2O(l)$, reduction (c) $ClO_3^-(aq) + 6\,H^+(aq) + 6e^- \longrightarrow Cl^-(aq) + 3\,H_2O(l)$, reduction (d) $N_2(g) + 8\,H^+(aq) + 6e^- \longrightarrow 2\,NH_4^+(aq)$, reduction (e) $4\,OH^-(aq) \longrightarrow O_2(g) + 2\,H_2O(l) + 4e^-$, oxidation (f) $SO_3^{2-}(aq) + 2\,OH^-(aq) \longrightarrow SO_4^{2-}(aq) + H_2O(l) + 2e^-$, oxidation (g) $N_2(g) + 6\,H_2O(l) + 6e^- \longrightarrow 2\,NH_3(g) + 6\,OH^-(aq)$, reducation **20.23** (a) $Cr_2O_7^{2-}(aq) + I^-(aq) + 8\,H^+(aq) \longrightarrow 2\,Cr^{3+}(aq) + IO_3^-(aq) + 4\,H_2O(l)$; oxidizing agent, $Cr_2O_7^{2-}$; reducing agent, I^- (b) $4\,MnO_4^-(aq) + 5\,CH_3OH(aq) + 12\,H^+(aq) \longrightarrow 4\,Mn^{2+}(aq) + 5\,HCO_2H(aq) + 12\,H_2O(aq)$; oxidizing agent, MnO_4^-; reducing agent, CH_3OH (c) $I_2(s) + 5\,OCl^-(aq) + H_2O(l) \longrightarrow 2\,IO_3^-(aq) + 5\,Cl^-(aq) + 2\,H^+(aq)$; oxidizing agent, OCl^-; reducing agent, l_2 (d) $As_2O_3(s) +$

$2\,NO_3^-(aq) + 2\,H_2O(l) + 2\,H^+(aq) \longrightarrow 2\,H_3AsO_4(aq) + N_2O_3(aq)$; oxidizing agent, NO_3^-; reducing agent, As_2O_3 (e) $2\,MnO_4^-(aq) + Br^-(aq) + H_2O(l) \longrightarrow 2\,MnO_2(s) + BrO_3^-(aq) + 2\,OH^-(aq)$; oxidizing agent, MnO_4^-; reducing agent, Br^- (f) $Pb(OH)_4^{2-}(aq) + ClO^-(aq) \longrightarrow PbO_2(s) + Cl^-(aq) + 2\,OH^-(aq) + H_2O(l)$; oxidizing agent, ClO^-; reducing agent, $Pb(OH)_4^{2-}$ **20.25** (a) The reaction $Cu^{2+}(aq) + Zn(s) \longrightarrow Cu(s) + Zn^{2+}(aq)$ is occurring in both figures. In Figure 20.3 the reactants are in contact, while in Figure 20.4 the oxidation half-reaction and reduction half-reaction are occurring in separate compartments. In Figure 20.3 the flow of electrons cannot be isolated or utilized; in Figure 20.4 electrical current is isolated and flows through the voltmeter. (b) Na^+ cations are drawn into the cathode compartment to maintain charge balance as Cu^{2+} ions are removed. **20.27** (a) $Fe(s)$ is oxidized, $Ag^+(aq)$ is reduced. (b) $Ag^+(aq) + e^- \longrightarrow Ag(s)$; $Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$ (c) $Fe(s)$ is the anode, $Ag(s)$ is the cathode. (d) $Fe(s)$ is negative; $Ag(s)$ is positive. (e) Electrons flow from the Fe electrode (−) toward the Ag electrode (+). (f) Cations migrate toward the $Ag(s)$ cathode; anions migrate toward the $Fe(s)$ anode. **20.29** *Electromotive force*, emf, is the potential energy difference between an electron at the anode and an electron at the cathode of a voltaic cell. (b)One *volt* is the potential energy difference required to impart 1 J of energy to a charge of 1 coulomb. (c) *Cell potential*, E_{cell}, is the emf of an electrochemical cell. **20.31** (a) $2\,H^+(aq) + 2e^- \longrightarrow H_2(g)$ (b) A *standard* hydrogen electrode, SHE, has components that are at standard conditions, 1 *M* $H^+(aq)$ and $H_2(g)$ at 1 atm. (c) The platinum foil in a SHE serves as an inert electron carrier and a solid reaction surface. **20.33** (a) A *standard reduction potential* is the relative potential of a reduction half-reaction measured at standard conditions. (b) $E^\circ_{red} = 0\,V$ **20.35** (a) $Cr^{2+}(aq) \longrightarrow Cr^{3+}(aq) + e^-$; $Tl^{3+}(aq) + 2e^- \longrightarrow Tl^+(aq)$ (b) $E^\circ_{red} = 0.78\,V$

(c)



20.37 (a) $E^\circ = 0.823\,V$ (b) $E^\circ = 1.89\,V$ (c) $E^\circ = 1.211\,V$ (d) $E^\circ = 0.62\,V$ **20.39** (a) $3\,Ag^+(aq) + Cr(s) \longrightarrow 3\,Ag(s) + Cr^{3+}(aq)$, $E^\circ = 1.54\,V$ (b) Two of the combinations have essentially equal E° values: $2\,Ag^+(aq) + Cu(s) \longrightarrow 2\,Ag(s) + Cu^{2+}(aq)$, $E^\circ = 0.462\,V$; $3\,Ni^{2+}(aq) + 2\,Cr(s) \longrightarrow 3\,Ni(s) + 2\,Cr^{3+}(aq)$, $E^\circ = 0.46\,V$ **20.41** (a) Anode, $Sn(s)$; cathode, $Cu(s)$. (b) The copper electrode gains mass as Cu is plated out, and the tin electrode loses mass as Sn is oxidized. (c) $Cu^{2+}(aq) + Sn(s) \longrightarrow Cu(s) + Sn^{2+}(aq)$. (d) $E^\circ = 0.473\,V$. **20.43** (a) $Mg(s)$ (b) $Ca(s)$ (c) $H_2(g)$ (d) $BrO_3^-(aq)$ **20.45** (a) $Cl_2(aq)$, strong oxidant (b) $MnO_4^-(aq)$, acidic, strong oxidant (c) $Ba(s)$ strong reductant (d) $Zn(s)$, reductant **20.47** (a) $Cu^{2+}(aq) < O_2(g) < Cr_2O_7^{2-}(aq) < Cl_2(g) < H_2O_2(aq)$ (b) $H_2O_2(aq) < I^-(aq) < Sn^{2+}(aq) < Zn(s) < Al(s)$ **20.49** Al and $H_2C_2O_4$ **20.51** (a) $2\,Fe^{2+}(aq) + S_2O_6^{2-}(aq) + 4\,H^+(aq) \longrightarrow 2\,Fe^{3+}(aq) + 2\,H_2SO_3(aq)$; $2\,Fe^{2+}(aq) + N_2O(aq) + 2\,H^+(aq) \longrightarrow 2\,Fe^{3+}(aq) + N_2(g) + H_2O(l)$; $Fe^{2+}(aq) + VO_2^+(aq) + 2\,H^+(aq) \longrightarrow Fe^{3+}(aq) + VO^{2+}(aq) + H_2O(l)$ (b) $E^\circ = -0.17\,V$, $\Delta G^\circ = 33\,kJ$; $E^\circ = -2.54\,V$, $\Delta G^\circ = 4.90 \times 10^2\,kJ$; $E^\circ = 0.23\,V$, $\Delta G^\circ = -22\,kJ$ (c) $K = 1.8 \times 10^{-6} = 10^{-6}$; $K = 1.2 \times 10^{-86} = 10^{-86}$; $K = 7.8 \times 10^3 = 8 \times 10^3$ **20.53** $\Delta G^\circ = 21.8\,kJ$, $E^\circ_{cell} = -0.113\,V$ **20.55** (a) $E^\circ = 0.16\,V$, $K = 2.54 \times 10^5 = 3 \times 10^5$ (b) $E^\circ = 0.277\,V$, $K = 2.3 \times 10^9$ (c) $E^\circ = 0.45\,V$, $K = 1.5 \times 10^{75} = 10^{75}$ **20.57** (a) $K = 9.8 \times 10^2$ (b) $K = 9.5 \times 10^5$ (c) $K = 9.3 \times 10^8$ **20.59** (a) $w_{max} = -130\,kJ/mol\,Sn$ **20.61** (a) The Nernst equation is applicable when the components of an electrochemical cell are at nonstandard conditions. (b) $Q = 1$ (c) Q decreases and E increases **20.63** (a) E decreases (b) E decreases (c) E decreases (d) no effect **20.65** (a) $E^\circ = 0.48\,V$ (b) $E = 0.53\,V$ (c) $E = 0.46\,V$ **20.67** (a) $E^\circ = 0.46\,V$ (b) $E = 0.37\,V$ **20.69** (a) The compartment with $[Zn^{2+}] = 1.00 \times 10^{-2}\,M$ is the anode. (b) $E^\circ = 0$ (c) $E = 0.0668\,V$ (d) In the anode compartment $[Zn^{2+}]$ increases; in the cathode compartment $[Zn^{2+}]$ decreases **20.71** $E^\circ = 0.763\,V$, pH = 1.6 **20.73** (a) The emf of a battery decreases as it is used. The concentrations of products increase and the concentrations of reactants decrease, causing Q to increase and E_{cell} to decrease. (b) A D-size battery contains more reactants than a AA, enabling the D to provide power for a longer time. **20.75** (a) 464 g PbO_2 (b) 3.74×10^5 C of charge transferred **20.77** (a) The anode (b) $E^\circ = 0.50\,V$ (c) The emf of the battery, 3.5 V, is exactly the standard cell potential calculated in part (b). (d) At ambient conditions, $E \approx E^\circ$, so $\log Q \approx 1$. Assuming that the value of E° is relatively constant with temperature, the value of the second term in the Nernst equation is approximately zero at 37 °C, and $E \approx 3.5\,V$. **20.79** (a) The cell emf will have a smaller value. (b) NiMH batteries use an alloy such as $ZrNi_2$ as the anode material. This eliminates the use and disposal problems associated with Cd, a toxic heavy metal. **20.81** The main advantage of a fuel cell is that fuel is continuously supplied, so that it can produce electrical current for a time limited only by the amount of available fuel. For the hydrogen-oxygen fuel cell, this is also a disadvantage because volatile and explosive hydrogen must be acquired and stored. Alkaline batteries are convenient, but they have a short lifetime, and the disposal of their zinc and manganese solids is more problematic than disposal of water produced by the hydrogen-oxygen fuel cell. **20.83** (a) anode: $Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$; cathode: $O_2(g) + 4\,H^+(aq) + 4e^- \longrightarrow 2\,H_2O(l)$ (b) $2\,Fe^{2+}(aq) + 3\,H_2O(l) + 3\,H_2O(l) \longrightarrow Fe_2O_3 \cdot 3\,H_2O(s) + 6\,H^+(aq) + 2e^-$; $O_2(g) + 4\,H^+(aq) + 4e^- \longrightarrow 2\,H_2O(l)$ **20.85** (a) Mg is called a "sacrificial anode" because it has a more negative E°_{red} than the pipe metal and is preferentially oxidized when the two are coupled. It is sacrificed to preserve the pipe. (b) E°_{red} for Mg^{2+} is −2.37 V, more negative than most metals present in pipes, including Fe and Zn. **20.87** Under acidic conditions, air (O_2) oxidation of $Zn(s)$, 1.99 V; $Fe(s)$, 1.67 V; and $Cu(s)$, 0.893 V are all spontaneous. When the three metals are in contact, Zn will act as a sacrificial anode for both Fe and Cu, but after the Zn is depleted, Fe will be oxidized (corroded). **20.89** (a) *Electrolysis* is an electrochemical process driven by an outside energy source. (b) By definition, electrolysis reactions are nonspontaneous. (c) $2\,Cl^-(l) \longrightarrow Cl_2(g) + 2e^-$ (d) When an aqueous solution of NaCl undergoes electrolysis, sodium metal is not formed because H_2O is preferentially reduced to form $H_2(g)$. **20.91** (a) 236 g $Cr(s)$ (b) 2.51 A **20.93** (a) 4.0×10^5 g Li (b) The minimum voltage required to drive the electrolysis is + 4.41 V. **20.95** Gold is less active than copper and thus more difficult to oxidize. When crude copper is refined by electrolysis, Cu is oxidized from the crude anode, but any metallic gold present in the crude copper is not oxidized,so it accumulates near the anode, available for collection.

20.97(a) $2\,Ni^+(aq) \longrightarrow Ni(s) + Ni^{2+}(aq)$ (b) $3\,MnO_4^{2-}(aq) + 4\,H^+(aq) \longrightarrow 2\,MnO_4^-(aq) + MnO_2(s) + 2\,H_2O(l)$

(c) $3\,H_2SO_3(aq) \longrightarrow S(s) + 2\,HSO_4^-(aq) + 2\,H^+(aq) + H_2O(l)$ (d) $Cl_2(aq) + 2\,OH^-(aq) \longrightarrow Cl^-(aq) + ClO^-(aq) + H_2O(l)$ **20.100** (a) $E° = 0.627\,V$, spontaneous (b) $E° = -0.82\,V$, nonspontaneous (c) $E° = 0.93\,V$, spontaneous (d) $E° = 0.183\,V$, spontaneous **20.104** $K = 1.6 \times 10^6$ **20.107** The ship's hull should be made negative. The ship, as a negatively charged "electrode," becomes the site of reduction, rather than oxidation, in an electrolytic process. **20.110** 3.0×10^4 kWh required **20.112** (a) H_2 is being oxidized and N_2 is being reduced. (b) $K = 6.9 \times 10^5$ (c) $E° = 0.05755\,V$ **20.115** (a) $E° = 0.028\,V$ (b) cathode: $Ag^+(aq) + e^- \longrightarrow Ag(s)$; anode: $Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-$ (c) $\Delta S° = 148.5\,J$. Since $\Delta S°$ is positive, $\Delta G°$ will become more negative and $E°$ will become more positive as temperature is increased. **20.118** K_{sp} for AgSCN is 1.0×10^{-12}.

CHAPTER 21

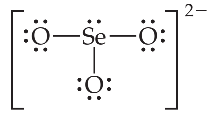
21.1 (a) ${}^{24}Ne$; outside; reduce neutron-to-proton ratio via β decay (b) ${}^{32}Cl$; outside; increase neutron-to-proton ratio via positron emission or orbital electron capture (c) ${}^{108}Sn$; outside; increase neutron-to-proton ratio via positron emission or orbital electron capture (d) ${}^{216}Po$; outside; nuclei with $Z \geq 84$ usually decay via α emission. **21.4** (a) 7 min (b) $0.1\,min^{-1}$ (c) 30% (3/10) of the sample remains after 12 min. (d) ${}^{88}_{41}Nb$ **21.5** (a) ${}^{10}_{5}B$, ${}^{11}_{5}B$; ${}^{12}_{6}C$, ${}^{13}_{6}C$; ${}^{14}_{7}N$, ${}^{15}_{7}N$; ${}^{16}_{8}O$, ${}^{17}_{8}O$, ${}^{18}_{8}O$; ${}^{19}_{9}F$ (b) ${}^{14}_{6}C$ (c) ${}^{11}_{6}C$, ${}^{13}_{7}N$, ${}^{15}_{8}O$, ${}^{18}_{9}F$ (d) ${}^{11}_{6}C$ **21.7** (a) 25 protons, 30 neutrons (b) 80 protons, 121 neutrons (c) 19 protons, 20 neutrons **21.9** (a) ${}^{1}_{0}n$ (b) ${}^{4}_{2}He$ or α (c) ${}^{0}_{0}\gamma$ or γ **21.11** (a) ${}^{90}_{37}Rb \longrightarrow {}^{90}_{38}Sr + {}^{0}_{-1}e$ (b) ${}^{72}_{34}Se + {}^{0}_{-1}e$ (orbital electron) $\longrightarrow {}^{72}_{33}As$ (c) ${}^{76}_{36}Kr \longrightarrow {}^{76}_{35}Br + {}^{0}_{1}e$ (d) ${}^{226}_{88}Ra \longrightarrow {}^{222}_{86}Rn + {}^{4}_{2}He$ **21.13** (a) ${}^{211}_{82}Pb \longrightarrow {}^{211}_{83}Bi + {}^{0}_{-1}\beta$ (b) ${}^{50}_{25}Mn \longrightarrow {}^{50}_{24}Cr + {}^{0}_{1}e$ (c) ${}^{179}_{74}W + {}^{0}_{-1}e \longrightarrow {}^{179}_{73}Ta$ (d) ${}^{230}_{90}Th \longrightarrow {}^{266}_{88}Ra + {}^{4}_{2}He$ **21.15** 7 alpha emissions, 4 beta emissions **21.17** (a) Positron emission (for low atomic numbers, positron emission is more common than electron capture) (b) beta emission (c) beta emission (d) beta emission **21.19** (a) Stable: ${}^{39}_{19}K$, 20 neutrons is a magic number (b) stable: ${}^{209}_{83}Bi$, 126 neutrons is a magic number (c) stable: ${}^{58}_{28}Ni$ even proton, even neutron more likely to be stable; ${}^{65}_{28}Ni$ has high neutron-to-proton ratio **21.21** (a) ${}^{4}_{2}He$ (c) ${}^{40}_{20}Ca$ (e) ${}^{126}_{82}Pb$ **21.23** The alpha particle, ${}^{4}_{2}He$, has a magic number of both protons and neutrons, while the proton is an odd proton, even neutron particle. Alpha is a very stable emitted particle, which makes alpha emission a favorable process. The proton is not a stable emitted particle, and its formation does not encourage proton emission as a process. **21.25** Protons and alpha particles are positively charged and must be moving very fast to overcome electrostatic forces that would repel them from the target nucleus. Neutrons are electrically neutral and not repelled by the nucleus. **21.27** (a) ${}^{252}_{98}Cf + {}^{10}_{5}B \longrightarrow 3\,{}^{1}_{0}n + {}^{259}_{103}Lr$ (b) ${}^{2}_{1}H + {}^{3}_{2}He \longrightarrow {}^{4}_{2}He + {}^{1}_{1}H$ (c) ${}^{1}_{1}H + {}^{11}_{5}B \longrightarrow 3\,{}^{4}_{2}He$ (d) ${}^{122}_{53}I \longrightarrow {}^{122}_{54}Xe + {}^{0}_{-1}e$ (e) ${}^{59}_{26}Fe \longrightarrow {}^{0}_{-1}e + {}^{59}_{27}Co$ **21.29** (a) ${}^{238}_{92}U + {}^{4}_{2}He \longrightarrow {}^{241}_{94}Pu + {}^{1}_{0}n$ (b) ${}^{14}_{7}N + {}^{4}_{2}He \longrightarrow {}^{17}_{8}O + {}^{1}_{1}H$ (c) ${}^{56}_{26}Fe + {}^{4}_{2}He \longrightarrow {}^{60}_{29}Cu + {}^{0}_{-1}e$ **21.31** (a) True. The decay rate constant and half-life are inversely related. (b) False. If X is not radioactive, its half-life is essentially infinity. (c) True. Changes in the amount of A would be substantial and measurable over the 40-year time frame, while changes in the amount of X would be very small and difficult to detect. **21.33** When the watch is 50 years old, only 6% of the tritium remains. The dial will be dimmed by 94%. **21.35** The source must be replaced after 2.18 yr or 26.2 months; this corresponds to August 2012. **21.37** (a) 1.1×10^{11} alpha particles emitted in 5.0 min (b) 9.9 mCi **21.39** $k = 1.21 \times 10^{-4}\,yr^{-1}$; $t = 4.3 \times 10^3\,yr$ **21.41** $k = 5.46 \times 10^{-10}\,yr^{-1}$; $t = 3.0 \times 10^9\,yr$ **21.43** The energy released when one mole of Fe_2O_3 reacts is $8.515 \times 10^3\,J$. The energy released when one mole of ${}^{4}_{2}He$ is formed from protons and neutrons is $2.73 \times 10^{12}\,J$. This is 3×10^8 or 300 million times as much energy as the thermite reaction. **21.45** $\Delta m = 0.2414960$ amu, $\Delta E = 3.604129 \times 10^{-11}\,J/{}^{27}Al$ nucleus required, $8.044234 \times 10^{13}\,J/100\,g\,{}^{27}Al$ **21.47** (a) Nuclear mass: ${}^{2}H$, 2.013553 amu; ${}^{4}He$, 4.001505 amu; ${}^{6}Li$, 6.0134771 amu (b) nuclear binding energy: ${}^{2}H$, $3.564 \times 10^{-13}\,J$; ${}^{4}He$, $4.5336 \times 10^{-12}\,J$; ${}^{6}Li$, $5.12602 \times 10^{-12}\,J$ (c) binding energy/nucleon: ${}^{2}H$, 1.782×10^{-13} J/nucleon; ${}^{4}He$, 1.1334×10^{-12} J/nucleon; ${}^{6}Li$, 8.54337×10^{-13} J/nucleon. This trend in binding energy/nucleon agrees with the curve in Figure 21.12. The anomalously high calculated value for ${}^{4}He$ is also apparent on the figure. **21.49** (a) 1.71×10^5 kg/d (b) $2.1 \times 10^8\,g\,{}^{235}U$ **21.51** (a) ${}^{59}Co$; it has the largest binding energy per nucleon, and binding energy gives rise to mass defect. **21.53** (a) NaI is a good source of iodine because iodine is a large percentage of its mass; it is completely dissociated into ions in aqueous solution, and iodine in the form of $I^-(aq)$ is mobile and immediately available for biouptake. (b) A Geiger counter placed near the thyroid immediately after ingestion will register background, then gradually increase in signal until the concentration of iodine in the thyroid reaches a maximum. Over time, iodine-131 decays, and the signal decreases. (c) The radioactive iodine will decay to 0.01% of the original amount in approximately 82 days. **21.55** ${}^{235}U$ **21.57** The *control rods* in a nuclear reactor regulate the flux of neutrons to keep the reaction chain self-sustaining and also prevent the reactor core from overheating. They are composed of materials such as boron or cadmium that absorb neutrons. **21.59** (a) ${}^{2}_{1}H + {}^{2}_{1}H \longrightarrow {}^{3}_{2}He + {}^{1}_{0}n$ (b) ${}^{239}_{92}U + {}^{1}_{0}n \longrightarrow {}^{133}_{51}Sb + {}^{98}_{41}Nb + 9\,{}^{1}_{0}n$ **21.61** (a) $\Delta m = 0.006627\,g/mol$; $\Delta E = 5.956 \times 10^{11}\,J = 5.956 \times 10^8\,kJ/mol\,{}^{1}_{1}H$ (b) The extremely high temperature is required to overcome electrostatic charge repulsions between the nuclei so that they can come together to react. **21.63** (a) Boiling water reactor (b) fast breeder reactor (c) gas-cooled reactor **21.65** Hydrogen abstraction: $RCOOH + {\cdot}OH \longrightarrow RCOO{\cdot} + H_2O$; deprotonation: $RCOOH + OH^- \longrightarrow RCOO^- + H_2O$. Hydroxyl radical is more toxic to living systems because it produces other radicals when it reacts with molecules in the organism. Hydroxide ion, OH^-, on the other hand, will be readily neutralized in the buffered cell environment. The acid–base reactions of OH^- are usually much less disruptive to the organism than the chain of redox reactions initiated by ·OH radical. **21.67** (a) 5.3×10^8 dis/s, 5.3×10^8 Bq (b) 6.1×10^2 mrad, 6.1×10^{-3} Gy (c) 5.8×10^3 mrem, 5.8×10^{-2} Sv **21.69** ${}^{210}_{82}Pb$ **21.71** (a) ${}^{36}_{17}Cl \rightarrow {}^{36}_{18}Ar + {}^{0}_{-1}e$ (b) ${}^{35}Cl$ and ${}^{37}Cl$ both have an odd number of protons but an even number of neutrons. ${}^{36}Cl$ has an odd number of protons and neutrons, so it is less stable than the other two isotopes. **21.73** (a) ${}^{6}_{3}Li + {}^{56}_{28}Ni \rightarrow {}^{62}_{31}Ga$ (b) ${}^{40}_{20}Ca + {}^{248}_{96}Cm \longrightarrow {}^{147}_{62}Sm + {}^{141}_{54}Xe$ (c) ${}^{88}_{38}Sr + {}^{84}_{36}Kr \longrightarrow {}^{116}_{46}Pd + {}^{56}_{28}Ni$ (d) ${}^{40}_{20}Ca + {}^{238}_{92}U \longrightarrow {}^{70}_{30}Zn + 4\,{}^{1}_{0}n + 2\,{}^{102}_{41}Nb$ **21.77** The C—OH bond of the acid and the O—H bond of the alcohol break in this reaction. Initially, ${}^{18}O$ is present in the C—^{18}OH group of the alcohol. In order for ${}^{18}O$ to end up in the ester, the ^{18}O—H bond of the alcohol must break. This requires that the C—OH bond in the acid also breaks. The unlabeled O from the acid ends up in the H_2O product. **21.79** ${}^{7}Be$, 8.612×10^{-13} J/nucleon; ${}^{9}Be$, 1.035×10^{-12} J/nucleon; ${}^{10}Be$: 1.042×10^{-12} J/nucleon. The binding energies/nucleon for ${}^{9}Be$ and ${}^{10}Be$ are very similar; that for ${}^{10}Be$ is slightly higher. **21.85** $1.4 \times 10^4\,kg\,C_8H_{18}$

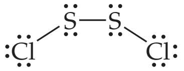
CHAPTER 22

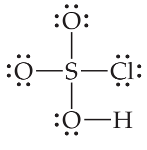
22.1 (a) C_2H_4, the structure on the left, is the stable compound. Carbon can form strong multiple bonds to satisfy the octet rule, while silicon cannot. (b) The geometry about the central atoms in C_2H_4 is trigonal planar. **22.3** Molecules (b) and (d) will have the seesaw structure shown in the figure. **22.6** (c) Density, the ratio of mass to volume, increases going down the family; only this trend is consistent with the data in the figure. Other properties do not match the trend because (a) electronegativity and (b) first ionization energy both decrease rather than increase going down the family. Trends for both (d) X—X single bond enthalpy and (e) electron affinity are

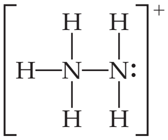
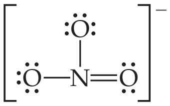
somewhat erratic, with the trends decreasing from S to Po, and anomalous values for the properties of O, probably owing to its small covalent radius. **22.9** The compound on the left, with the strained three-membered ring, will be the most generally reactive. The larger the deviation from ideal bond angles, the more strain in the molecule and the more generally reactive it is. **22.11** Metals: (b) Sr, (c) Mn, (e) Na; nonmetals: (a) P, (d) Se, (f) Kr; metalloids: none. **22.13** (a) O (b) Br (c) Ba (d) O (e) Co (f) Br **22.15** (a) N is too small a central atom to fit five fluorine atoms, and it does not have available *d* orbitals, which can help accommodate more than eight electrons. (b) Si does not readily form π bonds, which are necessary to satisfy the octet rule for both atoms in the molecule. (c) As has a lower electronegativity than N; that is, it more readily gives up electrons to an acceptor and is more easily oxidized. **22.17** (a) $NaOCH_3(s) + H_2O(l) \longrightarrow NaOH(aq) + CH_3OH(aq)$
(b) $CuO(s) + 2HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + H_2O(l)$
(c) $WO_3(s) + 3H_2(g) \longrightarrow W(s) + 3H_2O(g)$
(d) $4NH_2OH(l) + O_2(g) \longrightarrow 6H_2O(l) + 2N_2(g)$
(e) $Al_4C_3(s) + 12H_2O(l) \longrightarrow 4Al(OH)_3(s) + 3CH_4(g)$
22.19 (a) ${}^1_1H$, protium; ${}^2_1H$, deuterium; ${}^3_1H$, tritium (b) in order of decreasing natural abundance: protium > deuterium > tritium (c) Tritium is radioactive. (d) ${}^3_1H \longrightarrow {}^3_2He + {}^{0}_{-1}e$ **22.21** Like other elements in group 1A, hydrogen has only one valence electron and its most common oxidation number is +1.
22.23 (a) $Mg(s) + 2H^+(aq) \longrightarrow Mg^{2+}(aq) + H_2(g)$
(b) $C(s) + H_2O(g) \xrightarrow{1100\,°C} CO(g) + 3H_2(g)$
(c) $CH_4(g) + H_2O(g) \xrightarrow{1100\,°C} CO(g) + 3H_2(g)$
22.25 (a) $NaH(s) + H_2O(l) \longrightarrow NaOH(aq) + H_2(g)$
(b) $Fe(s) + H_2SO_4(aq) \longrightarrow Fe^{2+}(aq) + H_2(g) + SO_4{}^{2-}(aq)$
(c) $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$
(d) $2Na(l) + H_2(g) \longrightarrow 2NaH(s)$
(e) $PbO(s) + H_2(g) \xrightarrow{\Delta} Pb(s) + H_2O(g)$ **22.27** (a) Ionic (b) molecular (c) metallic **22.29** Vehicle fuels produce energy via combustion reactions. The combustion of hydrogen is very exothermic and its only product, H_2O, is a nonpollutant. **22.31** Xenon has a lower ionization energy than argon; because the valence electrons are not as strongly attracted to the nucleus, they are more readily promoted to a state in which the atom can form bonds with fluorine. Also, Xe is larger and can more easily accommodate an expanded octet of electrons. **22.33** (a) $Ca(OBr)_2$, Br, +1 (b) $HBrO_3$, Br, +5 (c) XeO_3, Xe, +6 (d) $ClO_4{}^-$, Cl, +7 (e) HIO_2, I, +3 (f) IF_5; I, +5; F, −1 **22.35** (a) iron(III) chlorate, Cl, +5 (b) chlorous acid, Cl, +3 (c) xenon hexafluoride, F, −1 (d) bromine pentafluoride; Br, + 5; F, −1 (e) xenon oxide tetrafluoride, F, −1 (f) iodic acid, I, +5 **22.37** (a) van der Waals intermolecular attractive forces increase with increasing number of electrons in the atoms. (b) F_2 reacts with water: $F_2(g) + H_2O(l) \longrightarrow 2HF(g) + O_2(g)$. That is, fluorine is too strong an oxidizing agent to exist in water. (c) HF has extensive hydrogen bonding. (d) Oxidizing power is related to electronegativity. Electronegativity and oxidizing power decrease in the order given. **22.39**(a) $2HgO(s) \xrightarrow{\Delta} 2Hg(l) + O_2(g)$
(b) $2Cu(NO_3)_2(s) \xrightarrow{\Delta} 2CuO(s) + 4NO_2(g) + O_2(g)$
(c) $PbS(s) + 4O_3(g) \longrightarrow PbSO_4(s) + 4O_2(g)$
(d) $2ZnS(s) + 3O_2(g) \longrightarrow 2ZnO(s) + 2SO_2(g)$
(e) $2K_2O_2(s) + 2CO_2(g) \longrightarrow 2K_2CO_3(s) + O_2(g)$
(f) $3O_2(g) \xrightarrow{h\nu} 2O_3(g)$ **22.41** (a) acidic (b) acidic (c) amphoteric (d) basic **22.43** (a) H_2SeO_3, Se, +4 (b) $KHSO_3$, S, +4 (c) H_2Te, Te, −2 (d) CS_2, S, −2 (e) $CaSO_4$, S, +6 (f) CdS, S, −2 (g) ZnTe, Te, −2
22.45 (a) $2Fe^{3+}(aq) + H_2S(aq) \longrightarrow 2Fe^{2+}(aq) + S(s) + 2H^+(aq)$
(b) $Br_2(l) + H_2S(aq) \longrightarrow 2Br^-(aq) + S(s) + 2H^+(aq)$
(c) $2MnO_4{}^-(aq) + 6H^+(aq) + 5H_2S(aq) \longrightarrow 2Mn^{2+}(aq) + 5S(s) + 8H_2O(l)$
(d) $2NO_3{}^-(aq) + H_2S(aq) + 2H^+(aq) \longrightarrow 2NO_2(aq) + S(s) + 2H_2O(l)$

22.47

(a)

Trigonal pyramidal

(b)

Bent (free rotation around S–S bond)

(c)

Tetrahedral (around S)

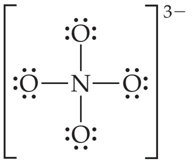
22.49 (a) $SO_2(s) + H_2O(l) \rightleftharpoons H_2SO_3(aq) \rightleftharpoons H^+(aq) + HSO_3{}^-(aq)$
(b) $ZnS(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2S(g)$
(c) $8SO_3{}^{2-}(aq) + S_8(s) \longrightarrow 8S_2O_3{}^{2-}(aq)$
(d) $SO_3(aq) + H_2SO_4(l) \longrightarrow H_2S_2O_7(l)$
22.51 (a) $NaNO_2$, +3 (b) NH_3, −3 (c) N_2O, +1 (d) NaCN, −3 (e) HNO_3, + 5 (f) NO_2, +4 (g) N_2, 0 (h) BN, −3
22.53 (a) $:\ddot{O}{=}\ddot{N}{-}\ddot{O}{-}H \longleftrightarrow :\ddot{O}{-}\ddot{N}{=}\ddot{O}{-}H$
The molecule is bent around the central oxygen and nitrogen atoms; the four atoms need not be coplanar. The right-most form does not minimize formal charges and is less important in the actual bonding model. The oxidation state of N is +3.
(b)
$$\left[:\ddot{N}{=}N{=}\ddot{N}:\right]^- \longleftrightarrow \left[:N{\equiv}N{-}\ddot{N}:\right]^- \longleftrightarrow \left[:\ddot{N}{-}N{\equiv}N:\right]^-$$
The molecule is linear. The oxidation state of N is −1/3.
(c)

The geometry is tetrahedral around the left nitrogen, trigonal pyramidal around the right. The oxidation state of N is −2.
(d)

The ion is trigonal planar; it has three equivalent resonance forms. The oxidation state of N is +5.
22.55 (a) $Mg_3N_2(s) + 6H_2O(l) \longrightarrow 3Mg(OH)_2(s) + 2NH_3(aq)$
(b) $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$, redox reaction
(c) $N_2O_5(g) + H_2O(l) \longrightarrow 2H^+(aq) + 2NO_3^-(aq)$
(d) $NH_3(aq) + H^+(aq) \longrightarrow NH_4{}^+(aq)$
(e) $N_2H_4(l) + O_2(g) \longrightarrow N_2(g) + 2H_2O(g)$, redox reaction
22.57 (a) $HNO_2(aq) + H_2O(l) \longrightarrow NO_3^-(aq) + 2e^-$
(b) $N_2(g) + H_2O(l) \longrightarrow N_2O(aq) + 2H^+(aq) + 2e^-$
22.59 (a) H_3PO_3, +3 (b) $H_4P_2O_7$, +5 (c) $SbCl_3$, +3 (d) Mg_3As_2, +5 (e) P_2O_5, +5 (f) Na_3PO_4, +5 **22.61** (a) Phosphorus is a larger atom than nitrogen, and P has energetically available 3*d* orbitals, which participate in the bonding, but nitrogen does not. (b) Only one of the three hydrogens in H_3PO_2 is bonded to oxygen. The other two are bonded directly to phosphorus and are not easily ionized. (c) PH_3 is a weaker base

than H_2O so any attempt to add H^+ to PH_3 in the presence of H_2O causes protonation of H_2O. (d) The P_4 molecules in white phosphorus have more severely strained bond angles than the chains in red phosphorus, causing white phosphorus to be more reactive.

22.63 (a)
$2\,Ca_3PO_4(s) + 6\,SiO_2(s) + 10\,C(s) \longrightarrow P_4(g) + 6\,CaSiO_3(l) + 10\,CO(g)$
(b) $PBr_3(l) + 3\,H_2O(l) \longrightarrow H_3PO_3(aq) + 3\,HBr(aq)$
(c) $4\,PBr_3(g) + 6\,H_2(g) \longrightarrow P_4(g) + 12\,HBr(g)$
22.65 (a) HCN (b) $Ni(CO)_4$ (c) $Ba(HCO_3)_2$ (d) CaC_2 (e) K_2CO_3
22.67 (a) $ZnCO_3(s) \xrightarrow{\Delta} ZnO(s) + CO_2(g)$
(b) $BaC_2(s) + 2\,H_2O(l) \longrightarrow Ba^{2+}(aq) + 2\,OH^-(aq) + C_2H_2(g)$
(c) $2\,C_2H_2(g) + 5\,O_2(g) \longrightarrow 4\,CO_2(g) + 2\,H_2O(g)$
(d) $CS_2(g) + 3\,O_2(g) \longrightarrow CO_2(g) + 2\,SO_2(g)$
(e) $Ca(CN)_2(s) + 2\,HBr(aq) \longrightarrow CaBr_2(aq) + 2\,HCN(aq)$
22.69
(a) $2\,CH_4(g) + 2\,NH_3(g) + 3\,O_2(g) \xrightarrow{800\,°C} 2\,HCN(g) + 6\,H_2O(g)$
(b) $NaHCO_3(s) + H^+(aq) \longrightarrow CO_2(g) + H_2O(l) + Na^+(aq)$
(c) $2\,BaCO_3(s) + O_2(g) + 2\,SO_2(g) \longrightarrow 2\,BaSO_4(s) + 2\,CO_2(g)$

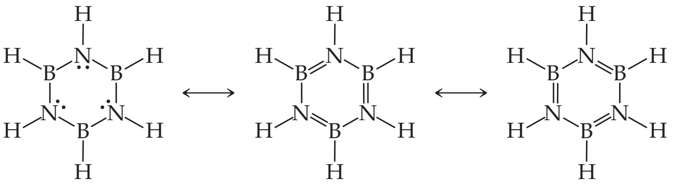
22.71 (a) H_3BO_3, +3 (b) $SiBr_4$, +4 (c) $PbCl_2$, +2 (d) $Na_2B_4O_7 \cdot 10\,H_2O$, +3 (e) B_2O_3, +3 (f) GeO_2, +4 **22.73** (a) Tin (b) carbon, silicon, and germanium (c) silicon **22.75** (a) Tetrahedral (b) Metasilicic acid will probably adopt the single-strand silicate chain structure shown in Figure 22.34 (b). The Si to O ratio is correct and there are two terminal O atoms per Si that can accommodate the two H atoms associated with each Si atom of the acid. **22.77** (a) Diborane has bridging H atoms linking the two B atoms. The structure of ethane has the C atoms bound directly, with no bridging atoms. (b) B_2H_6 is an electron-deficient molecule. The 6 valence electron pairs are all involved in B—H sigma bonding, so the only way to satisfy the octet rule at B is to have the bridging H atoms shown in Figure 22.36. (c) The term *hydridic* indicates that the H atoms in B_2H_6 have more than the usual amount of electron density for a covalently bound H atom.

22.81 (a) $SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq)$
(b) $Cl_2O_7(g) + H_2O(l) \rightleftharpoons 2\,HClO_4(aq)$
(c) $Na_2O_2(s) + 2\,H_2O(l) \longrightarrow H_2O_2(aq) + 2\,NaOH(aq)$
(d) $BaC_2(s) + 2\,H_2O(l) \longrightarrow Ba^{2+}(aq) + 2\,OH^-(aq) + C_2H_2(g)$
(e) $2\,RbO_2(s) + 2\,H_2O(l) \longrightarrow$
$2\,Rb^+(aq) + 2\,OH^-(aq) + O_2(g) + H_2O_2(aq)$
(f) $Mg_3N_2(s) + 6\,H_2O(l) \longrightarrow 3\,Mg(OH)_2(s) + 2\,NH_3(g)$
(g) $NaH(s) + H_2O(l) \longrightarrow NaOH(aq) + H_2(g)$ **22.85** (a) PO_4^{3-}, +5; NO_3^-, +5, (b) The Lewis structure for NO_4^{3-} would be:



The formal charge on N is +1 and on each O atom is −1. The four electronegative oxygen atoms withdraw electron density, leaving the nitrogen deficient. Since N can form a maximum of four bonds, it cannot form a π bond with one or more of the O atoms to regain electron density, as the P atom in PO_4^{3-} does. Also, the short N—O distance would lead to a tight tetrahedron of O atoms subject to steric repulsion. **22.89** (a) 1.94×10^3 g H_2 (b) 2.16×10^4 L H_2 (c) 2.76×10^5 kJ **22.91** (a) −285.83 kJ/mol H_2; −890.4 kJ/ mol CH_4 (b) −141.79 kJ/g H_2; −55.50 kJ/g CH_4 (c) 1.276×10^4 kJ/m^3 H_2; 3.975×10^4 kJ/m^3 CH_4 **22.95** (a) $SO_2(g) + 2\,H_2S(aq) \longrightarrow 3\,S(s) + 2\,H_2O(l)$ or $8\,SO_2(g) + 16\,H_2S(aq) \longrightarrow 3\,S_8(s) + 16\,H_2O(l)$ (b) 4.0×10^3 mol $= 9.7 \times 10^4$ L H_2S (c) 1.9×10^5 g S produced **22.97** The average bond enthalpies are H—O, 463 kJ; H—S, 367 kJ; H—Se, 316 kJ; H—Te, 266 kJ. The H—X bond enthalpy decreases steadily in the series. The origin of this effect is probably the increasing size of the orbital from X with which the hydrogen 1*s* orbital must overlap. **22.101** Dimethylhydrazine produces 0.0369 mol gas per gram of reactants, while methylhydrazine produces 0.0388 mol gas per gram of reactants. Methylhydrazine has marginally greater thrust.

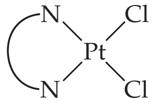
22.103 (a) $3\,B_2H_6(g) + 6\,NH_3(g) \longrightarrow 2\,(BH)_3(NH)_3(l) + 12\,H_2(g)$; $3\,LiBH_4(s) + 3\,NH_4Cl(s) \longrightarrow 2\,(BH)_3(NH)_3(l) + 9\,H_2(g) + 3\,LiCl(s)$
(b)



(c) 2.40 g $(BH)_3(NH)_3$

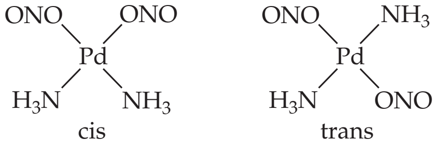
CHAPTER 23

23.2 (a)



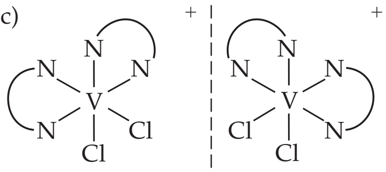
(b) Coordination number = 4, coordination geometry = square planar (c) oxidation state = +2 **23.4** aminotrichloroplatinate(II) **23.6** Molecules (1), (3), and (4) are chiral because their mirror images are not superimposible on the original molecules. **23.8** (a) diagram (4) (b) diagram (1) (c) diagram (3) (d) diagram (2) **23.11** The lanthanide contraction is the name given to the decrease in atomic size due to the build-up in effective nuclear charge as we move through the lanthanides (elements 58–71) and beyond them. This effect offsets the expected increase in atomic size, decrease in ionization energy, and increase in electron affinity going from period 5 to period 6 transition elements. This causes the chemical properties of period 5 and period 6 elements in the same family to be even more similar than we would expect. **23.13** (a) All transition metal atoms have two *s*-electrons in their valence shell. Loss of these *s*-electrons leads to the +2 oxidation state common for most of the transition metals. **23.15** (a) Ti^{3+}, $[Ar]3d^1$ (b) Ru^{2+}, $[Kr]4d^6$ (c) Au^{3+}, $[Xe]4f^{14}5d^8$ (d) Mn^{4+}, $[Ar]3d^3$ **23.17** (a) The unpaired electrons in a paramagnetic material cause it to be weakly attracted into a magnetic field. A diamagnetic material, where all electrons are paired, is very weakly repelled by a magnetic field. **23.19** The diagram shows a material with misaligned spins that become aligned in the direction of an applied magnetic field. This is a paramagnetic material. **23.21** (a) In Werner's theory, *primary valence* is the charge of the metal cation at the center of the complex. *Secondary valence* is the number of atoms bound or coordinated to the central metal ion. The modern terms for these concepts are *oxidation state* and *coordination number*, respectively. (b) Ligands are the Lewis base in metal–ligand interactions. As such, they must possess at least one unshared electron pair. NH_3 has an unshared electron pair but BH_3, with less than 8 electrons about B, has no unshared electron pair and cannot act as a ligand. **23.23** (a) +2 (b) 6 (c) 2 mol $AgBr(s)$ will precipitate per mole of complex. **23.25** (a) Coordination number = 4, oxidation number = +2; 4 Cl^- (b) 5, +4; 4 Cl^-, 1 O^{2-} (c) 6, +3; 4 N, 2 Cl^- (d) 5, +2; 5 C (e) 6, +3; 6 O (f) 4, +2; 4 N **23.27** (a) A monodentate ligand binds to a metal via one atom, a bidentate ligand binds through two atoms. (b) Three bidentate ligands fill the coordination sphere of a six-coordinate complex. (c) A tridentate ligand has at least three atoms with unshared electron pairs in the correct orientation to simultaneously bind one or more metal ions. **23.29** (a) *Ortho*-phenanthroline, *o*-phen, is bidentate (b) oxalate, $C_2O_4^{2-}$, is bidentate (c) ethylenediaminetetraacetate, EDTA, is pentadentate (d) ethylenediamine, en, is bidentate. **23.31** (a) The term *chelate effect* refers to the special stability associated with formation of a metal complex containing a polydentate (chelate) ligand relative to a complex containing only monodentate ligands. (b) The increase in entropy, $+\Delta S$, associated with the substitution of a chelating ligand for two or more monodentate ligands generally gives rise to the *chelate effect*. Chemical reactions with $+\Delta S$ tend to be spontaneous, have negative ΔG and large values of *K*. (c) Polydentate ligands are used as *sequestering agents* to bind metal ions and prevent them from undergoing unwanted chemical reactions without removing them from solution. **23.33** The ligand is not typically a chelate. The entire molecule is planar and the benzene rings on either side of the two N atoms inhibit their approach in the correct orientation for chelation. **23.35** (a) $[Cr(NH_3)_6](NO_3)_3$ (b) $[Co(NH_3)_4CO_3]_2SO_4$ (c) $[Pt(en)_2Cl_2]Br_2$ (d) $K[V(H_2O)_2Br_4]$ (e) $[Zn(en)_2][HgI_4]$ **23.37** (a) tetraamminedichlororhodium(III) chloride (b) potassium hexachlorotitanate(IV) (c) tetrachlorooxomolybdenum(VI) (d) tetraaqua(oxalato)platinum (IV) bromide

23.39 (a)



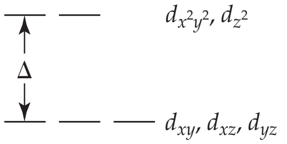
(b) $[Pd(NH_3)_2(ONO)_2]$, $[Pd(NH_3)_2(NO_2)_2]$

(c)



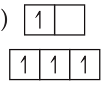
(d) $[Co(NH_3)_4Br_2]Cl$, $[Co(NH_3)_4BrCl]Br$ **23.41** Yes. No structural or stereoisomers are possible for a tetrahedral complex of the form MA_2B_2. The complex must be square planar with cis and trans geometric isomers. **23.43** (a) One isomer (b) trans and cis isomers with 180° and 90° Cl—Ir—Cl angles, respectively (c) trans and cis isomers with 180° and 90° Cl—Fe—Cl angles, respectively. The cis isomer is optically active. **23.45** (a) We cannot see the light with 300 nm wavelength, but we can see the 500 nm light. (b) *Complementary* colors are opposite each other on an artist's color wheel. (c) A colored metal complex absorbs visible light of its complementary color. (d) 196 kJ/mol **23.47** No. All 6 *d*-electrons in a low-spin octahedral Fe(II) complex will pair and occupy the low-energy d_{xy}, d_{xz}, and d_{yz} orbitals. With no unpaired electrons, the complex cannot be paramagnetic. **23.49** Most of the attraction between a metal ion and a ligand is electrostatic. Whether the interaction is ion–ion or ion–dipole, the ligand is strongly attracted to the metal center and can be modeled as a point negative charge.

23.51 (a)



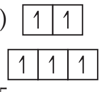
(b) The magnitude of Δ and the energy of the *d-d* transition for a d^1 complex are equal. (c) $\Delta = 220\,kJ/mol$ **23.53** A yellow color is due to absorption of light around 400 to 430 nm, a blue color to absorption near 620 nm. The shorter wavelength corresponds to a higher-energy electron transition and larger Δ value. Cyanide is a stronger-field ligand, and its complexes are expected to have larger Δ values than aqua complexes. **23.55** (a) Ti^{3+}, d^1 (b) Co^{3+}, d^6 (c) Ru^{3+}, d^5 (d) Mo^{5+}, d^1, (e) Re^{3+}, d^4 **23.57** Yes. A weak-field ligand leads to a small Δ value and a small *d*-orbital splitting energy. If the splitting energy of a complex is smaller than the energy required to pair electrons in an orbital, the complex is high spin. **23.59** (a) Mn, $[Ar]4s^23d^5$; Mn^{2+}, $[Ar]3d^5$; 1 unpaired electron (b) Ru, $[Kr]5s^14d^7$; Ru^{2+}, $[Kr]4d^6$; 0 unpaired electrons (c) Rh, $[Kr]5s^14d^8$; Rh^{2+}, $[Kr]4d^7$; 1 unpaired electron **23.61** All complexes in this exercise are six-coordinate octahedral.

(a)



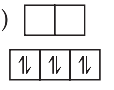
d^4, high spin

(b)



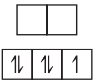
d^5, high spin

(c)



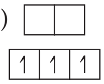
d^6, low spin

(d)



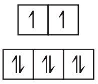
d^5, low spin

(e)



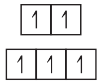
d^3

(f)



d^8

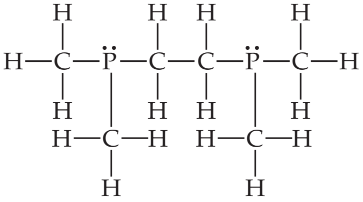
23.63



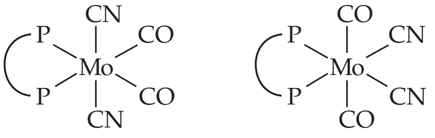
high spin

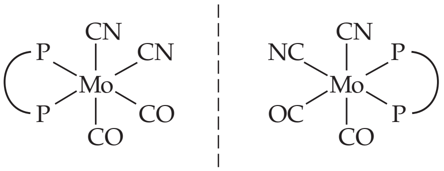
23.67 $[Pt(NH_3)_6]Cl_4$; $[Pt(NH_3)_4Cl_2]Cl_2$; $[Pt(NH_3)_3Cl_3]Cl$; $[Pt(NH_3)_2Cl_4]$; $K[Pt(NH_3)Cl_5]$

23.71 (a)



Both dmpe and en are bidentate ligands, binding through P and N, respectively. Because phosphorus is less electronegative than N, dmpe is a stronger electron pair donor and Lewis base than en. Dmpe creates a stronger ligand field and is higher on the spectrochemical series. Structurally, dmpe occupies a larger volume than en. M–P bonds are longer than M—N bonds and the two $-CH_3$ groups on each P atom in dmpe create more steric hindrance than the H atoms on N in en. (b) The oxidation state of Mo is zero. (c)The symbol $\widehat{P\ P}$ represents the bidentate dmpe ligand.

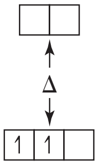




optical isomers

23.74 (a) Hemoglobin is the iron-containing protein that transports O_2 in human blood. (b) Chlorophylls are magnesium-containing porphyrins in plants. They are the key components in the conversion of solar energy into chemical energy that can be used by living organisms. (c) Siderophores are iron-binding compounds or ligands produced by a microorganism. They compete on a molecular level for iron in the medium outside the organism and carry needed iron into the cells of the organism. **23.76** (a) Pentacarbonyliron(0) (b) The oxidation state of iron must be zero. (c) Two. One isomer has CN in an axial position and the other has it in an equatorial position.

23.78 (a)

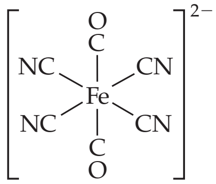


d^2

(b) Visible light with $\lambda = hc/\Delta$ is absorbed by the complex, promoting one of the *d* electrons into a higher-energy *d*-orbital. The remaining wavelengths are reflected or transmitted; the combination of these wavelengths is the color we see. (c) $[V(H_2O)_6]^{3+}$ will absorb light with higher energy because it has a larger Δ than $[VF_6]^{3-}$. H_2O is in the middle of the spectrochemical series and causes a larger Δ than F^-, a weak-field ligand. **23.80** $[Co(NH_3)_6]^{3+}$, yellow; $[Co(H_2O)_6]^{2+}$, pink; $[CoCl_4]^{2-}$, blue

23.85

(a)



(b) sodium dicarbonyltetracyanoferrate(II) (c) +2, 6 *d*-electrons (d) We expect the complex to be low spin. Cyanide (and carbonyl) are high on the spectrochemical series, which means the complex will have a large Δ splitting, characteristic of low-spin complexes. **23.91** (a) Yes, the oxidation state of Co is +3 in both complexes. (b) Compound A has SO_4^{2-} outside the coordination sphere and coordinated Br^-, so it forms a precipitate with $BaCl_2(aq)$ but not $AgNO_3(aq)$. Compound B has Br^- outside the coordination sphere and coordinated SO_4^{2-}, so it forms a precipitate with $AgNO_3(aq)$ but not $BaCl_2(aq)$. (c) Compounds A and B are coordination sphere isomers. (d) Both compounds are strong electrolytes. **23.94** The chemical formula is $[Pd(NC_5H_5)_2Br_2]$. This is an electrically neutral square-planar complex of Pd(II), a nonelectrolyte whose solutions do not conduct electricity. Because the dipole moment is zero, it must be the trans isomer. **23.96** 47.3 mg Mg^{2+}/L, 53.4 mg Ca^{2+}/L **23.99** $\Delta E = 3.02 \times 10^{-19}$ J/photon, $\lambda = 657$ nm. The complex will absorb in the visible around 660 nm and appear blue-green.

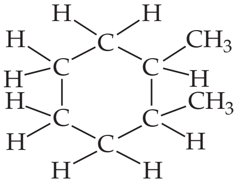
CHAPTER 24

24.1 Molecules (c) and (d) are the same molecule. **24.4** Compound (b), which has hydrogen bonding, has the highest boiling point. **24.7** (a) sp^3 (b) sp^2 (c) sp^2 (d) sp **24.9** Numbering from the right on the condensed structural formula, C1 has trigonal-planar electron-domain geometry, 120° bond angles, and sp^2 hybridization; C2 and C5 have tetrahedral electron-domain geometry, 109° bond angles, and sp^3 hybridization; C3 and C4 have linear electron-domain geometry, 180° bond angles, and sp hybridization. **24.11** NH_3 and CO are not typical organic molecules. NH_3 contains no carbon atoms. Carbon monoxide contains a C atom that does not form four bonds. **24.13** (a) A straight-chain alkane has all carbon atoms connected in a continuous chain. A carbon atom is bound to no more than two other carbon atoms and forms only σ bonds. A branched-chain hydrocarbon has a branch; at least one carbon atom is bound to three or more carbon atoms. (b) An alkane is a complete molecule composed of carbon and hydrogen in which all bonds are σ bonds. An alkyl group is a substituent formed by removing a hydrogen atom from an alkane. **24.15** (a) 2-methylhexane (b) 4-ethyl-2,4-dimethyldecane

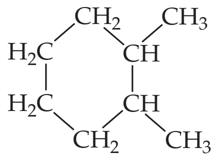
(c) $CH_3CH_2CH_2CH_2CH_2CH(CH_3)_2$

(d) $CH_3CH_2CH_2CH_2CH(CH_2CH_3)CH(CH_3)CH(CH_3)_2$

(e)

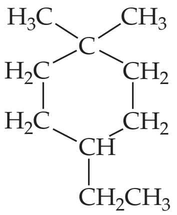


or



24.17 (a) 2,3-dimethylheptane (b) $CH_3CH_2CH_2C(CH_3)_3$

(c)



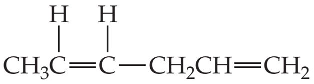
(d) 2,2,5-trimethylhexane (e) methylcyclobutane **24.19** 65 **24.21** (a) Alkanes are said to be saturated because they cannot undergo addition reactions, such as those characteristic of carbon–carbon double bonds. (b) No. The compound C_4H_6 does not contain the maximum possible number of hydrogen atoms and is unsaturated. **24.23** (a) C_5H_{12} (b) C_5H_{10} (c) C_5H_{10} (d) C_5H_8; saturated: (a), (b); unsaturated: (c), (d) **24.25** One possible structure is

$$CH{\equiv}C-CH{=}CH-C{\equiv}CH$$

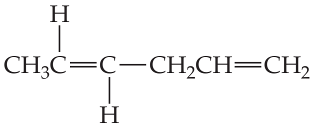
24.27 There are at least 46 structural isomers with the formula C_6H_{10}. A few of them are

$CH_3CH_2CH_2CH_2C{\equiv}CH$

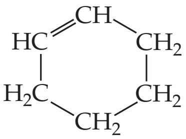
$CH_3CH_2CH_2C{\equiv}CCH_3$

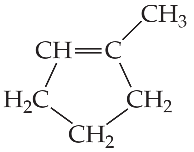


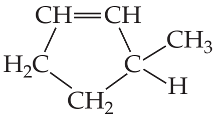
$$CH_3\overset{H}{C}=\overset{H}{C}-CH_2CH=CH_2$$



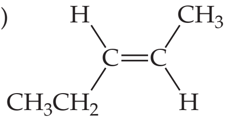
$$CH_3\overset{H}{C}=\underset{H}{C}-CH_2CH=CH_2$$



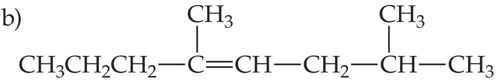




24.29 (a)



(b)

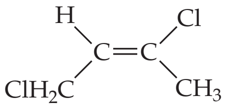


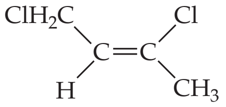
$$CH_3CH_2CH_2-\overset{CH_3}{C}=CH-CH_2-\overset{CH_3}{CH}-CH_3$$

(c) *cis*-6-methyl-3-octene (d) *para*-dibromobenzene (e) 4,4-dimethyl-1-hexyne **24.31** Geometric isomerism in alkenes is the result of restricted rotation about the double bond. In alkanes bonding sites are interchangeable by free rotation about the C—C single bonds. In alkynes there is only one additional bonding site on a triply bound carbon, so no isomerism results.

24.33 (a) No

(b)





(c) no (d) no **24.35** (a) An addition reaction is the addition of some reagent to the two atoms that form a multiple bond. In a substitution reaction one atom or group of atoms replaces another atom. Alkenes typically undergo addition, while aromatic hydrocarbons usually undergo substitution.

(b)

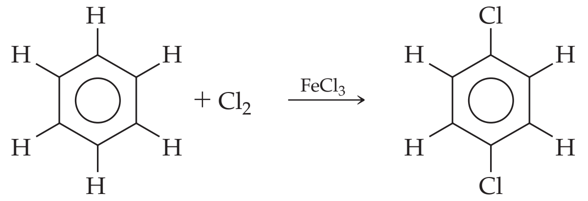
$CH_3CH_2CH{=}CH{-}CH_3 + Br_2 \longrightarrow$

2-pentene

$CH_3CH_2CH(Br)CH(Br)CH_3$

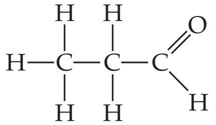
2, 3-dibromopentane

(c)

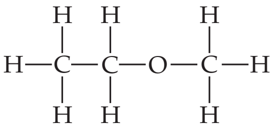


$C_6H_6 + Cl_2 \xrightarrow{FeCl_3} C_6H_4Cl_2$

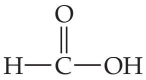
24.37 (a) The 60° C—C—C angles in the cyclopropane ring cause strain that provides a driving force for reactions that result in ring opening. There is no comparable strain in the five-or six-membered rings. (b) $C_2H_4(g) + HBr(g) \longrightarrow CH_3CH_2Br(l)$; $C_6H_6(l) + CH_3CH_2Br(l) \xrightarrow{AlCl_3} C_6H_5CH_2CH_3(l) + HBr(g)$ **24.39** Not necessarily. That the two rate laws are first order in both reactants and second order overall indicates that the activated complex in the rate-determining step in each mechanism is bimolecular and contains one molecule of each reactant. This is usually an indication that the mechanisms are the same, but it does not rule out the possibility of different fast steps or a different order of elementary steps. **24.41** $\Delta H_{comb}/\text{mol } CH_2$ for cyclopropane = 696.3 kJ, for cyclopentane = 663.4 kJ. $\Delta H_{comb}/CH_2$ group for cyclopropane is greater because C_3H_6 contains a strained ring. When combustion occurs, the strain is relieved and the stored energy is released. **24.43** (a) Alcohol (b) amine, alkene (c) ether (d) ketone, alkene (e) aldehyde (f) carboxylic acid, alkyne **24.45** (a) Propionaldehyde (or propanal):



(b) ethylmethyl ether:



24.47 (a)



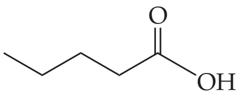
$H{-}\overset{O}{\overset{\|}{C}}{-}OH$

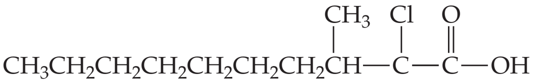
(b)

$CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}{-}OH$

or

(c)

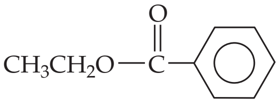




$CH_3CH_2CH_2CH_2CH_2CH_2CH_2\underset{}{\overset{CH_3}{\overset{|}{C}H}}{-}\overset{Cl}{\overset{|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OH$

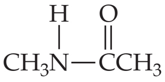
24.49

(a)



Ethylbenzoate

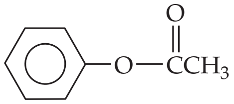
(b)



$CH_3\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}CH_3$

N-methylethanamide or
N-methylacetamide

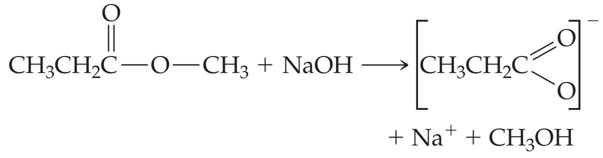
(c)



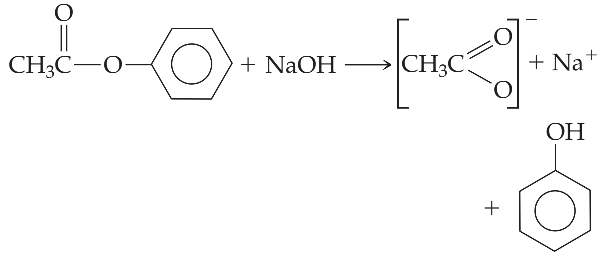
Phenylacetate

24.51

(a)



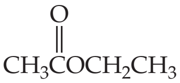
(b)



24.53 The presence of both —OH and —C=O groups in pure acetic acid leads us to conclude that it will be a strongly hydrogen-bonded substance. That the melting and boiling points of pure acetic acid are both higher than those of water, a substance we know to be strongly hydrogen-bonded, supports this conclusion.

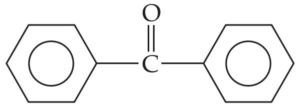
24.55 (a) $CH_3CH_2CH_2CH(OH)CH_3$ (b) $CH_3CH(OH)CH_2OH$

(c)



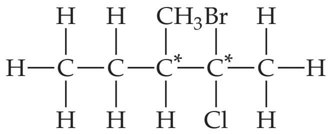
$CH_3\overset{O}{\overset{\|}{C}}OCH_2CH_3$

(d)



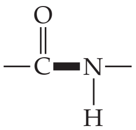
(e) $CH_3OCH_2CH_3$

24.57

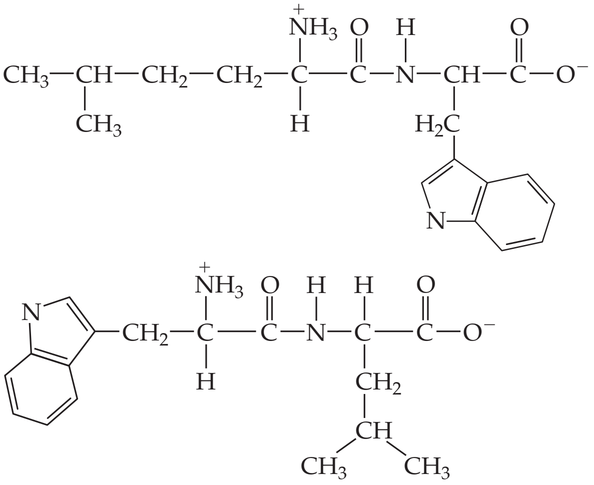


*chiral C atoms

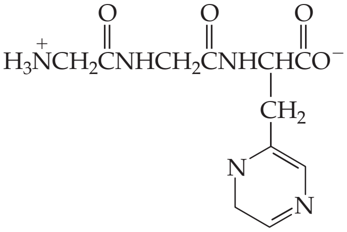
24.59 (a) An α -amino acid contains an NH_2 group attached to the carbon adjacent to the carboxcylic acid function. (b) In protein formation, amino acids undergo a condensation reaction between the amino group of one molecule and the carboxylic acid group of another to form the amide linkage. (c) The bond that links amino acids in proteins is called the peptide bond.



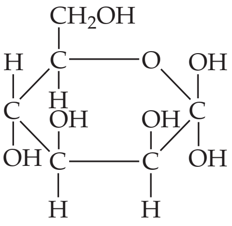
24.61

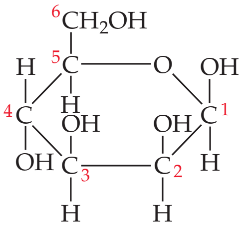


24.63 (a)



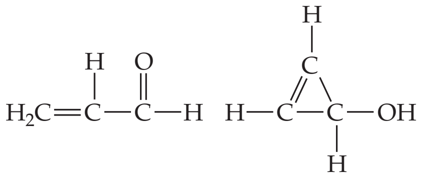
(b) Three tripeptides ar possible: Gly-Gly-His, GGH; Gly-His-Gly, GHG; His-Gly-Gly, HGG **24.65** The primary structure of a protein refers to the sequence of amino acids in the chain. The secondary structure is the configuration (helical, folded, open) of the protein chain. The tertiary structure is the overall shape of the protein determined by the way the segments fold together. (b) X-ray crystallography is the primary and preferred technique for determining protein structure. **24.67** (a) Carbohydrates, or sugars, are polyhydroxyaldehydes or ketones composed of carbon, hydrogen, and oxygen. They are derived primarily from plants and are a major food source for animals. (b) A monosaccharide is a simple sugar molecule that cannot be decomposed into smaller sugar molecules by hydrolysis. (c) A disaccharide is a carbohydrate composed of two simple sugar units. Hydrolysis breaks a disaccharide into two monosaccharides. (d) A polysaccharide is a polymer composed of many simple sugar units. **24.69** The empirical formula of cellulose is $C_6H_{10}O_5$. As in glycogen, the six-membered ring form of glucose forms the monomer unit that is the basis of the polymer cellulose. In cellulose, glucose monomer units are joined by β linkages. **24.71** (a) In the linear form of mannose, the aldehydic carbon is C1. Carbon atoms 2, 3, 4, and 5 are chiral because they each carry four different groups. (b) Both the α (left) and β (right) forms are possible.



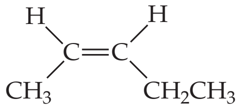


24.73 Two important kinds of lipids are fats and fatty acids. Structurally, fatty acids are carboxylic acids with a hydrocarbon chain of more than four carbon atoms (typically 16–20 carbon atoms). Fats are esters formed by condensation of an alcohol, often glycerol, and a fatty acid. Phospholipids are glycerol esters formed from one phosphoric acid $[RPO(OH)_2]$ and two fatty acid (RCOOH) molecules. At body pH, the phosphate group is depronated and has a negative charge. The long, nonpolar hydrocarbon chains do not readily mix with water, but they do interact with the nonpolar chains of other phospholipid molecules to form the inside of a bilayer. The charged phosphate heads interact with polar water molecules on the outsides of the bilayer. **24.75** *Purines*, with the larger electron cloud and molar mass, will have larger dispersion forces than *pyrimidines* in aqueous solution. **24.77** 5′−TACG−3′ **24.79** The complimentary strand for 5′−GCATTGGC−3′ is 3′−CGTAACCG−5′.

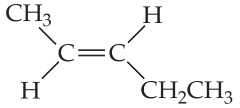
24.81



24.83



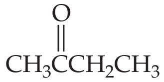
cis



trans

Cyclopentene does not show cis-trans isomerism because the existence of the ring demands that the C—C bonds be cis to one another. **24.86** (a) Aldehyde, trans-alkene, cis-alkene (b) ether, alcohol, alkene, amine (two of these, one aliphatic and one aromatic) (c) ketone (two of these), amine (two of these) (d) amide, alcohol (aromatic) **24.88** In a carboxylic acid, the electronegative carbonyl oxygen withdraws electron density from the O—H bond, rendering the bond more polar and the H more ionizable. And carboxylate anion is stabilized by resonance and encourages ionization of the carboxylic acid. In an alcohol no electronegative atoms are bound to the carbon that holds the —OH group, and the H is tightly bound to the O. **24.92** Glu-Cys-Gly is the only possible order. Glutamic acid has two carboxyl groups that can form a peptide bond with cysteine, so there are two possible structures for glutathione. **24.95** In both cases, stronger intermolecular forces lead to the higher boiling point. Ethanol contains O—H bonds, which form strong intermolecular hydrogen bonds, while dimethyl ether experiences only weak dipole–dipole and dispersion forces. The heavier and polar CH_2F_2 experiences dipole–dipole and stronger dispersion forces, while CH_4 experiences only weaker dispersion forces.

24.97



$CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_3$

24.99 $\Delta G^\circ = 13\,\text{kJ}$

ANSWERS TO GIVE IT SOME THOUGHT

CHAPTER 1

page 5 (a) 100 (b) atoms

page 10 Water is composed of two types of atoms: hydrogen and oxygen. Hydrogen is composed only of hydrogen atoms, and oxygen is composed only of oxygen atoms. Therefore, hydrogen and oxygen are elements and water is a compound.

page 13 (a) Chemical change: Carbon dioxide and water are different compounds than sugar. (b) Physical change: Water in the gas phase becomes water in the solid phase (frost). (c) Physical change: Gold in the solid state becomes liquid and then resolidifies.

page 16 pg, picogram (10^{-12} g)

page 19 $2.5 \times 10^2\ m^3$ is, because it has units of length to the third power.

page 21 (b) Mass of a penny

page 27 Use all digits given in the conversion factor. Conversion factors may be exact and then have “infinite” significant digits (for example, 2.54 cm = 1 inch exactly). Usually, your answer will have its number of significant digits limited by those of the quantities given in the problem.

CHAPTER 2

page 41 (a) The law of multiple proportions. (b) The second compound must contain two oxygen atoms for each carbon atom (that is, twice as many carbon atoms as the first compound).

page 44 Most α particles pass through the foil without being deflected because most of the volume of the atoms that comprise the foil is empty space.

page 45 (a) The atom has 15 electrons because atoms have equal numbers of electrons and protons. (b) The protons reside in the nucleus of the atom.

page 48 Any single atom of chromium must be one of the isotopes of that element. The isotope mentioned has a mass of 52.94 amu and is probably ^{53}Cr. The atomic weight differs from the mass of any particular atom because it is the average atomic mass of the naturally occurring isotopes of the element.

page 51 (a) Cl, (b) third period and group 7A, (c) 17, (d) nonmetal

page 54 (a) C_2H_6, (b) CH_3, (c) Probably the ball-and-stick model because the angles between the sticks indicate the angles between the atoms

page 57 We write the empirical formulas for ionic compounds. Thus, the formula is CaO.

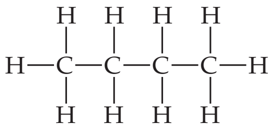
page 60 (a) The transition metals can form more than one type of cation, and the charges of these ions are therefore indicated explicitly with Roman numerals: Chromium(II) ion is Cr^{2+}. Calcium, on the other hand, always forms the Ca^{2+} ion, so there is no need to distinguish it from other calcium ions with different charges. (b) The *–ium* ending indicates that the ion is formed from nonmetals.

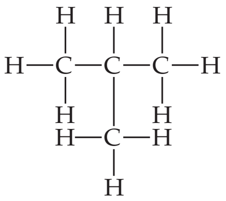
page 61 An *-ide* ending usually means a monatomic anion, although there are some anions with two atoms that are also named this way. An *-ate* ending indicates an oxyanion. The most common oxyanions have the *-ate* ending. An *-ite* ending also indicates an oxyanion, but one having less O than the anion whose name ends in *-ate*.

page 62 BO_3^{3-} and SiO_4^{4-}. The borate has three O atoms, like the other oxyanions of the second period in Figure 2.27, and its charge is 3−, following the trend of increasing negative charge as you move to the left in the period. The silicate has four O atoms, as do the other oxyanions in the third period in Figure 2.25, and its charge is 4−, also following the trend of increasing charge moving to the left.

page 65 Iodic acid, by analogy to the relationship between the chlorate ion and chloric acid

page 67





CHAPTER 3

page 78 Each $Mg(OH)_2$ has 1 Mg, 2 O, and 2 H; thus, 3 $Mg(OH)_2$ represents 3 Mg, 6 O, and 6 H.

page 83 The product is an ionic compound involving Na^+ and S^{2-}, and its chemical formula is therefore Na_2S.

page 88 (a) A mole of glucose. By inspecting their chemical formulas we find that glucose has more atoms of H and O than water and in addition it also has C atoms. Thus, a molecule of glucose has a greater mass than a molecule of water. (b) They both contain the same number of molecules because a mole of each substance contains 6.02×10^{23} molecules.

page 93 The N:H ratio is 2:4 = 1:2.

page 96 There are experimental uncertainties in the measurements.

page 97 3.14 mol because $2\ \text{mol}\ H_2 \hat{=} 1\ \text{mol}\ O_2$ based on the coefficients in the balanced equation

page 98 The number of grams of product formed is the sum of the masses of the two reactants, 50 g. When two substances react in a combination reaction, only one substance is formed as a product. According to the law of conservation of mass, the mass of the product must equal the masses of the two reactants.

CHAPTER 4

page 118 (a) $K^+(aq)$ and $CN^-(aq)$, (b) $Na^+(aq)$ and $ClO_4^-(aq)$

page 119 NaOH because it is the only solute that is a strong electrolyte

page 123 $Na^+(aq)$ and $NO_3^-(aq)$

page 125 Three. Each COOH group will partially ionize in water to form $H^+(aq)$.

page 126 Only soluble metal hydroxides are classified as strong bases and $Al(OH)_3$ is insoluble.

page 130 $SO_2(g)$

page 133 (a) −3, (b) +5

page 136 (a) Yes, nickel is below zinc in the activity series so $Ni^{2+}(aq)$ will oxidize $Zn(s)$ to form $Ni(s)$ and $Zn^{2+}(aq)$. (b) No reaction will occur because the $Zn^{2+}(aq)$ ions cannot be further oxidized.

page 139 The second solution is more concentrated, 2.50 *M*, than the first solution, which has a concentration of 1.00 *M*.

page 142 The concentration is halved to 0.25 *M*.

CHAPTER 5

page 162 No. The potential energy is lower at the bottom of the hill. (b) Once the bike comes to a stop, its kinetic energy is zero, just as it was at the top of the hill.

page 163 Open system. Humans exchange matter and energy with their surroundings.

page 167 Endothermic

page 169 The balance (current state) does not depend on the ways the money may have been transferred into the account or on the particular expenditures made in withdrawing money from the account. It depends only on the net total of all the transactions.

page 169 Because E, P, and V are state functions that don't depend on path, $H = E + PV$ must also be a state function.

page 170 No. If ΔV is zero, then the expression $w = -P\Delta V$ is also zero.

page 171 A thermometer to measure temperature changes

page 173 No. Because only half as much matter is involved, the value of ΔH would be $\frac{1}{2}(-483.6 \text{ kJ}) = -241.8 \text{ kJ}$.

page 176 Hg(l). Rearranging Equation 5.22 gives $\Delta T = \dfrac{q}{C_s \times m}$. When q and m are constant for a series of substances, then $\Delta T = \dfrac{\text{constant}}{C_s}$. Therefore, the element with the smallest C_s in Table 5.2 has the largest ΔT, Hg(l).

page 181 (a) The sign of ΔH changes. (b) The magnitude of ΔH doubles.

page 184 No. Because $O_3(g)$ is not the most stable form of oxygen at 25 °C, 1 atm $[O_2(g)$ is$]$, ΔH_f° for $O_3(g)$ is not necessarily zero. In Appendix C we see that it is 142.3 kJ/mol.

page 189 Fats, because they have the largest fuel value of the three

page 191 Combustion of $H_2(g)$ produces only $H_2O(g)$. No $CO_2(g)$ or other gases that might contribute to climate change issues are produced.

CHAPTER 6

page 210 No. Both visible light and X-rays are forms of electromagnetic radiation. They therefore both travel at the speed of light, c. Their differing ability to penetrate skin is due to their different energies, which we will discuss in the next section.

page 211 $E = h\nu = (6.63 \times 10^{-34} \text{ J-s})(5 \times 10^{-3} \text{ s}^{-1}) = 3 \times 10^{-30} \text{ J}$; this radiation cannot produce a burst of 5×10^{-36} J because it can only produce energy in multiples of 3×10^{-30} J.

page 212 Ultraviolet. Figure 6.4 shows that a photon in the ultraviolet region of the electromagnetic spectrum has a higher frequency and therefore a greater energy than a photon in the infrared region.

page 214 According to the third postulate, photons of only certain allowed frequencies can be absorbed or emitted as the electron changes energy state. The lines in the spectrum correspond to the allowed frequencies.

page 215 Absorb, because it is moving from a lower-energy state ($n = 3$) to a higher-energy state ($n = 7$)

page 217 Yes, all moving objects produce matter waves, but the wavelengths associated with macroscopic objects, such as the baseball, are too small to allow for any way of observing them.

page 219 The small size and mass of subatomic particles. The term $h/4\pi$ in the uncertainty principle is a very small number that becomes important only when considering extremely small objects, such as electrons.

page 220 Bohr proposed that the electron in the hydrogen atom moves in a well-defined circular path around the nucleus (an orbit). In the quantum-mechanical model, no effort is made to describe the motion of the electron. An orbital is a wave function related to the probability of finding the electron at any point in space.

page 221 The energy of an electron in the hydrogen atom is proportional to $-1/n^2$, as seen in Equation 6.5. The difference between $-1/(2)^2$ and $-1/(1)^2$ is much greater than the difference between $-1/(3)^2$ and $-1/(2)^2$.

page 226 (a) There is one $3s$ orbital, three $3p$ orbitals, and ten $3d$ orbitals, for a total of 14 orbitals. (b) $3s < 3p < 3d$.

page 232 The $6s$ orbital, which starts to hold electrons at element 55, Cs

page 237 We can't conclude anything! Each of the three elements has a different valence electron configuration for its $(n-1)d$ and ns subshells: For Ni, $3d^84s^2$; for Pd, $4d^{10}$; and for Pt, $5d^96s^1$.

CHAPTER 7

page 251 Atomic number is governed by the number of protons in the nucleus, but atomic weight is governed by both the number of protons and neutrons in the nucleus (electrons are too light to worry about). Co/Ni, Cu/Zn, and Te/I are other pairs of elements whose atomic weights are "off" compared to their atomic numbers.

page 254 The $2p$ electron in a Ne atom would experience a larger Z_{eff} than the $3s$ electron in Na, due to the better shielding by all the $2s$ and $2p$ electrons for Na's $3s$ electron.

page 256 These trends work against each other: Z_{eff} increasing would imply that the valence electrons are pulled tighter in to make the atom smaller, while orbital size "increasing" would imply that atomic size would also increase. The orbital size effect is larger: As you go down a column in the periodic table, atomic size generally increases.

page 259 It is harder to remove another electron from Na^+, so the process in Equation 7.3 would require more energy and, hence, shorter-wavelength light (see Sections 6.1 and 6.2).

page 260 Since Z_{eff} increases as you go from boron to carbon, we would expect that the first ionization energy would be larger for carbon. Therefore, I_2 for C is even greater.

page 262 The same

page 264 The numbers are the same; the signs are opposite.

page 265 Increasing metallic character is correlated with decreasing ionization energy.

page 268 Since the melting point is so low, we would expect a molecular rather than ionic compound. Thus, so PCl_3 is more likely than $ScCl_3$.

page 270 Its low ionization energy

page 272 In the acidic environment of the stomach, carbonate can react to give carbonic acid, which decomposes to water and carbon dioxide gas.

page 274 The longest wavelength of visible light is about 750 nm (Section 6.1). We can assume that this corresponds to the lowest energy of light (since $E = hc/\lambda$) needed to break bonds in hydrogen peroxide. If we plug in 750 nm for λ, we can calculate the energy to break one OO bond in one molecule of hydrogen peroxide, in joules. If we multiple by Avogadro's number, we can calculate how many joules it would take to break a mole of OO bonds in hydrogen peroxide (which is the number one normally finds).

page 275 The halogens all have ground-state electron configurations that are ns^2np^5; sharing an electron with only one other atom makes stable compounds.

page 276 We can estimate the radius to be 1.5 Å, and the first ionization energy to be 900 kJ/mol. In fact, its bonding radius is indeed 1.5 Å, and the experimental ionization energy is 920 kJ/mol.

CHAPTER 8

page 290 No. Cl has seven valence electrons. The first and second Lewis symbols are both correct—they both show seven valence electrons, and it doesn't matter which of the four sides has the single electron. The third symbol shows only five electrons and is incorrect.

page 292 CaF_2 is an ionic compound consisting of Ca^{2+} and F^- ions. When Ca and F_2 react to form CaF_2, each Ca atom loses two electrons to form a Ca^{2+} ion and each fluorine atom in F_2 takes up an electron, forming two F^- ions. Thus, we can say that each Ca atom transfers one electron to each of two fluorine atoms.

page 292 No. Figure 7.9 shows that the alkali metal with the smallest first ionization energy is Cs with a value of +376 kJ/mol. Figure 7.11 shows that the halogen with the largest electron affinity is Cl with a value of −349 kJ/mol. The sum of the two energies gives a positive energy (endothermic). Therefore, all other combinations of alkali metals with halogens will also have positive values.

page 296 Rhodium, Rh

page 297 Weaker. In both H_2 and H_2^+ the two H atoms are principally held together by the electrostatic attractions between the nuclei and the electron(s) concentrated between them. H_2^+ has only one electron between the nuclei whereas H_2 has two and this results in the H—H bond in H_2 being stronger.

page 298 Triple bond. CO_2 has two C—O double bonds. Because the C—O bond in carbon monoxide is shorter, it is likely to be a triple bond.

page 299 Electron affinity measures the energy released when an isolated atom gains an electron to form a 1− ion. The electronegativity measures the ability of the atom to hold on to its own electrons and attract electrons from other atoms in compounds.

page 300 Polar covalent. The difference in electronegativity between S and O is $3.5 - 2.5 = 1.0$. Based on the examples of F_2, HF, and LiF, the difference in electronegativity is great enough to introduce some polarity to the bond but not sufficient to cause a complete electron transfer from one atom to the other.

page 302 IF. Because the difference in electronegativity between I and F is greater than that between Cl and F, the magnitude of Q should be greater for IF. In addition, because I has a larger atomic radius than Cl, the bond length in IF is longer than that in ClF. Thus, both Q and r are larger for IF and, therefore, $\mu = Qr$ will be larger for IF.

page 303 Smaller dipole moment for C—H. The magnitude of Q should be similar for C—H and H—I bonds because the difference in electronegativity for each bond is 0.4. The C—H bond length is 1.1 Å and the H—I bond length is 1.6 Å. Therefore $\mu = Qr$ will be greater for H—I because it has a longer bond (larger r).

page 304 OsO_4. The data suggest that the yellow substance is a molecular species with its low melting and boiling points. Os in OsO_4 has an oxidation number of +8 and Cr in Cr_2O_3 has an oxidation number of +3. In Section 8.4, we learn that a compound with a metal in a high oxidation state should show a high degree of covalence and OsO_4 fits this situation.

page 308 There is probably a better choice of Lewis structure than the one chosen. Because the formal charges must add up to 0 and the formal charge on the F atom is +1, there must be an atom that has a formal charge of −1. Because F is the most electronegative element, we don't expect it to carry a positive formal charge.

page 310 Yes. There are two resonance structures for ozone that each contribute equally to the overall description of the molecule. Each O—O bond is therefore an average of a single bond and a double bond, which is a "one-and-a-half" bond.

page 310 As "one-and-a-third" bonds. There are three resonance structures, and each of the three N—O bonds is single in two of those structures and double in the third. Each bond in the actual ion is an average of these: $(1 + 1 + 2)/3 = 1\frac{1}{3}$.

page 312 No, it will not have multiple resonance structures. We can't "move" the double bonds, as we did in benzene, because the positions of the hydrogen atoms dictate specific positions for the double bonds. We can't write any other reasonable Lewis structures for the molecule.

page 312 The formal charge of each atom is shown here:

The first structure shows each atom with a zero formal charge and therefore it is the dominant Lewis structure. The second one shows a positive formal charge for an oxygen atom, which is a highly electronegative atom, and this is not a favorable situation.

page 315 The atomization of ethane produces $2\,C(g) + 6\,H(g)$. In this process, six C—H bonds and one C—C bond are broken. We can use $6D(C—H)$ to estimate the amount of enthalpy needed to break the six C—H bonds. The difference between that number and the enthalpy of atomization is an estimate of the bond enthalpy of the C—C bond, $D(C—C)$.

page 315 H_2O_2. From Table 8.4, the bond enthalpy of the O—O single bond in H_2O_2 (146 kJ/mol) is much lower than that of the O═O bond in O_2 (495 kJ/mol). The weaker bond in H_2O_2 is expected to make it more reactive than O_2.

CHAPTER 9

page 334 Octahedral. Removing two atoms that are opposite each other leads to a square-planar geometry.

page 335 The molecule does not follow the octet rule because it has ten electrons around the central A atom. There are four electron domains around A: two single bonds, one double bond, and one nonbonding pair.

page 336 Each of the three represents a single electron domain in the VSEPR model.

page 339 Yes. Based on one resonance structure, we might expect the electron domain that is due to the double bond to "push" the domains that are due to the single bonds, leading to angles slightly different from 120°. However, we must remember that there are two other equivalent resonance structures—each of the three O atoms has a double bond to N in one of the three resonance structures (Section 8.6). Because of resonance, all three O atoms are equivalent, and they will experience the same amount of repulsion, which leads to bond angles equal to 120°.

page 339 A tetrahedral arrangement of electron domains is preferred because the bond angles are 109.5° compared to 90°. bond angles in a square-planar arrangement of electron domains. The larger bond angles result in smaller repulsions among electron domains and a more stable structure.

page 343 Yes. The C—O and C—S bond dipoles exactly oppose each other, like in CO_2, but because O and S have different electronegativities, the magnitudes of the bond dipoles will be different. As a consequence, the bond dipoles will not cancel each other and the OCS molecule has a nonzero dipole moment.

page 348 Both p orbitals are perpendicular to the Be—F bond axes.

page 348 (bottom) The unhybridized p orbital is oriented perpendicular to the plane defined by the three sp^2 hybrids (trigonal-planar array of lobes) with one lobe on each side of the plane.

page 353 The molecule should not be linear. Because there are three electron domains around each N atom, we expect sp^2 hybridization and H—N—N angles of approximately 120°. The molecule is expected to be planar; the unhybridized $2p$ orbitals on the N atoms can form a π bond only if all four atoms lie in the same plane. You might notice that there are two ways in which the H atoms can be arranged: They can be both on the same side of the N═N bond or on opposite sides of the N═N bond.

page 358 The σ bond component is formed from sp hybrid orbitals.

page 360 The molecule would fall apart. With one electron in the bonding MO and one in the antibonding MO, there is no net stabilization of the electrons relative to two separate H atoms.

page 362 Yes. In Be_2^+ there would be two electrons in the σ_{2s} MO but only one electron in the $\sigma^{\star}_{2s}$ MO; therefore, the ion is predicted to have a bond order of $\frac{1}{2}$. It should (and does) exist.

page 366 No. If the σ_{2p} MO were lower in energy than the π_{2p} MOs, we would expect the σ_{2p} MO to hold two electrons and the π_{2p} MOs to hold one electron each, with the same spin. The molecule would therefore be paramagnetic.

CHAPTER 10

page 384 Small

page 385 1470 lb

page 389 It would be halved.

page 390 No—you have to convert *T* to Kelvin to calculate this properly.

page 392 Avogadro's number, 6.022×10^{23}

page 396 Less dense

page 399 The pressure due to N_2 would be the same, but the total pressure would increase.

page 404 HCl (slowest) $<$ O_2 $<$ H_2 (fastest)

page 406 3/2

page 409 (a) Decrease, (b) No change

page 410 (b) 100 K and 5 atm

page 411 They do have intermolecular attractions for each other, and they do take up space.

CHAPTER 11

page 430 $CH_4 < CCl_4 < CBr_4$. Because all three molecules are nonpolar, the strength of dispersion forces determines the relative boiling points. Polarizability increases in order of increasing molecular size and molecular weight, $CH_4 < CCl_4 < CBr_4$; hence, the dispersion forces and boiling points increase in the same order.

page 434 $Ca(NO_3)_2$ in water, because calcium nitrate is a strong electrolyte that forms ions and water is a polar molecule with a dipole moment. Ion–dipole forces cannot be present in a CH_3OH/H_2O mixture because CH_3OH does not form ions.

page 438 (a) Both viscosity and surface tension decrease with increasing temperature because of the increased molecular motion. (b) Both properties increase as the strength of intermolecular forces increases.

page 440 Melting (or fusion), endothermic

page 443 CCl_4. Both compounds are nonpolar; therefore, only dispersion forces exist between the molecules. Because dispersion forces are stronger for the larger, heavier CBr_4, it has a lower vapor pressure than CCl_4. The substance with the larger vapor pressure at a given temperature is more volatile.

CHAPTER 12

page 466 Tetragonal. There are two three-dimensional lattices that have a square base with a third vector perpendicular to the base, tetragonal and cubic, but in a cubic lattice the *a*, *b*, and *c* lattice vectors are all of the same length.

page 473 The packing efficiency decreases as the number of nearest neighbors decreases. The structures with the highest packing efficiency, hexagonal and cubic close packing, both have atoms with a coordination number of 12. Body-centered cubic packing, where the coordination number is 8, has a lower packing efficiency, and primitive cubic packing, where the coordination number is 6, has a lower packing efficiency still.

page 474 Interstitial, because boron is a small nonmetal atom that can fit in the voids between the larger palladium atoms

page 481 (a) Gold, Au. Tungsten, W, lies near the middle of the transition metal series where the bands arising from the *d* orbitals and the *s* orbital are approximately half-filled. This electron count should fill the bonding orbitals and leave the antibonding orbitals mostly empty. (b) Because both elements have similar numbers of electrons in the bonding orbitals but tungsten has fewer electrons in antibonding orbitals, it will have a higher melting point.

page 482 No. In a crystal the lattice points must be identical. Therefore, if an atom lies on top of a lattice point, then the same type of atom must lie on all lattice points. In an ionic compound there are at least two different types of atoms, and only one can lie on the lattice points.

page 484 Four. The empirical formula of potassium oxide is K_2O. Rearranging Equation 12.1 we can determine the potassium coordination number to be anion coordination number × (number of anions per formula unit/number of cations per formula unit) $= 8(1/2) = 4$.

page 494 A condensation polymer. The presence of both —COOH and $—NH_2$ groups allow molecules to react with one another forming C—N bonds and splitting out H_2O.

page 495 As the vinyl acetate content increases more side chain branching occurs which inhibits the formation of crystalline regions thereby lowering the melting point.

page 498 No. The emitted photons have energies that are similar in energy to the band gap of the semiconductor. If the size of the crystals is reduced into the nanometer range, the band gap will increase. However, because 340-nm light falls in the UV region of the electromagnetic spectrum, increasing the energy of the band gap will only shift the light deeper into the UV.

CHAPTER 13

page 514 Energy (or enthalpy) and entropy

page 515 The lattice energy of NaCl(*s*) must be overcome to separate Na^+ and Cl^- ions and disperse them into a solvent. C_6H_{14} is nonpolar. Interactions between ions and nonpolar molecules tend to be very weak. Thus, the energy required to separate the ions in NaCl is not recovered in the form of ion–C_6H_{14} interactions.

page 517 (a) Separating solvent molecules from each other requires energy and is therefore endothermic. (b) Forming the solute–solvent interactions is exothermic.

page 519 The added solute provides a template for the solid to begin to crystallize from solution, and the excess dissolved solute comes out of solution leaving a saturated solution.

page 522 The solubility in water would be considerably lower because there would no longer be hydrogen bonding with water, which promotes solubility.

page 526 Dissolved gases become less soluble as temperature increases, and they come out of solution, forming bubbles below the boiling point of water.

page 526 230 ppm (1 ppm is 1 part in 10^6); 2.30×10^5 ppb (1 ppb is 1 part in 10^9).

page 528 For dilute aqueous solutions the molality will be nearly equal to the molarity. Molality is the number of moles of solute per kilogram of solvent, whereas molarity is the number moles of solute per liter of solution. Because the solution is dilute, the mass of solvent is essentially equal to the mass of the solution. Furthermore, a dilute aqueous solution will have a density of 1.0 kg/L. Thus, the number of liters of solution and the number of kilograms of solvent will be essentially equal.

page 531 The lowering of the vapor pressure depends on the total solute concentration (Equation 13.11). One mole of NaCl (a strong electrolyte) provides 2 mol of particles (1 mol of Na^+ and 1 mol Cl), whereas one mole of (a nonelectrolyte) provides only 1 mol particles.

page 534 Not necessarily; if the solute is a strong or weak electrolyte, it could have a lower molality and still cause an increase of 0.51 °C. The total molality of all the particles in the solution is 1 *m*.

page 537 The 0.20-*m* solution is hypotonic with respect to the 0.5-*m* solution. (A hypotonic solution will have a lower concentration and hence a lower osmotic pressure.)

page 539 They would have the same osmotic pressure because they have the same concentration of particles. (Both are strong electrolytes that are 0.20 *M* in total ions.)

page 543 The smaller droplets carry negative charges because of the embedded stearate ions and thus repel one another.

CHAPTER 14

page 559 The rate will increase.

page 562 Average rate is for a large time interval; instantaneous rate is for an "instant" in time. Yes, they can have the same numeric value, especially if a plot of concentration versus time is linear.

page 565 (top) Reaction rate is what we measure as a reaction proceeds—change in concentration in time for one or more of the components in the mixture. Reaction rate always has units of concentration per time, usually M/s. A rate constant is what we calculate from reaction rate data, and its magnitude is proportional to the reaction rate, but its units depend on the reaction order. The rate law of a reaction is an equation that relates reaction rate to the rate constant: Rate $= k[\mathrm{A}]^m[\mathrm{B}]^n$, for components A and B in the reaction.

page 565 No. Rate is always change in concentration per time; rate constant has units that depend on the form of the rate law.

page 566 (a) The reaction is second order in NO, first order in H_2, and third order overall. (b) No. Doubling NO concentration will quadruple the rate, but doubling H_2 concentration will merely double the rate.

page 567 No reaction will take place.

page 573 1.25 g

page 575 The half-life will increase.

page 578 No—transition states are by definition not stable.

page 578 The collision may not have occurred with enough energy for reaction to occur, and/or the collision may not have occurred with the proper orientation of reactant molecules to favor product formation.

page 581 Bimolecular

page 585 Most reactions occur in elementary steps; the rate law is governed by the elementary steps, not by their sum (which is the overall balanced equation).

page 587 The odds of three molecules colliding with each other properly to react is very low.

page 590 By lowering the activation energy for the reaction or by increasing the frequency factor

page 591 A homogeneous catalyst will be harder to separate from the reaction mixture than a heterogeneous one.

page 593 People do say this, but we have to be careful. An enzyme-catalyzed reaction will have a lower transition state energy than the uncatalyzed reaction, but the nature of the transition state is probably different than the uncatalyzed version.

CHAPTER 15

page 614 (a) The rates of the forward and reverse reactions. (b) Greater than 1

page 614 When the concentrations of reactants and products are no longer changing

page 617 It does not depend on starting concentrations.

page 617 Units of moles/L are used to calculate K_c; units of partial pressure are used to calculate K_p.

page 618 0.00140

page 621 It is cubed.

page 623 $K_p = P_{H_2O}$

page 625 $K_c = [NH_4^+][OH^-]/[NH_3]$

page 633 (a) It shifts to the right. (b) It shifts to the left.

page 633 (bottom) It will shift to the left, the side with a larger number of moles of gas.

page 636 As the temperature increases, a larger fraction of molecules in the liquid phase have enough energy to overcome their intermolecular attractions and go into the vapor; the evaporation process is endothermic.

page 638 No

CHAPTER 16

page 652 The H^+ ion for acids and the OH^- ion for bases

page 654 CH_3NH_2 is the base because it accepts a H^+ from H_2S as the reaction moves from the left-hand to the right-hand side of the equation.

page 657 As the conjugate base of a strong acid, we would classify ClO_4^- as having negligible basicity.

page 661 pH is defined as $-\log[H^+]$. This quantity will become negative if the H^+ concentration exceeds 1 M, which is possible. Such a solution would be highly acidic.

page 662 pH $= 14.00 - 3.00 = 11.00$. This solution is basic because pH > 7.0.

page 665 Both NaOH and $Ba(OH)_2$ are soluble hydroxides. Therefore, the hydroxide concentrations will be 0.001 M for NaOH and 0.002 M for $Ba(OH)_2$. Because the $Ba(OH)_2$ solution has a higher $[OH^-]$, it is more basic and has a higher pH.

page 666 Because CH_3^- is the conjugate base of a substance that has negligible acidity, CH_3^- must be a strong base. Bases stronger than OH^- abstract H^+ from water molecules:

$$CH_3^- + H_2O \longrightarrow CH_4 + OH^-.$$

page 668 Oxygen

page 671 Because weak acids typically undergo very little ionization, often less than 1%. Normally we make this assumption and then check its validity based on the concentration of conjugate base formed in the calculation. If it is ≤5% of the initial concentration of the weak acid, we can generally use this assumption. If not, we must do an exact calculation.

page 674 This is the acid-dissociation constant for the loss of the third and final proton from H_3PO_4, corresponding to the equilibrium $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$.

page 680 The pK_a value is $-\log K_a = -\log(6.8 \times 10^{-4}) = 3.17$. The p$K_b$ value is $14.00 - \mathrm{p}K_a = 14.00 - 3.17 = 10.83$.

page 682 Nitrate is the conjugate base of nitric acid, HNO_3. The conjugate base of a strong acid does not act as a base, so NO_3^- ions will not affect the pH. Carbonate is the conjugate base of hydrogen carbonate, HCO_3^-, which is a weak acid. The conjugate base of a weak acid acts as a weak base, so CO_3^{2-} ions will increase the pH.

page 686 The increasing acidity going down a group is due mainly to decreasing H—X bond strength. The trend going across a period is due mainly to the increasing electronegativity of X, which weakens the H—X bond.

page 687 $HBrO_3$. For an oxyacid, acidity increases as the electronegativity of the central ion increases, which would make $HBrO_2$ more acidic than HIO_2. Acidity also increases as the number of oxygens bound to the central atom increases, which would make $HBrO_3$ more acidic than $HBrO_2$. Combining these two relationships we can order these acids in terms of increasing acid-dissociation constant, $HIO_2 < HBrO_2 < HBrO_3$.

page 689 The carboxyl group, —COOH

page 690 It must have an unshared pair of electrons that can be shared with another atom.

CHAPTER 17

page 707 (top) The Cl^- ion is the only spectator ion. The pH is determined by the equilibrium $NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$.

page 707 (bottom) HNO_3 and NO_3^-. To form a buffer we need comparable concentrations of a weak acid and its conjugate base.

HNO_3 and NO_3^- will not form a buffer because HNO_3 is a strong acid and the NO_3^- ion is merely a spectator ion.

page 708 (a) The OH^- of NaOH (a strong base) reacts with the acid member of the buffer (CH_3COOH), abstracting a proton. Thus, $[CH_3COOH]$ decreases and $[CH_3COO^-]$ increases. (b) The H^+ of HCl (a strong acid) reacts with the base member of the buffer $[CH_3COOH^-]$. Thus, $[CH_3COO^-]$ decreases and $[CH_3COOH]$ increases.

page 711 A buffer will be most resistant to changes in pH when the concentrations of the weak acid and its conjugate base are equal. When the two are exactly equal the Henderson–Hasselbach equation tells us that the pH of the buffer will be equal to the pK_a of the weak acid. The pK_a values of nitrous acid and hypochlorous acid are 3.35 and 7.52, respectively. Thus, HClO would be more suitable for a $pH = 7.0$ buffer solution. To make a buffer we would also need a salt containing ClO^-, such as NaClO.

page 716 The $pH = 7$. The neutralization of a strong base with a strong acid gives a salt solution at the equivalence point. The salt contains ions that do not change the pH of water.

page 721 The following titration curve shows the titration of 25 mL of Na_2CO_3 with HCl, both with 0.1 M concentrations. The overall reaction between the two is

$$Na_2CO_3(aq) + HCl(aq) \longrightarrow 2\,NaCl(aq) + CO_2(g) + H_2O(l)$$

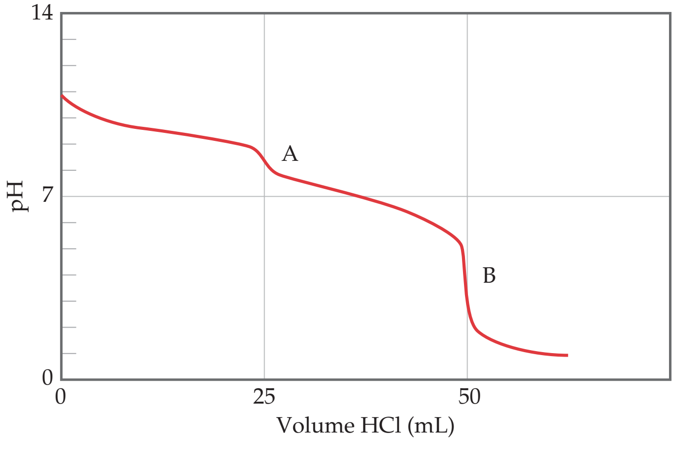
The initial pH (sodium carbonate in water only) is near 11 because CO_3^{2-} is a weak base in water. The graph shows two equivalence points, **A** and **B**. The first point, **A**, is reached at a pH of about 9:

$$Na_2CO_3(aq) + HCl(aq) \longrightarrow NaCl(aq) + NaHCO_3(aq)$$

HCO_3^- is weakly basic in water and is a weaker base than the carbonate ion. The second point, **B**, is reached at a pH of about 4:

$$NaHCO_3(aq) + HCl(aq) \longrightarrow NaCl(aq) + CO_2(g) + H_2O(l)$$

H_2CO_3, a weak acid, forms and decomposes to carbon dioxide and water.



page 722 The nearly vertical portion of the titration curve at the equivalence point is smaller for a weak acid–strong base titration; as a result fewer indicators undergo their color change within this narrow range.

page 724 AgCl. Because all three compounds produce the same number of ions, their relative stabilities correspond directly to the K_{sp} values, with the compound with the largest K_{sp} value being the most soluble.

page 734 Amphoteric substances are insoluble in water but dissolve in the presence of sufficient acid or base. Amphiprotic substances can both donate and accept protons.

page 738 The solution must contain one or more of the cations in group 1 of the qualitative analysis scheme, Ag^+, Pb^{2+} or Hg_2^{2+}.

CHAPTER 18

page 754 Photoionization is a process in which a molecule breaks into ions upon illumination with light; photodissociation is a process in which molecules break up upon illumination with light but the products bear no charge.

page 755 Because those molecules do not absorb light at those wavelengths

page 757 Yes—Cl is neither a product nor a reactant in the overall reaction, and its presence does speed the reaction up.

page 760 SO_2 in the atmosphere reacts with oxygen to form SO_3. SO_3 in the atmosphere reacts with water in the atmosphere to form H_2SO_4, sulfuric acid. The sulfuric acid dissolves in water droplets that fall to Earth, causing "acid rain" that has a pH of 4 or so.

page 761 NO_2 photodissociates to NO and O; the O atoms react with O_2 in the atmosphere to form ozone, which is a key ingredient in photochemical smog.

page 763 Higher humidity means there is more water in the air. Water absorbs infrared light, which we feel as heat. After sundown, the ground that has been warmed earlier in the day reradiates heat out. In locations with higher humidity, this energy is absorbed somewhat by the water and in turn is reradiated to some extent back to the Earth, resulting in warmer temperatures compared to a low-humidity location.

page 764 We need to be below water's critical point. Therefore, to sublime water we need to be below 0.006 atm. A wide range of temperatures will work for sublimation at this pressure—the most environmentally relevant ones are -50 °C to 100 °C.

page 768 The pollutants are capable of being oxidized (either directly by reaction with dissolved oxygen or indirectly by the action of organisms such as bacteria).

page 772 With a catalyst, the reaction is always faster, therefore costing less energy to run. In addition, with a catalyst the reaction may occur readily at a lower temperature, also costing less energy.

page 773 Fossil fuel combustion puts a great deal more CO_2 in the atmosphere right now than any supercritical use of CO_2. Compared to other (halogenated organic) solvents, supercritical CO_2 is far less toxic to life. Therefore, at present, using CO_2 as a solvent or a reactant in industrial processes is a reasonable choice for environmental sustainability.

page 774 Use room temperature and room pressure; use water as a solvent if possible; use O_2 as the oxidizing agent instead of hydrogen peroxide if possible.

page 775 sp before reaction; sp^2 after reaction

CHAPTER 19

page 787 No, nonspontaneous processes can occur so long as they receive some continuous outside assistance. Examples of nonspontaneous processes with which we may be familiar include the building of a brick wall and the electrolysis of water to form hydrogen gas and oxygen gas.

page 789 No. Just because the system is restored to its original condition doesn't mean that the surroundings have likewise been restored to their original condition, so it is not necessarily reversible.

page 791 ΔS depends not merely on q but on q_{rev}. Although there are many possible paths that could take a system from its initial to final state, there is always only one reversible isothermal path between two states. Thus, ΔS has only one particular value regardless of the path taken between states.

page 793 Because rusting is a spontaneous process, ΔS_{univ} must be positive. Therefore, the entropy of the surroundings must increase, and that increase must be larger than the entropy decrease of the system.

page 795 $S = 0$, based on Equation 19.5 and the fact that $\ln 1 = 0$.

page 796 A molecule can vibrate (atoms moving relative to one another) and rotate (tumble), whereas a single atom cannot undergo these motions.

page 799 It must be a perfect crystal at 0 K (third law of thermodynamics), which means it has only a single accessible microstate.

page 803 ΔS_{surr} always increases. For simplicity, assume that the process is isothermal. The change in entropy of the surroundings in an isothermal process is $\Delta S_{\text{surr}} = \frac{-q_{\text{sys}}}{T}$. Because the reaction is exothermic, $-q_{\text{sys}}$ is a positive number. Thus, ΔS_{surr} is a positive number and the entropy of the surroundings increases.

page 805 (a) In any spontaneous process the entropy of the universe increases. (b) In any spontaneous process operating at constant temperature, the free energy of the system decreases.

page 806 It indicates that the process to which the thermodynamic quantity refers has taken place under standard conditions, as summarized in Table 19.2.

page 810 Above the boiling point, vaporization is spontaneous, and $\Delta G < 0$. Therefore, $\Delta H - T\Delta S < 0$, and $\Delta H < T\Delta S$.

CHAPTER 20

page 829 Oxygen is first assigned an oxidation number of -2. Nitrogen must then have a $+3$ oxidation number for the sum of oxidation numbers to equal -1, the charge of the ion.

page 832 No. Electrons should appear in the two half-reactions but cancel when the half-reactions are added properly.

page 839 Yes. A redox reaction with a positive standard cell potential is spontaneous under standard conditions.

page 840 1 atm pressure of $Cl_2(g)$ and 1 M concentration of $Cl^-(aq)$

page 846 Using data from Appendix E, we have $E^\circ_{\text{red}} = -0.126\text{ V}$ for $Pb^{2+}(aq) \longrightarrow Pb(s)$ and $E^\circ_{\text{red}} = 0.854\text{ V}$ for $Hg^{2+}(aq) \longrightarrow Hg(l)$. Because Pb($s$) has the most negative value for E°_{red}, it is the stronger reducing agent. (See Figure 20.12.) The comparison can also be made by reference to the activity series where Pb lies also above Hg, indicating that Pb is oxidized more readily than Hg. The more readily a substance is oxidized, the stronger it is as a reducing agent.

page 859 Al, Zn. Both are easier to oxidize than Fe.

CHAPTER 21

page 877 The mass number decreases by 4.

page 879 Only the neutron, as it is the only neutral particle listed.

page 883 From Figure 21.4 we can see that each of these four elements has only one stable isotope, and from their atomic numbers we see that they each have an odd number of protons. Given the rarity of stable isotopes with odd numbers of neutrons and protons, we expect that each isotope will possess an even number of neutrons. From their atomic weights we see that this is the case: F (10 neutrons), Na (12 neutrons), Al (14 neutrons), and P (16 neutrons).

page 885 No. Electric and magnetic fields are only effective at accelerating charged particles and a neutron is not charged.

page 889 top Spontaneous radioactive decay is a unimolecular process: $A \longrightarrow$ Products. The rate law that fits this observation is a first-order kinetic rate law, rate $= k[A]$. A second-order kinetic process has rate $= k[A]^2$ and the elementary reaction is bimolecular: $A + A \longrightarrow$ Products. A zero-order kinetic process has rate $= k$, and the rate does not change until the limiting reactant is entirely consumed. The latter two rate laws do not fit a unimolecular process.

page 889 (bottom) (a) Yes; doubling the mass would double the amount of radioactivity of the sample as shown in Equation 21.18. (b) No; changing the mass would not change the half-life as shown in Equation 21.20.

page 892 No. Alpha particles are more readily absorbed by matter than beta or gamma rays. Geiger counters must be calibrated for the radiation they are being used to detect.

page 896 (top) The values in Table 21.7 only reflect the mass of the nucleus, while the atomic mass is the sum of the mass of the nucleus and the electrons. So the atomic mass of iron-56 is $26 \times m_e$ larger than the nuclear mass.

page 896 (bottom) No. Stable nuclei having mass numbers around 100 are the most stable nuclei. They could not form a still more stable nucleus with an accompanying release of energy.

page 905 The absorbed dose is equal to $0.10\text{ J} \times (1\text{ rad}/1 \times 10^{-2}\text{ J}) =$ 10 rads. The effective dosage is calculated by multiplying the absorbed dose by the relative biological effectiveness (RBE) factor, which is 10 for alpha radiation. Thus, the effective dosage is 100 rems.

CHAPTER 22

page 919 (top) No.

page 919 No. N can form triple bonds but P cannot, as it would have to form P_2.

page 921 H^-, hydride.

page 923 $+1$ for everything except H_2, for which the oxidation state of H is 0.

page 924 No—it is the volume of Pd that can increase to accommodate hydrogen, not its mass.

page 927 0 for Cl_2; -1 for Cl^-; $+1$ for ClO^-

page 929 They should both be strong, since the central halogen is in the $+5$ oxidation state for both of them. We need to look up the redox potentials to see which ion, BrO_3^- or ClO_3^-, has the larger reduction potential. The ion with the larger reduction potential is the stronger oxidizing agent. BrO_3^- is the stronger oxidizing agent on this basis ($+1.52$ V standard reduction potential in acid compared to $+1.47$ V for ClO_3^-).

page 931 The standard energy to dissociate one mole of oxygen atoms from one mole of ozone was given as 105 kJ. If we assume, as usual, that one photon will dissociate one molecule, that means the energy of the photons should be 105 kJ per mole (of photons). Using Avogadro's number, we can calculate that one photon would then have 1.744×10^{-19} J of energy. Using equations from Chapter 6, $c = \lambda\nu$ and $E = h\nu$, we can find that a photon with 1.744×10^{-19} J of energy will have a wavelength λ of 1140 nm, or 1.14×10^6 m, which is in the infrared part of the spectrum.

page 932 HIO_3

page 936 $SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(l)$

page 940 (a) $+5$ (b) $+3$

page 948 $CO_2(g)$

page 949 Yes, it must, since CS_2 is a liquid at room temperature and pressure, and CO_2 is a gas.

page 952 Silicon is the element, Si. Silica is SiO_2. Silicones are polymers that have an $O{-}Si{-}O$ backbone and hydrocarbon groups on the Si.

page 953 $+3$

CHAPTER 23

page 965 Sc is the biggest.

page 967 You would have to remove core electrons.

page 968 (top) The larger the distance, the weaker the spin–spin interactions.

page 968 (bottom) Yes, it is a Lewis acid–base interaction; the metal ion is the Lewis acid (electron pair acceptor).

page 972 $[Fe(H_2O)_6]^{3+}(aq) + SCN^-(aq) \longrightarrow$ $[Fe(H_2O)_5SCN]^{2+}(aq) + H_2O(l)$

page 974 (a) tetrahedral (b) octahedral

page 976 Bidentate

page 978 Its conjugation (alternating single and double CC bonds)

page 981 No, ammonia cannot engage in linkage isomerism—the only atom that can coordinate to a metal is the nitrogen.

page 985 Both isomers have the same chemical formulas and the same donor atoms on the ligands bonding to the metal ion. The difference is that the *d* isomer has a right-handed "twist" and the *l* isomer has a "left-handed" twist.

page 987 Co is $1s^22s^22p^63s^23p^64s^23d^7$. Co^{3+} is $1s^22s^22p^63s^23p^63d^6$. Co has 3 unpaired electrons; Co^{3+} has 4 unpaired electrons, assuming all 5 *d* orbitals have the same energy.

page 989 It has lost all of the Ti valence electrons; only core electrons remain, and the energy gap between filled and empty orbitals is large, corresponding to light in the ultraviolet, which we cannot perceive as colored.

page 991 Low spin

page 992 The ligands are in the *xy* plane. The d_{xy} orbital has its lobes mostly in that plane, so its energy is higher than d_{xz} and d_{yz}.

CHAPTER 24

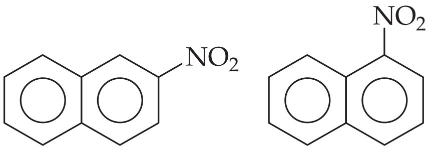
page 1007 $C{=}N$, because it is a polar double bond. $C{-}H$ and $C{-}C$ bonds are relatively unreactive.

page 1009 Two $C{-}H$ bonds and two $C{-}C$ bonds

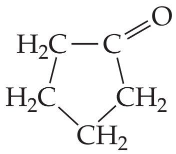
page 1010 The isomers have different properties, as seen in Table 24.3.

page 1015 Only two of the four possible $C{=}C$ bond sites are distinctly different in the linear chain of five carbon atoms with one double bond.

page 1021



page 1025



page 1029 All four groups must be different from one another.

page 1033 No. Breaking the hydrogen bonds between $N{-}H$ and $O{=}C$ groups in a protein by heating causes the α-helix structure to unwind and the β-sheet structure to separate.

page 1037 The α form of the $C{-}O{-}C$ linkage. Glycogen serves as a source of energy in the body, which means that the body's enzymes must be able to hydrolyze it to sugars. The enzymes work only on polysaccharides having the α linkage.

ANSWERS TO GO FIGURE

CHAPTER 1

Figure 1.1 9

Figure 1.4 Vapor (gas)

Figure 1.5 Molecules of a compound are composed of more than one type of atom, and molecules of an element are composed of only one type of atom.

Figure 1.6 Earth is rich in silicon and aluminum; the human body is rich in carbon and hydrogen

Figure 1.7 They are the same; there are twice as many hydrogen molecules as oxygen molecules, and the hydrogen gas takes up twice the volume of the oxygen gas.

Figure 1.17 True

Figure 1.18 1000

Figure 1.23 The darts would be scattered widely (poor precision) but their average position would be at the center (good accuracy).

CHAPTER 2

Figure 2.3 We know the rays travel from the cathode because of the way the magnetic field diverts the path (b).

Figure 2.4 The electron beam would be deflected downward because of repulsion by the negative plate and attraction toward the positive plate.

Figure 2.8 The beta rays, whose path is diverted away from the negative plate and toward the positive plate, consist of electrons. Because the electrons are much less massive than the alpha particles, their motion is affected more strongly by the electric field.

Figure 2.10 The beam consists of alpha particles, which carry a $+2$ charge.

Figure 2.14 Based on the periodic trend, we expect that elements that precede a nonreactive gas, as F does, will also be reactive nonmetals. The elements fitting this pattern are H and Cl.

Figure 2.19 The ball-and-stick model more clearly shows the connections between atoms, so we can see the angles at which the atoms are attached in the molecule.

Figure 2.20 The elements are in the following groups: Ag^+ is 1B, Zn^{2+} is 2B, and Sc^{3+} is 3B. Sc^{3+} has the same number of electrons as Ar (element 18).

Figure 2.24 Removing one O atom from the perbromate ion gives the bromate ion, BrO_3^-.

CHAPTER 3

Figure 3.3 The formula CO_2 represents one molecule containing one C and two O atoms, whereas 2 CO represents two molecules, each containing one C atom and one O atom for a total of two C and two O atoms.

Figure 3.8 Both figures show combustion reactions in which the fuel is a hydrocarbon (CH_4 in Figure 3.4 and C_3H_8 in Figure 3.8). In both cases the reactants are the hydrocarbon and O_2, and the products are CO_2 and H_2O.

Figure 3.9 As shown, $18.0\ g\ H_2O = 1\ mol\ H_2O = 6.02 \times 10^{23}$ molecules H_2O. Thus, $9.00\ g\ H_2O = 0.500\ mol\ H_2O = 3.01 \times 10^{23}$ molecules H_2O.

Figure 3.12 (a) The molar mass of CH_4, $16.0\ g\ CH_4/1\ mol\ CH_4$. (b) Avogadro's number, $1\ mol\ CH_4/6.02 \times 10^{23}$ formula units CH_4, where a formula unit in this case is a molecule.

Figure 3.13 The mole ratio is obtained by dividing the molecular weight by the empirical formula weight, Equation 3.11.

Figure 3.17 There are 7 mol O_2, and each mol O_2 yields 2 mol H_2O. Thus, 14 mol H_2O would have formed.

CHAPTER 4

Figure 4.3 $NaCl(aq)$

Figure 4.4 K^+ and NO_3^-

Figure 4.9 Two moles of hydrochloric acid are needed to react with each mole of $Mg(OH)_2$.

Figure 4.19 The volume needed to reach the end point if $Ba(OH)_2(aq)$ were used would be one-half the volume needed for titration with $NaOH(aq)$.

CHAPTER 5

Figure 5.1 In the act of throwing, the pitcher transfers energy to the ball, which then becomes kinetic energy of the ball. For a given amount of energy E transferred to the ball, Equation 5.1 tells us that the speed of the ball is $v = \sqrt{2E/m}$ where m is the mass of the ball. Because a baseball has less mass than a bowling bowl, it will have a higher speed for a given amount of energy transferred.

Figure 5.2 When she starts going uphill, kinetic energy is converted to potential energy and her speed decreases.

Figure 5.3 The electrostatic potential energy of two oppositely charged particles is negative (Equation 5.2). As the particles become closer, the electrostatic potential energy becomes even more negative—that is, it decreases.

Figure 5.4 Yes, the system is still closed—matter can't escape the system to the surroundings unless the piston is pulled completely out of the cylinder.

Figure 5.5 If $E_{final} = E_{initial}$, then $\Delta E = 0$.

Figure 5.6

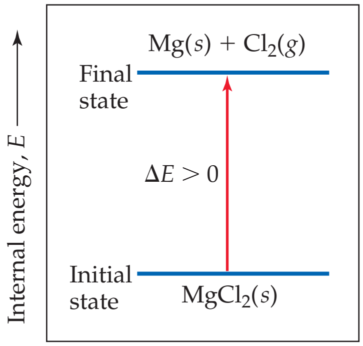


Figure 5.7 No. The sign on w is positive and the sign on q is negative. We need to know the magnitudes of q and w to determine whether $\Delta E = q + w$ is positive or negative.

Figure 5.10 The battery is doing work on the surroundings, so $w < 0$.

Figure 5.11 We need to know whether $Zn(s)$ or $HCl(aq)$ is the limiting reagent of the reaction. If it is $Zn(s)$, then the addition of more Zn will lead to the generation of more $H_2(g)$ and more work will be done.

Figure 5.17 Endothermic—heat is being added to the system to raise the temperature of the water.

Figure 5.18 Two cups provide more thermal insulation so less heat will escape the system.

Figure 5.19 The stirrer ensures that all of the water in the bomb is at the same temperature.

Figure 5.21 The condensation of 2 $H_2O(g)$ to 2 $H_2O(l)$

Figure 5.22 Yes, ΔH_3 would remain the same as it is the enthalpy change for the process $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$.

Figure 5.24 Grams of fat

CHAPTER 6

Figure 6.3 The wavelength of (a) is twice that of (b) and the frequency of (a) is consequently half that of (b). Thus, the wavelength of (b) is 0.50 m and its frequency is 6.0×10^8 cycles/s.

Figure 6.4 The X-ray has a shorter wavelength and, consequently, higher frequency than the red light.

Figure 6.5 The hottest area is the white or yellowish white area in the center.

Figure 6.7 If the tube is not evacuated, the electrons that are freed from the metal surface will strike gas molecules near that surface. As a result, they will become attached to the gas molecules and never arrive at the positive terminal.

Figure 6.12 The $n = 2$ to $n = 1$ transition involves a larger energy change than the $n = 3$ to $n = 2$ transition. (Compare the space differences between the states in the figure.) If the $n = 2$ to $n = 1$ transition produces visible light, the $n = 3$ to $n = 2$ transition must produce radiation of lower energy. The infrared radiation has lower frequency and, hence, lower energy than visible light, whereas the ultraviolet has greater frequency and greater energy. Thus, the $n = 2$ to $n = 1$ transition will produce ultraviolet radiation.

Figure 6.16 The region of highest electron density is where the density of dots is highest, which is near the nucleus.

Figure 6.17 The fourth shell ($n = 4$) would contain four subshells, labeled $4s$, $4p$, $4d$, and $4f$.

Figure 6.18 There would be four maxima and three nodes.

Figure 6.22 (a) The intensity of the color indicates that the probability of finding the electron is greater at the interior of the lobes than on the edges. (b) $2p_x$.

Figure 6.24 The $4d$ and $4f$ subshells are not shown.

CHAPTER 7

Figure 7.1 Row 7—these elements are generally radioactive and not stable.

Figure 7.3 $2s$

Figure 7.6 Bottom and left

Figure 7.7 They get larger, just like the atoms do.

Figure 7.9 Ar; it has a larger Z_{eff}.

Figure 7.10 There is more electron–electron repulsion in the case of oxygen because two electrons have to occupy the same orbital.

Figure 7.11 The halogens (group 7A); it does make sense because we know that they are very stable as anions.

Figure 7.12 Ionization energy—lower ionization energy is correlated with increasing metallic character.

Figure 7.14 Anions are above the lines; cations are below the line.

Figure 7.22 Lilac

CHAPTER 8

Figure 8.1 Covalent

Figure 8.2 Yes, the same sort of reaction should occur between any of the alkali metals and any of the elemental halogens.

Figure 8.3 Cations have a smaller radius than their neutral atoms and anions have a larger radius. Because Na and Cl are in the same row of the periodic table, we would expect Na^+ to have a smaller radius than Cl^-, so we would guess that the larger green spheres represent Cl^-.

Figure 8.4 The distance between ions in KF should be larger than that in NaF and smaller than that in KCl. We would thus expect the lattice energy of KF to be between 701 and 910 kJ/mol.

Figure 8.6 The repulsions between the nuclei would decrease, the attractions between the nuclei and the electrons would decrease, and the repulsions between the electrons would be unaffected.

Figure 8.7 The electronegativity decreases with increasing atomic number.

Figure 8.9 μ will decrease

Figure 8.10 The bonds are not polar enough to cause enough excess electron density on the halogen atom to lead to a red shading.

Figure 8.12 The lengths of the bonds of the outer O atoms to the inner O atom are the same.

Figure 8.13 Yes. The electron densities on the left and right parts of the molecule are the same, indicating that resonance has made the two O—O bonds equivalent to one another.

Figure 8.14 The dashed bonds represent the "half bonds" that result when the two resonance structures are averaged.

Figure 8.15 Exothermic

Figure 8.17 As the bond gets longer, it gets weaker. We would therefore expect a plot of bond enthalpy versus bond length to have a negative slope.

CHAPTER 9

Figure 9.1 The atomic radii (Figure 7.7)

Figure 9.3 Octahedral

Figure 9.7 The electron pair in the bonding domain is attracted toward two nuclear centers, whereas the nonbonding pair is attracted toward just one.

Figure 9.8 90°

Figure 9.9 The nonbonding electron pairs exert a greater repulsive force than the bonding electron pairs.

Figure 9.10 The heads of the arrows point toward regions of highest electron density, as indicated by the red color.

Figure 9.14 As the internuclear distance decreases, nucleus–nucleus repulsion becomes a dominant component of the potential energy.

Figure 9.16 The small lobes of the *sp* hybrid orbitals are very much smaller in spatial extent and, therefore, provide very little overlap with the F orbitals.

Figure 9.17 Three: one *s* and two *p* orbitals

Figure 9.23 The two *p* orbitals that form the π bond must align, and each of them is perpendicular to the plane of the sp^2 hybrid orbitals.

Figure 9.24 Acetylene, because it has two C—C π bonds, whereas ethylene has one π bond

Figure 9.26 C—H and C—C

Figure 9.33 The σ^*_{1s}

Figure 9.34 The two electrons in the σ_{1s} MO

Figure 9.35 The $1s$ orbitals of Li are small in spatial extent because they experience a strong nuclear attraction. In addition, both the bonding and antibonding MOs formed from them are occupied, so that there is no significant net bonding.

Figure 9.36 Nodal planes between the atoms are found in antibonding MOs.

Figure 9.42 The σ_{2p} and π_{2p} orbitals. Because the σ_{2p} orbital mixes with the σ_{2s}, it is pushed to higher energy and the σ_{2s} is moved to lower energy. The σ_{2p} orbital thus rises above the π_{2p} in energy.

Figure 9.43 F_2 contains four more electrons than N_2. These electrons go into the antibonding π^*_{2p} orbitals, thus lowering the bond order.

Figure 9.45 Because N_2 has no unpaired electrons, it is diamagnetic. Therefore, it would simply flow down with no tendency to remain in the magnetic field.

Figure 9.46 11. All the electrons in the $n = 2$ level are valence-shell electrons.

CHAPTER 10

Figure 10.2 It will increase.

Figure 10.5 Decrease

Figure 10.6 1520 torr

Figure 10.7 Linear

Figure 10.10 one

Figure 10.11 It is small and inert.

Figure 10.17 About a third

Figure 10.18 Higher speeds are correlated with smaller molar masses (assuming constant T).

Figure 10.20 n, moles of gas

Figure 10.22 Not really—CO_2 is least ideal and does have the largest molar mass, but H_2, the lightest gas, deviates more from the ideal line than the heavier N_2.

Figure 10.23 True

Figure 10.25 It would increase.

CHAPTER 11

Figure 11.2 The density in a liquid is much closer to a solid than it is to a gas.

Figure 11.9 Both compounds are nonpolar and incapable of forming hydrogen bonds. Therefore, the boiling point is determined by the dispersion forces, which are stronger for the larger, heavier SnH_4.

Figure 11.10 The non-hydrogen atom must possess a nonbonding electron pair.

Figure 11.11 There are four electron pairs surrounding oxygen in a water molecule. Two of the electron pairs are used to make covalent bonds to hydrogen within the H_2O molecule, while the other two are available to make hydrogen bonds to neighboring molecules. Because the electron-pair geometry is tetrahedral (four electron domains around the central atom), the $H—O\cdots H$ bond angle is approximately 109°.

Figure 11.19 Wax is a hydrocarbon that cannot form hydrogen bonds. Therefore, coating the inside of tube with wax will dramatically decrease the adhesive forces between water and the tube and change the shape of the water meniscus to an inverted U-shape. Neither wax nor glass can form metallic bonds with mercury so the shape of the mercury meniscus will be qualitatively the same, an inverted U-shape.

Figure 11.21 Because we are dealing with a state function, the energy of going straight from a solid to a gas must be the same as going from a solid to a gas through an intermediate liquid state. Therefore, the heat of sublimation must be equal to the sum of the heat of fusion and the heat of vaporization: $\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$.

Figure 11.24 Increases, because the molecules have more kinetic energy as the temperature increases and can escape more easily

Figure 11.25 All liquids including ethylene glycol reach their normal boiling point when their vapor pressure is equal to atmospheric pressure, 760 torr.

Figure 11.27 Freezing, because for most substances the solid phase is denser than the liquid phase and increasing the pressure will eventually drive a phase transition from the liquid to the solid state (provided the temperature is below the critical temperature)

CHAPTER 12

Figure 12.13 A hexagonal lattice

Figure 12.15 The solvent is the majority component and the solute the minority component. Therefore, there will be more solvent atoms than solute atoms.

Figure 12.17 The samarium atoms sit on the corners of the unit cell so there is only $8 \times (1/8) = 1$ Sm atom per unit cell. Eight of the nine cobalt atoms sit on faces of the unit cell, and the other sits in the middle of the unit cell so there are $8 \times (1/2) + 1 = 5$ Co atoms per unit cell.

Figure 12.19 The atoms are randomly arranged in red gold, which is a substitutional alloy. Purple gold is an intermetallic compound in which the atoms are arranged in a specific ordered pattern.

Figure 12.20 By drawing Lewis structures you can show that there are three (chlorine), two (sulfur), one (phosphorus), and zero (silicon) nonbonding electron pairs per atom.

Figure 12.22 In the fourth period, vanadium and chromium have very similar melting points. Molybdenum and tungsten have the highest melting points in the fifth and sixth periods, respectively. All of these elements are located near the middle of the period where the bonding orbitals are mostly filled and the antibonding orbitals mostly empty.

Figure 12.23 The molecular orbitals become more closely spaced in energy.

Figure 12.24 Potassium has only one valence electron per atom. If we fill the 4*s* band halfway probably a small amount of electron density will leak over and start to fill the 3*d* orbitals as well. The 4*p* orbitals should be empty.

Figure 12.25 Ionic substances cleave because the nearest neighbor interactions switch from attractive to repulsive if the atoms slide so that ions of like charge (cation–cation and anion–anion) touch each other. Metals don't cleave because the atoms are attracted to all other atoms in the crystal through metallic bonding.

Figure 12.26 No, ions of like charge do not touch in an ionic compound because they are repelled from one another. In an ionic compound the cations touch the anions.

Figure 12.28 In NaF there are four Na^+ ions $(12 \times 1/4)$ and four F^- ions $(8 \times 1/8 + 6 \times 1/2)$ per unit cell. In MgF_2 there are two Mg^{2+} ions $(8 \times 1/8 + 1)$ and four F^- ions $(4 \times 1/2 + 2)$ per unit cell. In ScF_3 there is one Sc^{3+} ion $(8 \times 1/8)$ and three F^- ions $(12 \times 1/4)$ per unit cell.

Figure 12.29 The intermolecular forces are stronger in toluene, as shown by its higher boiling point. The molecules pack more efficiently in benzene, which explains its higher melting point, even though the intermolecular forces are weaker.

Figure 12.44 Decrease. As the quantum dots get smaller, the band gap increases and the emitted light shifts to shorter wavelength.

Figure 12.47 Each carbon atom in C_{60} is bonded to three neighboring carbon atoms through covalent bonds. Thus, the bonding is more like graphite, where carbon atoms also bond to three neighbors, than diamond, where carbon atoms bond to four neighbors.

CHAPTER 13

Figure 13.2 Opposite charges attract. The electron-rich O atom of the H_2O molecule, which is the negative end of the dipole, is attracted to the positive Na^+ ion.

Figure 13.3 The negative end of the water dipole (the O) is attracted to the positive Na^+ ion, whereas the positive end of the dipole (the H) is attracted to the negative Cl^- ion.

Figure 13.4 For exothermic solution processes the magnitude of ΔH_{mix} will be larger than the magnitude of $\Delta H_{solute} + \Delta H_{solvent}$

Figure 13.8 The dissolving of the crystal and the crystallization by which ions in solution become reattached to the solid

Figure 13.9 If the solution wasn't supersaturated, solute would not crystallize from it.

Figure 13.14 If the partial pressure of a gas over a solution is doubled, the concentration of gas in the solution would double.

Figure 13.15 The slopes increase as the molecular weight increases. The larger the molecular weight, the greater the polarizability of the gas molecules, leading to greater intermolecular attractive forces between gas molecules and water molecules.

Figure 13.18 Looking at where the solubility curves for KCl and NaCl intersect the 80 °C line, we see that the solubility of KCl is about 51 g/100 g H_2O, whereas NaCl has a solubility of about 39 g/100 g H_2O. Thus, KCl is more soluble than NaCl at this temperature.

Figure 13.19 N_2 has the same molecular weight as CO but is nonpolar, so we can predict that its curve will be just below that of CO.

Figure 13.25 The water will move through the semipermeable membrane toward the more concentrated solution. Thus, the liquid level in the left arm will increase.

Figure 13.26 Water will move toward the more concentrated solute solution, which is inside the red blood cells, causing them to undergo hemolysis.

Figure 13.30 The two negatively charged groups both have the composition $-CO_2^-$.

Figure 13.32 Recall the rule that likes dissolve likes. The oil drop is composed of nonpolar molecules, which interact with the nonpolar part of the stearate ion with dispersion forces.

CHAPTER 14

Figure 14.3 B

Figure 14.4 It decreases.

Figure 14.8 The reaction is first order in CH_3NC.

Figure 14.10 At early times in the reaction; both graphs look linear close to $t = 0$.

Figure 14.17 The energy needed to overcome the energy barrier (the activation energy) looks about twice as large as the overall energy change for the reaction.

Figure 14.23 For the blue curve: The transition states are at the top of the peaks (2) and the intermediate is in the "valley" between the two peaks. For the red curve: The top of the peak is the transition state; no intermediates are shown.

Figure 14.27 Substrate; if products bound tightly, they would not leave and the active site would not be free.

CHAPTER 15

Figure 15.1 The color in the tube stops changing.

Figure 15.2 No

Figure 15.6 The boxes would be approximately the same size.

Figure 15.7 It will be lower; some CO_2 has to react with CaO to make some $CaCO_3$.

Figure 15.9 500 atm and 400 °C

Figure 15.10 Nitrogen (and some of the added hydrogen) is converted into ammonia.

Figure 15.14 About two to three times faster, based on the graph

Figure 15.15 About 5×10^{-4}

CHAPTER 16

Figure 16.2 Hydrogen bonds

Figure 16.3 $O^{2-}(aq) + H_2O(l) \longrightarrow 2\,OH^-(aq)$

Figure 16.7 Phenolphthalein changes from colorless, for pH values less than 8, to pink for pH values greater than 10. A pink color indicates $pH > 10$.

Figure 16.8 Bromothymol blue would be most suitable because it changes pH over a range that brackets $pH = 7$. Methyl red is not sensitive to pH changes when $pH > 6$, while phenolphthalein is not sensitive to pH changes when $pH < 8$, so neither changes color at $pH = 7$.

Figure 16.11 Yes. The equilibrium of interest is $H_3CCOOH \rightleftharpoons H^+ + H_3CCOO^-$. If the percent dissociation remained constant as the acid concentration increased, the concentration of all three species would increase at the same rate. However, because there are two products and only one reactant, the total concentration of products would increase faster than the concentration of reactants. To offset this effect the percent dissociation decreases as the acid concentration increases.

Figure 16.12 The acidic hydrogens belong to carboxlyate ($-COOH$) groups, whereas the fourth proton bound to oxygen is part of a hydroxyl ($-OH$) group. In organic acids, like citric acid, the acidic protons are almost always part of a carboxylate group.

Figure 16.13 The nitrogen atom in hydroxylamine accepts a proton to form NH_3OH^+. As a general rule, nonbonding electron pairs on nitrogen atoms are more basic than nonbonding electron pairs on oxygen atoms.

CHAPTER 17

Figure 17.6 The pH will increase on addition of the base.

Figure 17.7 25.00 mL. The number of moles of added base needed to reach the equivalence point remains the same. Therefore, by doubling the concentration of added base the volume needed to reach the equivalence point is halved.

Figure 17.9 The volume of base needed to reach the equivalence point would not change because this quantity does not depend on the strength of the acid. However, the pH at the equivalence point, which is greater than 7 for a weak acid–strong base titration, would decrease to 7 because hydrochloric acid is a strong acid.

Figure 17.11 The pH at the equivalence point increases (becomes more basic) as the acid becomes weaker. The volume of added base needed to reach the equivalence point remains unchanged.

Figure 17.13 Yes. Any indicator that changes color between $pH = 3$ and $pH = 11$ could be used for a strong acid–strong base titration. Methyl red changes color between pH values of approximately 4 and 6.

Figure 17.22 ZnS and CuS would both precipitate on addition of H_2S, preventing separation of the two ions.

Figure 17.23 Yes. CuS would precipitate in step 2 on addition of H_2S to an acidic solution, while the Zn^{2+} ions remained in solution.

CHAPTER 18

Figure 18.1 About 85 km

Figure 18.3 The atmosphere absorbs a significant fraction of solar radiation.

Figure 18.4 The peak value is about 5×10^{12} molecules per cm^3. If we use Avogadro's number to convert molecules to moles, and the conversion factor of $1000\ cm^3 = 1000\ mL = 1\ L$, we find that the concentration of ozone at the peak is 8×10^{-9} mole/L.

Figure 18.16 This is ambiguous; both temperature and salinity vary with density in similar ways; but temperature seems to parallel density better. Temperature decreases down to 1000 m, then remains relatively constant; density increases down to 1000 m, and then remains relatively constant.

Figure 18.17 The depth of the aquifer; the nature of the intervening layers (how porous or dense they are)

Figure 18.19 Water is the chemical species that is crossing the membrane, not the ions.

CHAPTER 19

Figure 19.1 Yes, the potential energy of the eggs decreases as they fall.

Figure 19.2 Because the final volume would be less than twice the volume of Flask A, the final pressure would be greater than 0.5 atm.

Figure 19.3 The freezing of liquid water to ice is exothermic.

Figure 19.4 To be truly reversible, the temperature change δT must be infinitesimally small.

Figure 19.8 There are two other independent rotational motions of the H_2O molecule:

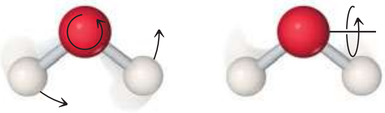


Figure 19.9 Ice, because it is the phase in which the molecules are held most rigidly

Figure 19.11 The decrease in the number of molecules due to the formation of new bonds.

Figure 19.13 During a phase change, the temperature remains constant but the entropy change can be large.

Figure 19.14 Based on the three molecules shown, the addition of each C increases $S°$ by 40–45 J/mol-K. Based on this observation, we would predict that $S°(C_4H_{10})$ would 310–315 J/mol-K. Appendix C confirms that this is a good prediction: $S°(C_4H_{10}) = 310.0$ J/mol-K.

Figure 19.16 Spontaneous

Figure 19.17 If we plot progress of the reaction versus free energy, equilibrium is at a minimum point in free energy, as shown in the figure. In that sense, the reaction runs "downhill" until it reaches that minimum point.

CHAPTER 20

Figure 20.1 (a) The bubbling is caused by the hydrogen gas formed in the reaction. (b) The reaction is exothermic, and the heat causes the formation of steam.

Figure 20.2 The permanganate, MnO_4^-, is reduced, as the half-reactions in the text show.

Figure 20.3 The blue color is due to $Cu^{2+}(aq)$. As this ion is reduced, forming $Cu(s)$, the blue color fades.

Figure 20.4 The Zn is oxidized and, therefore, serves as the anode of the cell.

Figure 20.5 The electrical balance is maintained in two ways: Anions migrate into the half-cell, and cations migrate out.

Figure 20.9 As the cell operates, H^+ is reduced to H_2 in the cathode half-cell. As H^+ is depleted, the positive Na^+ ions are drawn into the half-cell to maintain electrical balance in the solution.

Figure 20.10 The reduction reaction occurs at the cathode. The substance that is reduced most easily is the one with the larger standard reduction potential, $E°_{red}$.

Figure 20.12 Oxidation is the loss of electrons. An oxidizing agent causes another substance to lose electrons by gaining them itself. A strong oxidizing agent readily gains electrons, meaning that it is easily reduced.

Figure 20.14 The variable n is the number of moles of electrons transferred in the process.

Figure 20.15 The $Ni^{2+}(aq)$ and the cations in the salt bridge migrate toward the cathode. The $NO_3^-(aq)$ and the anions in the salt bridge migrate toward the anode.

Figure 20.19 The cathode consists of $PbO_2(s)$. Because each oxygen has an oxidation state of −2, lead must have an oxidation state of +4 in this compound.

Figure 20.22 The oxidizing agent of $O_2(g)$ from the air

CHAPTER 21

Figure 21.2 From Figure 21.2 we see that the belt of stability for a nucleus containing 70 protons lies at approximately 102 neutrons.

Figure 21.4 Only three of the elements with an even number of protons have fewer than three isotopes: He, Be, and C. Note that these three elements are the lightest elements that have an even atomic number. Because they are so light, any change in the number of neutrons will change the neutron/proton ratio significantly. This helps to explain why they do not have more stable isotopes. None of the elements in Figure 21.4 that have an odd number of protons have more than two stable isotopes.

Figure 21.6 6.25 g. After one half-life, the amount of the radioactive material will have dropped to 25.0 g. After two half-lives, it will have dropped to 12.5 g. After three half-lives, it will have dropped to 6.25 g.

Figure 21.19 Because large quantities of water are needed to condense the secondary coolant once it passes through the turbine

Figure 21.21 The United States has the most reactors in operation. China has the most reactors under construction. France generates the largest percentage of its electricity from nuclear power.

Figure 21.24 Alpha rays are less dangerous when outside the body because they cannot penetrate the skin. However, once inside the body they can do great harm to any cells they come in contact with.

CHAPTER 22

Figure 22.5 Beaker on the right is warmer.

Figure 22.6 HF is the most stable, SbH_3 the least stable.

Figure 22.8 More soluble in CCl_4—the colors are deeper.

Figure 22.9 CF_2

Figure 22.10 Redox reactions: The halides are being oxidized.

Figure 22.14 No

Figure 22.16 Based on this structure—yes, it would have a dipole moment. In fact, if you look it up, hydrogen peroxide's dipole moment is larger than water's!

Figure 22.20 They have been converted into water.

Figure 22.21 Formally they could both be +2. If we consider that the central sulfur is like SO_4^{2-}, however, then the central sulfur would be +6, like SO_4^{2-}, and then the terminal sulfur would be −2.

Figure 22.22 Nitrite

Figure 22.23 Longer

Figure 22.26 The NO double bond

Figure 22.28 In P_4O_6 the electron domains about the P atoms are trigonal pyramidal; in P_4O_{10} the electron domains about the P atoms are tetrahedral.

Figure 22.33 The minimum temperature should be the melting point of silicon; the temperature of the heating coil should not be so high that the silicon rod starts to melt outside the zone of the heating coil.

CHAPTER 23

Figure 23.3 Zn (it is colorless)

Figure 23.4 The increase parallels the linear increase in valence electron count.

Figure 23.5 All the electron spins would align with the direction of the magnetic field.

Figure 23.9 109.5 degrees for the tetrahedral Zn complex; 90 degrees for the square-planar Pt complex

Figure 23.13 4 for both (assuming no other ligands come in to bind)

Figure 23.15 In the same place as O_2

Figure 23.16 The peak with a maximum at 650 nm, the longest wavelength and lowest energy

Figure 23.21 The *cis* one

Figure 23.24 Larger, since ammonia can displace water

Figure 23.26 The peak would stay in the same position in terms of wavelength, but its absorbance would decrease.

Figure 23.28 $d_{x^2-y^2}$ and d_{z^2}

Figure 23.29 Convert the wavelength of light, 495 nm, into energy in joules using $E = hc/\lambda$.

Figure 23.30 It would be to the right of the "yellow" member of the series, but the energy gap between filled and empty *d* orbitals would be even larger than that of the "yellow" one.

Figure 23.34 That orbital has the lobes that point directly at the ligands.

CHAPTER 24

Figure 24.1 Tetrahedral

Figure 24.2 The OH group is polar whereas the CH_3 group is nonpolar. Hence, adding CH_3 will (a) reduce the substance's solubility in polar solvents and (b) increase its solubility in nonpolar solvents.

Figure 24.5 C_nH_{2n}, because there are no CH_3 groups, each carbon has two hydrogens.

Figure 24.7 Just one

Figure 24.9 Intermediates are minima and transition states are maxima on energy profiles.

Figure 24.14 Both lactic acid and citric acid

Figure 24.15 No, because there are not four different groups around any carbon

Figure 24.18 Those labeled "basic amino acids," which have basic side groups that are protonated at pH 7

Figure 24.25 The long hydrocarbon chains, which are nonpolar

Figure 24.27 The polar parts of the phospholipids seek to interact with water whereas the nonpolar parts seek to interact with other nonpolar substances and to avoid water.

Figure 24.29 Negative charge because of charge on phosphate groups

Figure 24.31 GC because each base has three hydrogen bonding sites, whereas there are only two in AT

GLOSSARY

absolute zero The lowest attainable temperature; 0 K on the Kelvin scale and -273.15 °C on the Celsius scale. (Section 1.4)

absorption spectrum A pattern of variation in the amount of light absorbed by a sample as a function of wavelength. (Section 23.5)

accuracy A measure of how closely individual measurements agree with the correct value. (Section 1.5)

acid A substance that is able to donate a H^+ ion (a proton) and, hence, increases the concentration of $H^+(aq)$ when it dissolves in water. (Section 4.3)

acid-dissociation constant (K_a) An equilibrium constant that expresses the extent to which an acid transfers a proton to solvent water. (Section 16.6)

acidic anhydride (acidic oxide) An oxide that forms an acid when added to water; soluble nonmetal oxides are acidic anhydrides. (Section 22.5)

acidic oxide (acidic anhydride) An oxide that either reacts with a base to form a salt or with water to form an acid. (Section 22.5)

acid rain Rainwater that has become excessively acidic because of absorption of pollutant oxides, notably SO_3, produced by human activities. (Section 18.2)

actinide element Element in which the 5*f* orbitals are only partially occupied. (Section 6.8)

activated complex (transition state) The particular arrangement of atoms found at the top of the potential-energy barrier as a reaction proceeds from reactants to products. (Section 14.5)

activation energy (E_a) The minimum energy needed for reaction; the height of the energy barrier to formation of products. (Section 14.5)

active site Specific site on a heterogeneous catalyst or an enzyme where catalysis occurs. (Section 14.7)

activity The decay rate of a radioactive material, generally expressed as the number of disintegrations per unit time. (Section 21.4)

activity series A list of metals in order of decreasing ease of oxidation. (Section 4.4)

addition polymerization Polymerization that occurs through coupling of monomers with one another, with no other products formed in the reaction. (Section 12.8)

addition reaction A reaction in which a reagent adds to the two carbon atoms of a carbon–carbon multiple bond. (Section 24.3)

adsorption The binding of molecules to a surface. (Section 14.7)

alcohol An organic compound obtained by substituting a hydroxyl group ($-OH$) for a hydrogen on a hydrocarbon. (Sections 2.9 and 24.4)

aldehyde An organic compound that contains a carbonyl group ($C{=}O$) to which at least one hydrogen atom is attached. (Section 24.4)

alkali metals Members of group 1A in the periodic table. (Section 7.7)

alkaline earth metals Members of group 2A in the periodic table. (Section 7.7)

alkanes Compounds of carbon and hydrogen containing only carbon–carbon single bonds. (Sections 2.9 and 24.2)

alkenes Hydrocarbons containing one or more carbon–carbon double bonds. (Section 24.2)

alkyl group A group that is formed by removing a hydrogen atom from an alkane. (Section 25.3)

alkynes Hydrocarbons containing one or more carbon–carbon triple bonds. (Section 24.2)

alloy A substance that has the characteristic properties of a metal and contains more than one element. Often there is one principal metallic component, with other elements present in smaller amounts. Alloys may be homogeneous or heterogeneous. (Section 12.3)

alpha decay A type of radioactive decay in which an atomic nucleus emits an alpha particle and thereby transforms (or "decays") into an atom with a mass number 4 less and atomic number 2 less. (Section 21.1)

alpha (α) helix A protein structure in which the protein is coiled in the form of a helix with hydrogen bonds between $C{=}O$ and $N{-}H$ groups on adjacent turns. (Section 24.7)

alpha particles Particles that are identical to helium-4 nuclei, consisting of two protons and two neutrons, symbol $^{4}_{2}He$ or $^{4}_{2}\alpha$. (Section 21.1)

amide An organic compound that has an NR_2 group attached to a carbonyl. (Section 24.4)

amine A compound that has the general formula R_3N, where R may be H or a hydrocarbon group. (Section 16.7)

amino acid A carboxylic acid that contains an amino ($-NH_2$) group attached to the carbon atom adjacent to the carboxylic acid ($-COOH$) functional group. (Section 24.7)

amorphous solid A solid whose molecular arrangement lacks the regularly repeating long-range pattern of a crystal. (Section 12.2)

amphiprotic Refers to the capacity of a substance to either add or lose a proton (H^+). (Section 16.2)

amphoteric oxides and hydroxides Oxides and hydroxides that are only slightly soluble in water but that dissolve in either acidic or basic solutions. (Section 17.5)

angstrom A common non-SI unit of length, denoted Å, that is used to measure atomic dimensions: $1 \text{Å} = 10^{-10}$ m. (Section 2.3)

anion A negatively charged ion. (Section 2.7)

anode An electrode at which oxidation occurs. (Section 20.3)

antibonding molecular orbital A molecular orbital in which electron density is concentrated outside the region between the two nuclei of bonded atoms. Such orbitals, designated as σ^* or π^*, are less stable (of higher energy) than bonding molecular orbitals. (Section 9.7)

antiferromagnetism A form of magnetism in which unpaired electron spins on adjacent sites point in opposite directions and cancel each other's effects. (Section 23.1)

aqueous solution A solution in which water is the solvent. (Chapter 4: Introduction)

aromatic hydrocarbons Hydrocarbon compounds that contain a planar, cyclic arrangement of carbon atoms linked by both σ and delocalized π bonds. (Section 24.2)

Arrhenius equation An equation that relates the rate constant for a reaction to the frequency factor, A, the activation energy, E_a, and the temperature, T: $k = Ae^{-E_a/RT}$. In its logarithmic form it is written $\ln k = -E_a/RT + \ln A$. (Section 14.5)

atmosphere (atm) A unit of pressure equal to 760 torr; 1 atm = 101.325 kPa. (Section 10.2)

atom The smallest representative particle of an element. (Sections 1.1 and 2.1)

atomic mass unit (amu) A unit based on the value of exactly 12 amu for the mass of the isotope of carbon that has six protons and six neutrons in the nucleus. (Sections 2.3 and 3.3)

atomic number The number of protons in the nucleus of an atom of an element. (Section 2.3)

atomic radius An estimate of the size of an atom. See **bonding atomic radius**. (Section 7.3)

atomic weight The average mass of the atoms of an element in atomic mass units (amu); it is numerically equal to the mass in grams of one mole of the element. (Section 2.4)

autoionization The process whereby water spontaneously forms low concentrations of $H^+(aq)$ and $OH^-(aq)$ ions by proton transfer from one water molecule to another. (Section 16.3)

Avogadro's hypothesis A statement that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules. (Section 10.3)

Avogadro's law A statement that the volume of a gas maintained at constant temperature and pressure is directly proportional to the number of moles of the gas. (Section 10.3)

Avogadro's number (N_A) The number of ^{12}C atoms in exactly 12 g of ^{12}C; it equals 6.022×10^{23} mol^{-1}. (Section 3.4)

band An array of closely spaced molecular orbitals occupying a discrete range of energy. (Section 12.4)

band gap The energy gap between a fully occupied band called a valence band and an empty band called the conduction band. (Section 12.7)

band structure The electronic structure of a solid, defining the allowed ranges of energy for electrons in a solid. (Section 12.7)

bar A unit of pressure equal to 10^5 Pa. (Section 10.2)

base A substance that is an H^+ acceptor; a base produces an excess of $OH^-(aq)$ ions when it dissolves in water. (Section 4.3)

base-dissociation constant (K_b) An equilibrium constant that expresses the extent to which a base reacts with solvent water, accepting a proton and forming $OH^-(aq)$. (Section 16.7)

basic anhydride (basic oxide) An oxide that forms a base when added to water; soluble metal oxides are basic anhydrides. (Section 22.5)

basic oxide (basic anhydride) An oxide that either reacts with water to form a base or reacts with an acid to form a salt and water. (Section 22.5)

battery A self-contained electrochemical power source that contains one or more voltaic cells. (Section 20.7)

becquerel The SI unit of radioactivity. It corresponds to one nuclear disintegration per second. (Section 21.4)

Beer's law The light absorbed by a substance (A) equals the product of its extinction coefficient (ε), the path length through which the light passes (b), and the molar concentration of the substance (c): $A = \varepsilon bc$.(Section 14.2)

beta emission A nuclear decay process where a beta particle is emitted from the nucleus; also called beta decay. (Section 21.1)

beta particles Energetic electrons emitted from the nucleus, symbol $_{-1}^{0}e$. (Section 21.1)

beta sheet A structural form of protein in which two strands of amino acids are hydrogen-bonded together in a zipperlike configuration. (Section 24.7)

bidentate ligand A ligand in which two linked coordinating atoms are bound to a metal. (Section 23.3)

bimolecular reaction An elementary reaction that involves two molecules. (Section 14.6)

biochemistry The study of the chemistry of living systems. (Chapter 24: Introduction)

biodegradable Organic material that bacteria are able to oxidize. (Section 18.4)

body-centered lattice A crystal lattice in which the lattice points are located at the center and corners of each unit cell. (Section 12.2)

bomb calorimeter A device for measuring the heat evolved in the combustion of a substance under constant-volume conditions. (Section 5.5)

bond angles The angles made by the lines joining the nuclei of the atoms in a molecule. (Section 9.1)

bond dipole The dipole moment that is due to unequal electron sharing between two atoms in a covalent bond. (Section 9.3)

bond enthalpy The enthalpy change, ΔH, required to break a particular bond when the substance is in the gas phase. (Section 8.8)

bonding atomic radius The radius of an atom as defined by the distances separating it from other atoms to which it is chemically bonded. (Section 7.3)

bonding molecular orbital A molecular orbital in which the electron density is concentrated in the internuclear region. The energy of a bonding molecular orbital is lower than the energy of the separate atomic orbitals from which it forms. (Section 9.7)

bonding pair In a Lewis structure a pair of electrons that is shared by two atoms. (Section 9.2)

bond length The distance between the centers of two bonded atoms. (Section 8.3)

bond order The number of bonding electron pairs shared between two atoms, minus the number of antibonding electron pairs: bond order = (number of bonding electrons − number of antibonding electrons)/2. (Section 9.7)

bond polarity A measure of the degree to which the electrons are shared unequally between two atoms in a chemical bond. (Section 8.4)

boranes Covalent hydrides of boron. (Section 22.11)

Born–Haber cycle A thermodynamic cycle based on Hess's law that relates the lattice energy of an ionic substance to its enthalpy of formation and to other measurable quantities. (Section 8.2)

Boyle's law A law stating that at constant temperature, the product of the volume and pressure of a given amount of gas is a constant. (Section 10.3)

Brønsted–Lowry acid A substance (molecule or ion) that acts as a proton donor. (Section 16.2)

Brønsted–Lowry base A substance (molecule or ion) that acts as a proton acceptor. (Section 16.2)

buffer capacity The amount of acid or base a buffer can neutralize before the pH begins to change appreciably. (Section 17.2)

buffered solution (buffer) A solution that undergoes a limited change in pH upon addition of a small amount of acid or base. (Section 17.2)

calcination The heating of an ore to bring about its decomposition and the elimination of a volatile product. For example, a carbonate ore might be calcined to drive off CO_2. (Section 23.2)

calorie A unit of energy, it is the amount of energy needed to raise the temperature of 1 g of water by 1 °C from 14.5 °C to 15.5 °C. A related unit is the joule: 1 cal = 4.184 J. (Section 5.1)

calorimeter An apparatus that measures the heat released or absorbed in a chemical or physical process. (Section 5.5)

calorimetry The experimental measurement of heat produced in chemical and physical processes. (Section 5.5)

capillary action The process by which a liquid rises in a tube because of a combination of adhesion to the walls of the tube and cohesion between liquid particles. (Section 11.3)

carbide A binary compound of carbon with a metal or metalloid. (Section 22.9)

carbohydrates A class of substances formed from polyhydroxy aldehydes or ketones. (Section 24.8)

carbon black A microcrystalline form of carbon. (Section 22.9)

carbonyl group The $C{=}O$ double bond, a characteristic feature of several organic functional groups, such as ketones and aldehydes. (Section 24.4)

carboxylic acid A compound that contains the $-COOH$ functional group. (Sections 16.10 and 24.4)

catalyst A substance that changes the speed of a chemical reaction without itself undergoing a permanent chemical change in the process. (Section 14.7)

cathode An electrode at which reduction occurs. (Section 20.3)

cathode rays Streams of electrons that are produced when a high voltage is applied to electrodes in an evacuated tube. (Section 2.2)

cathodic protection A means of protecting a metal against corrosion by making it the cathode in a voltaic cell. This can be achieved by attaching a more easily oxidized metal, which serves as an anode, to the metal to be protected. (Section 20.8)

cation A positively charged ion. (Section 2.7)

cell potential The potential difference between the cathode and anode in an electrochemical cell; it is measured in volts: 1 V = 1 J/C. Also called electromotive force. (Section 20.4)

cellulose A polysaccharide of glucose; it is the major structural element in plant matter. (Section 24.8)

Celsius scale A temperature scale on which water freezes at 0° and boils at 100° at sea level. (Section 1.4)

chain reaction A series of reactions in which one reaction initiates the next. (Section 21.7)

changes of state Transformations of matter from one state to a different one, for example, from a gas to a liquid. (Section 1.3)

charcoal A form of carbon produced when wood is heated strongly in a deficiency of air. (Section 22.9)

Charles's law A law stating that at constant pressure, the volume of a given quantity of gas is proportional to absolute temperature. (Section 10.3)

chelate effect The generally larger formation constants for polydentate ligands as compared with the corresponding *monodentate* ligands. (Section 23.3)

chelating agent A polydentate ligand that is capable of occupying two or more sites in the coordination sphere. (Section 23.3)

chemical bond A strong attractive force that exists between atoms in a molecule. (Section 8.1)

chemical changes Processes in which one or more substances are converted into other substances; also called **chemical reactions**. (Section 1.3)

chemical equation A representation of a chemical reaction using the chemical formulas of the reactants and products; a balanced chemical equation contains equal numbers of atoms of each element on both sides of the equation. (Section 3.1)

chemical equilibrium A state of dynamic balance in which the rate of formation of the products of a reaction from the reactants equals the rate of formation of the reactants from the products; at equilibrium the concentrations of the reactants and products remain constant. (Section 4.1; Chapter 15: Introduction)

chemical formula A notation that uses chemical symbols with numerical subscripts to convey the relative proportions of atoms of the different elements in a substance. (Section 2.6)

chemical kinetics The area of chemistry concerned with the speeds, or rates, at which chemical reactions occur. (Chapter 14: Introduction)

chemical nomenclature The rules used in naming substances. (Section 2.8)

chemical properties Properties that describe a substance's composition and its reactivity; how the substance reacts or changes into other substances. (Section 1.3)

chemical reactions Processes in which one or more substances are converted into other substances; also called **chemical changes**. (Section 1.3)

chemistry The scientific discipline that studies the composition, properties, and transformations of matter. (Chapter 1: Introduction)

chiral A term describing a molecule or an ion that cannot be superimposed on its mirror image. (Sections 23.4 and 24.5)

chlorofluorocarbons Compounds composed entirely of chlorine, fluorine, and carbon. (Section 18.3)

chlorophyll A plant pigment that plays a major role in conversion of solar energy to chemical energy in photosynthesis. (Section 23.3)

cholesteric liquid crystalline phase A liquid crystal formed from flat, disc-shaped molecules that align through a stacking of the molecular discs. (Section 11.7)

coal A naturally occurring solid containing hydrocarbons of high molecular weight, as well as compounds containing sulfur, oxygen, and nitrogen. (Section 5.8)

colligative property A property of a solvent (vapor-pressure lowering, freezing-point lowering, boiling-point elevation, osmotic pressure) that depends on the total concentration of solute particles present. (Section 13.5)

collision model A model of reaction rates based on the idea that molecules must collide to react; it explains the factors influencing reaction rates in terms of the frequency of collisions, the number of collisions with energies exceeding the activation energy, and the probability that the collisions occur with suitable orientations. (Section 14.5)

colloids (colloidal dispersions) Mixtures containing particles larger than normal solutes but small enough to remain suspended in the dispersing medium. (Section 13.6)

combination reaction A chemical reaction in which two or more substances combine to form a single product. (Section 3.2)

combustion reaction A chemical reaction that proceeds with evolution of heat and usually also a flame; most combustion involves reaction with oxygen, as in the burning of a match. (Section 3.2)

common-ion effect A shift of an equilibrium induced by an ion common to the equilibrium. For example, added Na_2SO_4 decreases the solubility of the slightly soluble salt $BaSO_4$, or added NaF decreases the percent ionization of HF. (Section 17.1)

complementary colors Colors that, when mixed in proper proportions, appear white or colorless. (Section 23.5)

complete ionic equation A chemical equation in which dissolved strong electrolytes (such as dissolved ionic compounds) are written as separate ions. (Section 4.2)

complex ion (complex) An assembly of a metal ion and the Lewis bases (ligands) bonded to it. (Section 17.5)

compound A substance composed of two or more elements united chemically in definite proportions. (Section 1.2)

compound semiconductor A semiconducting material formed from two or more elements. (Section 12.7)

concentration The quantity of solute present in a given quantity of solvent or solution. (Section 4.5)

concentration cell A voltaic cell containing the same electrolyte and the same electrode materials in both the anode and cathode compartments. The emf of the cell is derived from a difference in the concentrations of the same electrolyte solutions in the compartments. (Section 20.6)

condensation polymerization Polymerization in which molecules are joined together through condensation reactions. (Section 12.8)

condensation reaction A chemical reaction in which a small molecule (such as a molecule of water) is split out from between two reacting molecules. (Sections 12.6 and 22.8)

conduction band A band of molecular orbitals lying higher in energy than the occupied valence band and distinctly separated from it. (Section 12.7)

conjugate acid A substance formed by addition of a proton to a Brønsted–Lowry base. (Section 16.2)

conjugate acid–base pair An acid and a base, such as H_2O and OH^-, that differ only in the presence or absence of a proton. (Section 16.2)

conjugate base A substance formed by the loss of a proton from a Brønsted–Lowry acid. (Section 16.2)

continuous spectrum A spectrum that contains radiation distributed over all wavelengths. (Section 6.3)

conversion factor A ratio relating the same quantity in two systems of units that is used to convert the units of measurement. (Section 1.6)

coordination compound A compound containing a metal ion bonded to a group of surrounding molecules or ions that act as ligands. (Section 23.2)

coordination number The number of adjacent atoms to which an atom is directly bonded. In a complex the coordination number of the metal ion is the number of donor atoms to which it is bonded. (Sections 12.37 and 24.2)

coordination sphere The metal ion and its surrounding ligands. (Section 23.2)

coordination-sphere isomers Structural isomers of coordination compounds in which the ligands within the coordination sphere differ. (Section 23.4)

copolymer A complex polymer resulting from the polymerization of two or more chemically different monomers. (Section 12.8)

core electrons The electrons that are not in the outermost shell of an atom. (Section 6.8)

corrosion The process by which a metal is oxidized by substances in its environment. (Section 20.8)

covalent bond A bond formed between two or more atoms by a sharing of electrons. (Section 8.1)

covalent-network solids Solids in which the units that make up the three-dimensional network are joined by covalent bonds. (Section 12.1)

critical mass The amount of fissionable material necessary to maintain a nuclear chain reaction. (Section 21.7)

critical pressure The pressure at which a gas at its critical temperature is converted to a liquid state. (Section 11.4)

critical temperature The highest temperature at which it is possible to convert the gaseous form of a substance to a liquid. The critical temperature increases with an increase in the magnitude of intermolecular forces. (Section 11.4)

crystal-field theory A theory that accounts for the colors and the magnetic and other properties of transition-metal complexes in terms of the splitting of the energies of metal ion *d* orbitals by the electrostatic interaction with the ligands. (Section 23.6)

crystal lattice An imaginary network of points on which the repeating motif of a solid may be imagined to be laid down so that the structure of the crystal is obtained. The motif may be a single atom or a group of atoms. Each lattice point represents an identical environment in the crystal. (Section 12.2)

crystalline solid (crystal) A solid whose internal arrangement of atoms, molecules, or ions possesses a regularly repeating pattern in any direction through the solid. (Section 12.2)

crystallization The process in which molecules, ions, or atoms come together to form a crystalline solid. (Section 13.2)

cubic close packing A crystal structure where the atoms are packed together as close as possible, and the close-packed layers of atoms adopt a three-layer repeating pattern that leads to a face-centered cubic unit cell. (Section 12.3)

curie A measure of radioactivity: $1 \text{ curie} = 3.7 \times 10^{10}$ nuclear disintegrations per second. (Section 21.4)

cycloalkanes Saturated hydrocarbons of general formula C_nH_{2n} in which the carbon atoms form a closed ring. (Section 24.2)

Dalton's law of partial pressures A law stating that the total pressure of a mixture of gases is the sum of the pressures that each gas would exert if it were present alone. (Section 10.6)

***d-d* transition** The transition of an electron in a transition-metal compound from a lower-energy *d* orbital to a higher-energy *d* orbital. (Section 23.6)

decomposition reaction A chemical reaction in which a single compound reacts to give two or more products. (Section 3.2)

degenerate A situation in which two or more orbitals have the same energy. (Section 6.7)

delocalized electrons Electrons that are spread over a number of atoms in a molecule or a crystal rather than localized on a single atom or a pair of atoms. (Section 9.6)

density The ratio of an object's mass to its volume. (Section 1.4)

deoxyribonucleic acid (DNA) A polynucleotide in which the sugar component is deoxyribose. (Section 24.10)

desalination The removal of salts from seawater, brine, or brackish water to make it fit for human consumption. (Section 18.4)

deuterium The isotope of hydrogen whose nucleus contains a proton and a neutron: ${}^{2}_{1}H$. (Section 22.2)

dextrorotatory, or merely dextro or *d* A term used to label a chiral molecule that rotates the plane of polarization of plane-polarized light to the right (clockwise). (Section 23.4)

diamagnetism A type of magnetism that causes a substance with no unpaired electrons to be weakly repelled from a magnetic field. (Section 9.8)

diatomic molecule A molecule composed of only two atoms. (Section 2.6)

diffusion The spreading of one substance through a space occupied by one or more other substances. (Section 10.8)

dilution The process of preparing a less concentrated solution from a more concentrated one by adding solvent. (Section 4.5)

dimensional analysis A method of problem solving in which units are carried through all calculations. Dimensional analysis ensures that the final answer of a calculation has the desired units. (Section 1.6)

dipole A molecule with one end having a partial negative charge and the other end having a partial positive charge; a polar molecule. (Section 8.4)

dipole–dipole force A force that becomes significant when polar molecules come in close contact with one another. The force is attractive when the positive end of one polar molecule approaches the negative end of another. (Section 11.2)

dipole moment A measure of the separation and magnitude of the positive and negative charges in polar molecules. (Section 8.4)

dispersion forces Intermolecular forces resulting from attractions between induced dipoles. Also called London dispersion forces. (Section 11.2)

displacement reaction A reaction in which an element reacts with a compound, displacing an element from it. (Section 4.4)

donor atom The atom of a ligand that bonds to the metal. (Section 23.2)

doping Incorporation of a hetero atom into a solid to change its electrical properties. For example, incorporation of P into Si. (Section 12.7)

double bond A covalent bond involving two electron pairs. (Section 8.3)

double helix The structure for DNA that involves the winding of two DNA polynucleotide chains together in a helical arrangement. The two strands of the double helix are complementary in that the organic bases on the two strands are paired for optimal hydrogen bond interaction. (Section 24.10)

dynamic equilibrium A state of balance in which opposing processes occur at the same rate. (Section 11.5)

effective nuclear charge The net positive charge experienced by an electron in a many-electron atom; this charge is not the full nuclear charge because there is some shielding of the nucleus by the other electrons in the atom. (Section 7.2)

effusion The escape of a gas through an orifice or hole. (Section 10.8)

elastomer A material that can undergo a substantial change in shape via stretching, bending, or compression and return to its original shape upon release of the distorting force. (Section 12.6)

electrochemistry The branch of chemistry that deals with the relationships between electricity and chemical reactions. (Chapter 20: Introduction)

electrolysis reaction A reaction in which a nonspontaneous redox reaction is brought about by the passage of current under a sufficient external electrical potential. The devices in which electrolysis reactions occur are called electrolytic cells. (Section 20.9)

electrolyte A solute that produces ions in solution; an electrolytic solution conducts an electric current. (Section 4.1)

electrolytic cell A device in which a nonspontaneous oxidation-reduction reaction is caused to occur by passage of current under a sufficient external electrical potential. (Section 20.9)

electromagnetic radiation (radiant energy) A form of energy that has wave characteristics and that propagates through a vacuum at the characteristic speed of 3.00×10^8 m/s. (Section 6.1)

electrometallurgy The use of electrolysis to reduce or refine metals. (Section 20.9)

electromotive force (emf) A measure of the driving force, or *electrical pressure*, for the completion of an electrochemical reaction. Electromotive force is measured in volts: $1 \text{ V} = 1 \text{ J/C}$. Also called the cell potential. (Section 20.4)

electron A negatively charged subatomic particle found outside the atomic nucleus; it is a part of all atoms. An electron has a mass 1/1836 times that of a proton. (Section 2.3)

electron affinity The energy change that occurs when an electron is added to a gaseous atom or ion. (Section 7.5)

electron capture A mode of radioactive decay in which an inner-shell orbital electron is captured by the nucleus. (Section 21.1)

electron configuration The arrangement of electrons in the orbitals of an atom or molecule (Section 6.8)

electron density The probability of finding an electron at any particular point in an atom; this probability is equal to ψ^2, the square of the wave function. Also called the probability density. (Section 6.5)

electron domain In the VSEPR model, a region about a central atom in which an electron pair is concentrated. (Section 9.2)

electron-domain geometry The three-dimensional arrangement of the electron domains around an atom according to the VSEPR model. (Section 9.2)

electronegativity A measure of the ability of an atom that is bonded to another atom to attract electrons to itself. (Section 8.4)

electronic charge The negative charge carried by an electron; it has a magnitude of 1.602×10^{-19} C. (Section 2.3)

electronic structure The arrangement of electrons in an atom or molecule. (Chapter 6: Introduction)

electron-sea model A model for the behavior of electrons in metals. (Section 12.4)

electron shell A collection of orbitals that have the same value of n. For example, the orbitals with $n = 3$ (the $3s$, $3p$, and $3d$ orbitals) comprise the third shell. (Section 6.5)

electron spin A property of the electron that makes it behave as though it were a tiny magnet. The electron behaves as if it were spinning on its axis; electron spin is quantized. (Section 6.7)

element A substance consisting of atoms of the same atomic number. Historically defined as a substance that cannot be separated into simpler substances by chemical means. (Sections 1.1 and 1.2)

elemental semiconductor A semiconducting material composed of just one element. (Section 12.7)

elementary reaction A process in a chemical reaction that occurs in a single event or step. An overall chemical reaction consists of one or more elementary reactions or steps. (Section 14.6)

empirical formula A chemical formula that shows the kinds of atoms and their relative numbers in a substance in the smallest possible whole-number ratios. (Section 2.6)

enantiomers Two mirror-image molecules of a chiral substance. The enantiomers are nonsuperimposable. (Section 23.4)

endothermic process A process in which a system absorbs heat from its surroundings. (Section 5.2)

energy The capacity to do work or to transfer heat. (Section 5.1)

energy-level diagram A diagram that shows the energies of molecular orbitals relative to the atomic orbitals from which they are derived. Also called a **molecular-orbital diagram**. (Section 9.7)

enthalpy A quantity defined by the relationship $H = E + PV$; the enthalpy change, ΔH, for a reaction that occurs at constant pressure is the heat evolved or absorbed in the reaction: $\Delta H = q_p$. (Section 5.3)

enthalpy of formation The enthalpy change that accompanies the formation of a substance from the most stable forms of its component elements. (Section 5.7)

enthalpy of reaction The enthalpy change associated with a chemical reaction. (Section 5.4)

entropy A thermodynamic function associated with the number of different equivalent energy states or spatial arrangements in which a system may be found. It is a thermodynamic state function, which means that once we specify the conditions for a system—that is, the temperature, pressure, and so on—the entropy is defined. (Section 19.2)

enzyme A protein molecule that acts to catalyze specific biochemical reactions. (Section 14.7)

equilibrium constant The numerical value of the equilibrium-constant expression for a system at equilibrium. The equilibrium constant is most usually denoted by K_p for gas-phase systems or K_c for solution-phase systems. (Section 15.2)

equilibrium-constant expression The expression that describes the relationship among the concentrations (or partial pressures) of the substances present in a system at equilibrium. The numerator is obtained by multiplying the concentrations of the substances on the product side of the equation, each raised to a power equal to its coefficient in the chemical equation. The denominator similarly contains the concentrations of the substances on the reactant side of the equation. (Section 15.2)

equivalence point The point in a titration at which the added solute reacts completely with the solute present in the solution. (Section 4.6)

ester An organic compound that has an OR group attached to a carbonyl; it is the product of a reaction between a carboxylic acid and an alcohol. (Section 24.4)

ether A compound in which two hydrocarbon groups are bonded to one oxygen. (Section 24.4)

exchange (metathesis) reaction A reaction between compounds that when written as a molecular equation appears to involve the exchange of ions between the two reactants. (Section 4.2)

excited state A higher energy state than the ground state. (Section 6.3)

exothermic process A process in which a system releases heat to its surroundings. (Section 5.2)

extensive property A property that depends on the amount of material considered; for example, mass or volume. (Section 1.3)

face-centered lattice A crystal lattice in which the lattice points are located at the faces and corners of each unit cell. (Section 12.2)

Faraday's constant (*F*) The magnitude of charge of one mole of electrons: 96,500 C/mol. (Section 20.5)

***f*-block metals** Lanthanide and actinide elements in which the 4*f* or 5*f* orbitals are partially occupied. (Section 6.9)

ferrimagnetism A form of magnetism in which unpaired electron spins on different-type ions point in opposite directions but do not fully cancel out. (Section 23.1)

ferromagnetism A form of magnetism in which unpaired electron spins align parallel to one another. (Section 23.1)

first law of thermodynamics A statement that energy is conserved in any process. One way to express the law is that the change in internal energy, ΔE, of a system in any process is equal to the heat, q, added to the system, plus the work, w, done on the system by its surroundings: $\Delta E = q + w$. (Section 5.2)

first-order reaction A reaction in which the reaction rate is proportional to the concentration of a single reactant, raised to the first power. (Section 14.4)

fission The splitting of a large nucleus into two smaller ones. (Section 21.6)

folding The process by which a protein adopts its biologically active shape. (Section 24.7)

force A push or a pull. (Section 5.1)

formal charge The number of valence electrons in an isolated atom minus the number of electrons assigned to the atom in the Lewis structure. (Section 8.5)

formation constant For a metal ion complex, the equilibrium constant for formation of the complex from the metal ion and base species present in solution. It is a measure of the tendency of the complex to form. (Section 17.5)

formula weight The mass of the collection of atoms represented by a chemical formula. For example, the formula weight of NO_2 (46.0 amu) is the sum of the masses of one nitrogen atom and two oxygen atoms. (Section 3.3)

fossil fuels Coal, oil, and natural gas, which are presently our major sources of energy. (Section 5.8)

free energy (Gibbs free energy, *G*) A thermodynamic state function that gives a criterion for spontaneous change in terms of enthalpy and entropy: $G = H - TS$. (Section 19.5)

free radical A substance with one or more unpaired electrons. (Section 21.9)

frequency The number of times per second that one complete wavelength passes a given point. (Section 6.1)

frequency factor (*A*) A term in the Arrhenius equation that is related to the frequency of collision and the probability that the collisions are favorably oriented for reaction. (Section 14.5)

fuel cell A voltaic cell that utilizes the oxidation of a conventional fuel, such as H_2 or CH_4, in the cell reaction. (Section 20.7)

fuel value The energy released when 1 g of a substance is combusted. (Section 5.8)

functional group An atom or group of atoms that imparts characteristic chemical properties to an organic compound. (Section 24.1)

fusion The joining of two light nuclei to form a more massive one. (Section 21.6)

galvanic cell See **voltaic cell**. (Section 20.3)

gamma radiation Energetic electromagnetic radiation emanating from the nucleus of a radioactive atom. (Section 21.1)

gas Matter that has no fixed volume or shape; it conforms to the volume and shape of its container. (Section 1.2)

gas constant (*R*) The constant of proportionality in the ideal-gas equation. (Section 10.4)

geometric isomerism A form of isomerism in which compounds with the same type and number of atoms and the same chemical bonds have different spatial arrangements of these atoms and bonds. (Sections 23.4 and 24.4)

Gibbs free energy A thermodynamic state function that combines enthalpy and entropy, in the form $G = H - TS$. For a change occurring at constant temperature and pressure, the change in free energy is $\Delta G = \Delta H - T\Delta S$. (Section 19.5)

glass An amorphous solid formed by fusion of SiO_2, CaO, and Na_2O. Other oxides may also be used to form glasses with differing characteristics. (Section 22.10)

glucose A polyhydroxy aldehyde whose formula is $CH_2OH(CHOH)_4CHO$; it is the most important of the monosaccharides. (Section 24.8)

glycogen The general name given to a group of polysaccharides of glucose that are synthesized in mammals and used to store energy from carbohydrates. (Section 24.7)

Graham's law A law stating that the rate of effusion of a gas is inversely proportional to the square root of its molecular weight. (Section 10.8)

gray (Gy) The SI unit for radiation dose corresponding to the absorption of 1 J of energy per kilogram of biological material; 1 Gy = 100 rads. (Section 21.9)

green chemistry Chemistry that promotes the design and application of chemical products and processes that are compatible with human health and that preserve the environment. (Section 18.5)

greenhouse gases Gases in an atmosphere that absorb and emit infrared radiation (radiant heat), "trapping" heat in the atmosphere. (Section 18.2)

ground state The lowest-energy, or most stable, state. (Section 6.3)

group Elements that are in the same column of the periodic table; elements within the same group or family exhibit similarities in their chemical behavior. (Section 2.5)

Haber process The catalyst system and conditions of temperature and pressure developed by Fritz Haber and coworkers for the formation of NH_3 from H_2 and N_2. (Section 15.2)

half-life The time required for the concentration of a reactant substance to decrease to half its initial value; the time required for half of a sample of a particular radioisotope to decay. (Sections 14.4 and 21.4)

half-reaction An equation for either an oxidation or a reduction that explicitly shows the electrons involved, for example, $Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$. (Section 20.2)

Hall–Héroult process A process used to obtain aluminum by electrolysis of Al_2O_3 dissolved in molten cryolite, Na_3AlF_6. (Section 20.9)

halogens Members of group 7A in the periodic table. (Section 7.8)

hard water Water that contains appreciable concentrations of Ca^{2+} and Mg^{2+}; these ions react with soaps to form an insoluble material. (Section 18.4)

heat The flow of energy from a body at higher temperature to one at lower temperature when they are placed in thermal contact. (Section 5.1)

heat capacity The quantity of heat required to raise the temperature of a sample of matter by 1 °C (or 1 K). (Section 5.5)

heat of fusion The enthalpy change, ΔH, for melting a solid. (Section 11.4)

heat of sublimation The enthalpy change, ΔH, for vaporization of a solid. (Section 11.4)

heat of vaporization The enthalpy change, ΔH, for vaporization of a liquid. (Section 11.4)

Henderson–Hasselbalch equation The relationship among the pH, pK_a, and the concentrations of acid and conjugate base in an aqueous solution: $\text{pH} = pK_a + \log\dfrac{[\text{base}]}{[\text{acid}]}$. (Section 17.2)

Henry's law A law stating that the concentration of a gas in a solution, S_g, is proportional to the pressure of gas over the solution: $S_g = kP_g$. (Section 13.3)

Hess's law The heat evolved in a given process can be expressed as the sum of the heats of several processes that, when added, yield the process of interest. (Section 5.6)

heterogeneous alloy An alloy in which the components are not distributed uniformly; instead, two or more distinct phases with characteristic compositions are present. (Section 12.3)

heterogeneous catalyst A catalyst that is in a different phase from that of the reactant substances. (Section 14.7)

heterogeneous equilibrium The equilibrium established between substances in two or more different phases, for example, between a gas and a solid or between a solid and a liquid. (Section 15.4)

hexagonal close packing A crystal structure where the atoms are packed together as closely as possible. The close-packed layers adopt a two-layer repeating pattern, which leads to a primitive hexagonal unit cell. (Section 12.3)

high-spin complex A complex whose electrons populate the d orbitals to give the maximum number of unpaired electrons. (Section 23.6)

hole A vacancy in the valence band of a semiconductor, created by doping. (Section 12.7)

homogeneous catalyst A catalyst that is in the same phase as the reactant substances. (Section 14.7)

homogeneous equilibrium The equilibrium established between reactant and product substances that are all in the same phase. (Section 15.4)

Hund's rule A rule stating that electrons occupy degenerate orbitals in such a way as to maximize the number of electrons with the same spin. In other words, each orbital has one electron placed in it before pairing of electrons in orbitals occurs. (Section 6.8)

hybridization The mixing of different types of atomic orbitals to produce a set of equivalent hybrid orbitals. (Section 9.5)

hybrid orbital An orbital that results from the mixing of different kinds of atomic orbitals on the same atom. For example, an sp^3 hybrid results from the mixing, or hybridizing, of one *s* orbital and three *p* orbitals. (Section 9.5)

hydration Solvation when the solvent is water. (Section 13.1)

hydride ion An ion formed by the addition of an electron to a hydrogen atom: H^-. (Section 7.7)

hydrocarbons Compounds composed of only carbon and hydrogen. (Section 2.9)

hydrogen bonding Bonding that results from intermolecular attractions between molecules containing hydrogen bonded to an electronegative element. The most important examples involve OH, NH, and HF. (Section 11.2)

hydrolysis A reaction with water. When a cation or anion reacts with water, it changes the pH. (Sections 16.9 and 24.4)

hydronium ion (H_3O^+) The predominant form of the proton in aqueous solution. (Section 16.2)

hydrophilic Water attracting. The term is often used to describe a type of colloid. (Section 13.6)

hydrophobic Water repelling. The term is often used to describe a type of colloid. (Section 13.6)

hypothesis A tentative explanation of a series of observations or of a natural law. (Section 1.3)

ideal gas A hypothetical gas whose pressure, volume, and temperature behavior is completely described by the ideal-gas equation. (Section 10.4)

ideal-gas equation An equation of state for gases that embodies Boyle's law, Charles's law, and Avogadro's hypothesis in the form $PV = nRT$. (Section 10.4)

ideal solution A solution that obeys Raoult's law. (Section 13.5)

immiscible liquids Liquids that do not dissolve in one another to a significant extent. (Section 13.3)

indicator A substance added to a solution that changes color when the added solute has reacted with all the solute present in solution. The most common type of indicator is an acid–base indicator whose color changes as a function of pH. (Section 4.6)

instantaneous rate The reaction rate at a particular time as opposed to the average rate over an interval of time. (Section 14.2)

intensive property A property that is independent of the amount of material considered, for example, density. (Section 1.3)

interhalogens Compounds formed between two different halogen elements. Examples include IBr and BrF_3. (Section 22.4)

intermediate A substance formed in one elementary step of a multistep mechanism and consumed in another; it is neither a reactant nor an ultimate product of the overall reaction. (Section 14.6)

intermetallic compound A homogeneous alloy with definite properties and a fixed composition. Intermetallic compounds are stoichiometric compounds that form between metallic elements. (Section 12.3)

intermolecular forces The short-range attractive forces operating between the particles that make up the units of a liquid or solid substance. These same forces also cause gases to liquefy or solidify at low temperatures and high pressures. (Chapter 11: Introduction)

internal energy The total energy possessed by a system. When a system undergoes a change, the change in internal energy, ΔE, is defined as the heat, q, added to the system, plus the work, w, done on the system by its surroundings: $\Delta E = q + w$. (Section 5.2)

interstitial alloy An alloy in which smaller atoms fit into spaces between larger atoms. The larger atoms are metallic elements and the smaller atoms are typically nonmetallic elements. (Section 12.3)

ion Electrically charged atom or group of atoms (polyatomic ion); ions can be positively or negatively charged, depending on whether electrons are lost (positive) or gained (negative) by the atoms. (Section 2.7)

ion–dipole force The force that exists between an ion and a neutral polar molecule that possesses a permanent dipole moment. (Section 11.2)

ion exchange A process by which ions in solution are exchanged for other ions held on the surface of an ion-exchange resin; the exchange of a hard-water cation such as Ca^{2+} for a soft-water cation such as Na^+ is used to soften water. (Section 18.4)

ionic bond A bond between oppositely charged ions. The ions are formed from atoms by transfer of one or more electrons. (Section 8.1)

ionic compound A compound composed of cations and anions. (Section 2.7)

ionic hydrides Compounds formed when hydrogen reacts with alkali metals and also the heavier alkaline earths (Ca, Sr, and Ba); these compounds contain the hydride ion, H^-. (Section 22.2)

ionic solids Solids that are composed of ions. (Section 12.1)

ionization energy The energy required to remove an electron from a gaseous atom when the atom is in its ground state. (Section 7.4)

ionizing radiation Radiation that has sufficient energy to remove an electron from a molecule, thereby ionizing it. (Section 21.9)

ion-product constant For water, K_w is the product of the aquated hydrogen ion and hydroxide ion concentrations: $[H^+][OH^-] = K_w = 1.0 \times 10^{-14}$ at 25 °C. (Section 16.3)

irreversible process A process that cannot be reversed to restore both the system and its surroundings to their original states. Any spontaneous process is irreversible. (Section 19.1)

isoelectronic series A series of atoms, ions, or molecules having the same number of electrons. (Section 7.3)

isomers Compounds whose molecules have the same overall composition but different structures. (Sections 2.9 and 23.4)

isothermal process One that occurs at constant temperature. (Section 19.1)

isotopes Atoms of the same element containing different numbers of neutrons and therefore having different masses. (Section 2.3)

joule (J) The SI unit of energy, 1 kg-m^2/s^2. A related unit is the calorie: 4.184 J $=$ 1 cal. (Section 5.1)

Kelvin scale The absolute temperature scale; the SI unit for temperature is the kelvin. Zero on the Kelvin scale corresponds to -273.15 °C. (Section 1.4)

ketone A compound in which the carbonyl group ($C{=}O$) occurs at the interior of a carbon chain and is therefore flanked by carbon atoms. (Section 24.4)

kinetic energy The energy that an object possesses by virtue of its motion. (Section 5.1)

kinetic-molecular theory A set of assumptions about the nature of gases. These assumptions, when translated into mathematical form, yield the ideal-gas equation. (Section 10.7)

lanthanide contraction The gradual decrease in atomic and ionic radii with increasing atomic number among the lanthanide elements, atomic numbers 57 through 70. The decrease arises because of a gradual increase in effective nuclear charge through the lanthanide series. (Section 23.1)

lanthanide (rare earth) element Element in which the 4*f* subshell is only partially occupied. (Sections 6.8 and 6.9)

lattice energy The energy required to separate completely the ions in an ionic solid. (Section 8.2)

lattice points Points in a crystal all of which have identical environments. (Section 12.2)

lattice vectors The vectors ***a***, ***b***, and ***c*** that define a crystal lattice. The position of any lattice point in a crystal can be represented by summing integer multiples of the lattice vectors. (Section 12.2)

law of constant composition A law that states that the elemental composition of a pure compound is always the same, regardless of its source; also called the **law of definite proportions**. (Section 1.2)

law of definite proportions A law that states that the elemental composition of a pure substance is always the same, regardless of its source; also called the **law of constant composition**. (Section 1.2)

law of mass action The rules by which the equilibrium constant is expressed in terms of the concentrations of reactants and products, in accordance with the balanced chemical equation for the reaction. (Section 15.2)

Le Châtelier's principle A principle stating that when we disturb a system at chemical equilibrium, the relative concentrations of reactants and products shift so as to partially undo the effects of the disturbance. (Section 15.7)

levorotatory, or merely levo or *l* A term used to label a chiral molecule that rotates the plane of polarization of plane-polarized light to the left (counterclockwise). (Section 24.4)

Lewis acid An electron-pair acceptor. (Section 16.11)

Lewis base An electron-pair donor. (Section 16.11)

Lewis structure A representation of covalent bonding in a molecule that is drawn using Lewis symbols. Shared electron pairs are shown as lines, and unshared electron pairs are shown as pairs of dots. Only the valence-shell electrons are shown. (Section 8.3)

Lewis symbol (electron-dot symbol) The chemical symbol for an element, with a dot for each valence electron. (Section 8.1)

ligand An ion or molecule that coordinates to a metal atom or to a metal ion to form a complex. (Section 23.2)

lime-soda process A method used in large-scale water treatment to reduce water hardness by removing Mg^{2+} and Ca^{2+}. The substances added to the water are lime, CaO [or slaked lime, $Ca(OH)_2$], and soda ash, Na_2CO_3, in amounts determined by the concentrations of the undesired ions. (Section 18.4)

limiting reactant (limiting reagent) The reactant present in the smallest stoichiometric quantity in a mixture of reactants; the amount of product that can form is limited by the complete consumption of the limiting reactant. (Section 3.7)

line spectrum A spectrum that contains radiation at only certain specific wavelengths. (Section 6.3)

linkage isomers Structural isomers of coordination compounds in which a ligand differs in its mode of attachment to a metal ion. (Section 23.4)

lipid A nonpolar molecule derived from glycerol and fatty acids that is used by organisms for long-term energy storage. (Section 24.9)

liquid Matter that has a distinct volume but no specific shape. (Section 1.2)

liquid crystal A substance that exhibits one or more partially ordered liquid phases above the melting point of the solid form. By contrast, in nonliquid crystalline substances the liquid phase that forms upon melting is completely unordered. (Section 11.7)

lock-and-key model A model of enzyme action in which the substrate molecule is pictured as fitting rather specifically into the active site on the enzyme. It is assumed that in being bound to the active site, the substrate is somehow activated for reaction. (Section 14.7)

low-spin complex A metal complex in which the electrons are paired in lower-energy orbitals. (Section 23.6)

magic numbers Numbers of protons and neutrons that result in very stable nuclei. (Section 21.2)

main-group elements Elements in the *s* and *p* blocks of the periodic table. (Section 6.9)

mass A measure of the amount of material in an object. It measures the resistance of an object to being moved. In SI units, mass is measured in kilograms. (Section 1.4)

mass defect The difference between the mass of a nucleus and the total masses of the individual nucleons that it contains. (Section 21.6)

mass number The sum of the number of protons and neutrons in the nucleus of a particular atom. (Section 2.3)

mass percentage The number of grams of solute in each 100 g of solution. (Section 13.4)

mass spectrometer An instrument used to measure the precise masses and relative amounts of atomic and molecular ions. (Section 2.4)

matter Anything that occupies space and has mass; the physical material of the universe. (Section 1.1)

matter waves The term used to describe the wave characteristics of a moving particle. (Section 6.4)

mean free path The average distance traveled by a gas molecule between collisions. (Section 10.8)

metal complex An assembly of a metal ion and the Lewis bases bonded to it. (Section 23.2)

metallic bond Bonding, usually in solid metals, in which the bonding electrons are relatively free to move throughout the three-dimensional structure. (Section 8.1)

metallic character The extent to which an element exhibits the physical and chemical properties characteristic of metals, for example, luster, malleability, ductility, and good thermal and electrical conductivity. (Section 7.6)

metallic elements (metals) Elements that are usually solids at room temperature, exhibit high electrical and heat conductivity, and appear lustrous. Most of the elements in the periodic table are metals. (Sections 2.5 and 12.1)

metallic hydrides Compounds formed when hydrogen reacts with transition metals; these compounds contain the hydride ion, H^-. (Section 22.2)

metallic solids Solids that are composed of metal atoms. (Section 12.1)

metalloids Elements that lie along the diagonal line separating the metals from the nonmetals in the periodic table; the properties of metalloids are intermediate between those of metals and nonmetals. (Section 2.5)

metallurgy The science of extracting metals from their natural sources by a combination of chemical and physical processes. It is also concerned with the properties and structures of metals and alloys. (Section 23.1)

metathesis (exchange) reaction A reaction in which two substances react through an exchange of their component ions: $AX + BY \longrightarrow AY + BX$. Precipitation and acid–base neutralization reactions are examples of metathesis reactions. (Section 4.2)

metric system A system of measurement used in science and in most countries. The meter and the gram are examples of metric units. (Section 1.4)

microstate The state of a system at a particular instant; one of many possible energetically equivalent ways to arrange the components of a system to achieve a particular state. (Section 19.3)

mineral A solid, inorganic substance occurring in nature, such as calcium carbonate, which occurs as calcite. (Section 23.1)

miscible liquids Liquids that mix in all proportions. (Section 13.3)

mixture A combination of two or more substances in which each substance retains its own chemical identity. (Section 1.2)

molal boiling-point-elevation constant (K_b) A constant characteristic of a particular solvent that gives the increase in boiling point as a function of solution molality: $\Delta T_b = K_b m$. (Section 13.5)

molal freezing-point-depression constant (K_f) A constant characteristic of a particular solvent that gives the decrease in freezing point as a function of solution molality: $\Delta T_f = K_f m$. (Section 13.5)

molality The concentration of a solution expressed as moles of solute per kilogram of solvent; abbreviated *m*. (Section 13.4)

molar heat capacity The heat required to raise the temperature of one mole of a substance by 1 °C. (Section 5.5)

molarity The concentration of a solution expressed as moles of solute per liter of solution; abbreviated *M*. (Section 4.5)

molar mass The mass of one mole of a substance in grams; it is numerically equal to the formula weight in atomic mass units. (Section 3.4)

mole A collection of Avogadro's number (6.022×10^{23}) of objects; for example, a mole of H_2O is 6.022×10^{23} H_2O molecules. (Section 3.4)

molecular compound A compound that consists of molecules. (Section 2.6)

molecular equation A chemical equation in which the formula for each substance is written without regard for whether it is an electrolyte or a nonelectrolyte. (Section 4.2)

molecular formula A chemical formula that indicates the actual number of atoms of each element in one molecule of a substance. (Section 2.6)

molecular geometry The arrangement in space of the atoms of a molecule. (Section 9.2)

molecular hydrides Compounds formed when hydrogen reacts with nonmetals and metalloids. (Section 22.2)

molecularity The number of molecules that participate as reactants in an elementary reaction. (Section 14.6)

molecular orbital (MO) An allowed state for an electron in a molecule. According to molecular-orbital theory, a molecular orbital is entirely analogous to an atomic orbital, which is an allowed state for an electron in an atom. Most bonding molecular orbitals can be classified as σ or π, depending on the disposition of electron density with respect to the internuclear axis. (Section 9.7)

molecular-orbital diagram A diagram that shows the energies of molecular orbitals relative to the atomic orbitals from which they are derived; also called an **energy-level diagram**. (Section 9.7)

molecular-orbital theory A theory that accounts for the allowed states for electrons in molecules. (Section 9.7)

molecular solids Solids that are composed of molecules. (Sections 12.1 and 12.6)

molecular weight The mass of the collection of atoms represented by the chemical formula for a molecule. (Section 3.3)

molecule A chemical combination of two or more atoms. (Sections 1.1 and 2.6)

mole fraction The ratio of the number of moles of one component of a mixture to the total moles of all components; abbreviated *X*, with a subscript to identify the component. (Section 10.6)

momentum The product of the mass, *m*, and velocity, *v*, of an object. (Section 6.4)

monodentate ligand A ligand that binds to the metal ion via a single donor atom. It occupies one position in the coordination sphere. (Section 23.3)

monomers Molecules with low molecular weights, which can be joined together (polymerized) to form a polymer. (Section 12.8)

monosaccharide A simple sugar, most commonly containing six carbon atoms. The joining together of monosaccharide units by condensation reactions results in formation of polysaccharides. (Section 24.8)

nanomaterial A solid whose dimensions range from 1 to 100 nm and whose properties differ from those of a bulk material with the same composition. (Section 12.1)

natural gas A naturally occurring mixture of gaseous hydrocarbon compounds composed of hydrogen and carbon. (Section 5.8)

nematic liquid crystalline phase A liquid crystal in which the molecules are aligned in the same general direction, along their long axes, but in which the ends of the molecules are not aligned. (Section 11.7)

Nernst equation An equation that relates the cell emf, E, to the standard emf, E°, and the reaction quotient, $Q: E = E^\circ - (RT/nF) \ln Q$. (Section 20.6)

net ionic equation A chemical equation for a solution reaction in which soluble strong electrolytes are written as ions and spectator ions are omitted. (Section 4.2)

neutralization reaction A reaction in which an acid and a base react in stoichiometrically equivalent amounts; the neutralization reaction between an acid and a metal hydroxide produces water and a salt. (Section 4.3)

neutron An electrically neutral particle found in the nucleus of an atom; it has approximately the same mass as a proton. (Section 2.3)

noble gases Members of group 8A in the periodic table. (Section 7.8)

node Points in an atom at which the electron density is zero. For example, the node in a 2*s* orbital is a spherical surface. (Section 6.6)

nonbonding pair In a Lewis structure a pair of electrons assigned completely to one atom; also called a lone pair. (Section 9.2)

nonelectrolyte A substance that does not ionize in water and consequently gives a nonconducting solution. (Section 4.1)

nonionizing radiation Radiation that does not have sufficient energy to remove an electron from a molecule. (Section 21.9)

nonmetallic elements (nonmetals) Elements in the upper right corner of the periodic table; nonmetals differ from metals in their physical and chemical properties. (Section 2.5)

nonpolar covalent bond A covalent bond in which the electrons are shared equally. (Section 8.4)

normal boiling point The boiling point at 1 atm pressure. (Section 11.5)

normal melting point The melting point at 1 atm pressure. (Section 11.6)

nuclear binding energy The energy required to decompose an atomic nucleus into its component protons and neutrons. (Section 21.6)

nuclear disintegration series A series of nuclear reactions that begins with an unstable nucleus and terminates with a stable one; also called a **radioactive series**. (Section 21.2)

nuclear model Model of the atom with a nucleus containing protons and neutrons and with electrons in the space outside the nucleus. (Section 2.2)

nuclear transmutation A conversion of one kind of nucleus to another. (Section 21.3)

nucleic acids Polymers of high molecular weight that carry genetic information and control protein synthesis. (Section 24.10)

nucleon A particle found in the nucleus of an atom. (Section 21.1)

nucleotide Compounds formed from a molecule of phosphoric acid, a sugar molecule, and an organic nitrogen base. Nucleotides form linear polymers called DNA and RNA, which are involved in protein synthesis and cell reproduction. (Section 24.10)

nucleus The very small, very dense, positively charged portion of an atom; it is composed of protons and neutrons. (Section 2.2)

octet rule A rule stating that bonded atoms tend to possess or share a total of eight valence-shell electrons. (Section 8.1)

optical isomerism A form of isomerism in which the two forms of a compound (stereoisomers) are nonsuperimposable mirror images. (Section 23.4)

optically active Possessing the ability to rotate the plane of polarized light. (Section 23.4)

orbital An allowed energy state of an electron in the quantum mechanical model of the atom; the term *orbital* is also used to describe the spatial distribution of the electron. An orbital is defined by the values of three quantum numbers: n, l, and m_l (Section 6.5)

organic chemistry The study of carbon-containing compounds, typically containing carbon–carbon bonds. (Section 2.9; Chapter 24: Introduction)

osmosis The net movement of solvent through a semipermeable membrane toward the solution with greater solute concentration. (Section 13.5)

osmotic pressure The pressure that must be applied to a solution to stop osmosis from pure solvent into the solution. (Section 13.5)

Ostwald process An industrial process used to make nitric acid from ammonia. The NH_3 is catalytically oxidized by O_2 to form NO; NO in air is oxidized to NO_2; HNO_3 is formed in a disproportionation reaction when NO_2 dissolves in water. (Section 22.7)

overall reaction order The sum of the reaction orders of all the reactants appearing in the rate expression when the rate can be expressed as rate $= k[A]^a[B]^b \ldots$. (Section 14.3)

overlap The extent to which atomic orbitals on different atoms share the same region of space. When the overlap between two orbitals is large, a strong bond may be formed. (Section 9.4)

oxidation A process in which a substance loses one or more electrons. (Section 4.4)

oxidation number (oxidation state) A positive or negative whole number assigned to an element in a molecule or ion on the basis of a set of formal rules; to some degree it reflects the positive or negative character of that atom. (Section 4.4)

oxidation-reduction (redox) reaction A chemical reaction in which the oxidation states of certain atoms change. (Section 4.4; Chapter 20: Introduction)

oxidizing agent, or oxidant The substance that is reduced and thereby causes the oxidation of some other substance in an oxidation-reduction reaction. (Section 20.1)

oxyacid A compound in which one or more OH groups, and possibly additional oxygen atoms, are bonded to a central atom. (Section 16.10)

oxyanion A polyatomic anion that contains one or more oxygen atoms. (Section 2.8)

ozone The name given to O_3, an allotrope of oxygen. (Section 7.8)

paramagnetism A property that a substance possesses if it contains one or more unpaired electrons. A paramagnetic substance is drawn into a magnetic field. (Section 9.8)

partial pressure The pressure exerted by a particular gas in a mixture. (Section 10.6)

particle accelerator A device that uses strong magnetic and electrostatic fields to accelerate charged particles. (Section 21.3)

parts per billion (ppb) The concentration of a solution in grams of solute per 10^9 (billion) grams of solution; equals micrograms of solute per liter of solution for aqueous solutions. (Section 13.4)

parts per million (ppm) The concentration of a solution in grams of solute per 10^6 (million) grams of solution; equals milligrams of solute per liter of solution for aqueous solutions. (Section 13.4)

pascal (Pa) The SI unit of pressure: $1\ \text{Pa} = 1\ \text{N/m}^2$. (Section 10.2)

Pauli exclusion principle A rule stating that no two electrons in an atom may have the same four quantum numbers (n, l, m_l, and $m_{s)}$). As a reflection of this principle, there can be no more than two electrons in any one atomic orbital. (Section 6.7)

peptide bond A bond formed between two amino acids. (Section 24.7)

percent ionization The percent of a substance that undergoes ionization on dissolution in water. The term applies to solutions of weak acids and bases. (Section 16.6)

percent yield The ratio of the actual (experimental) yield of a product to its theoretical (calculated) yield, multiplied by 100. (Section 3.7)

period The row of elements that lie in a horizontal row in the periodic table. (Section 2.5)

periodic table The arrangement of elements in order of increasing atomic number, with elements having similar properties placed in vertical columns. (Section 2.5)

petroleum A naturally occurring combustible liquid composed of hundreds of hydrocarbons and other organic compounds. (Section 5.8)

pH The negative log in base 10 of the aquated hydrogen ion concentration: $\text{pH} = -\log[H^+]$. (Section 16.4)

pH titration curve A graph of pH as a function of added titrant. (Section 17.3)

phase change The conversion of a substance from one state of matter to another. The phase changes we consider are melting and freezing (solid $\rightleftharpoons$ liquid), sublimation and deposition, and vaporization and condensation (liquid $\rightleftharpoons$ gas). (Section 11.4)

phase diagram A graphic representation of the equilibria among the solid, liquid, and gaseous phases of a substance as a function of temperature and pressure. (Section 11.6)

phospholipid A form of lipid molecule that contains charged phosphate groups. (Section 24.9)

photochemical smog A complex mixture of undesirable substances produced by the action of sunlight on an urban atmosphere polluted with automobile emissions. The major starting ingredients are nitrogen oxides and organic substances, notably olefins and aldehydes. (Section 18.2)

photodissociation The breaking of a molecule into two or more neutral fragments as a result of absorption of light. (Section 18.2)

photoelectric effect The emission of electrons from a metal surface induced by light. (Section 6.2)

photoionization The removal of an electron from an atom or molecule by absorption of light. (Section 18.2)

photon The smallest increment (a quantum) of radiant energy; a photon of light with frequency ν has an energy equal to $h\nu$. (Section 6.2)

photosynthesis The process that occurs in plant leaves by which light energy is used to convert carbon dioxide and water to carbohydrates and oxygen. (Section 23.3)

physical changes Changes (such as a phase change) that occur with no change in chemical composition. (Section 1.3)

physical properties Properties that can be measured without changing the composition of a substance, for example, color and freezing point. (Section 1.3)

pi (π) bond A covalent bond in which electron density is concentrated above and below the internuclear axis. (Section 9.6)

pi (π) molecular orbital A molecular orbital that concentrates the electron density on opposite sides of an imaginary line that passes through the nuclei. (Section 9.8)

Planck's constant (h) The constant that relates the energy and frequency of a photon, $E = h\nu$. Its value is 6.626×10^{-34} J-s. (Section 6.2)

plastic A material that can be formed into particular shapes by application of heat and pressure. (Section 12.8)

polar covalent bond A covalent bond in which the electrons are not shared equally. (Section 8.4)

polarizability The ease with which the electron cloud of an atom or a molecule is distorted by an outside influence, thereby inducing a dipole moment. (Section 11.2)

polar molecule A molecule that possesses a nonzero dipole moment. (Section 8.4)

polyatomic ion An electrically charged group of two or more atoms. (Section 2.7)

polydentate ligand A ligand in which two or more donor atoms can coordinate to the same metal ion. (Section 23.3)

polymer A large molecule of high molecular mass, formed by the joining together, or polymerization, of a large number of molecules of low molecular mass. The individual molecules forming the polymer are called monomers. (Sections 12.1 and 12.8)

polypeptide A polymer of amino acids that has a molecular weight of less than 10,000. (Section 24.7)

polyprotic acid A substance capable of dissociating more than one proton in water; H_2SO_4 is an example. (Section 16.6)

polysaccharide A substance made up of many monosaccharide units joined together. (Section 24.8)

porphyrin A complex derived from the porphine molecule. (Section 23.3)

positron emission A nuclear decay process where a positron, a particle with the same mass as an electron but with a positive charge, symbol ${}^{0}_{1}e$, is emitted from the nucleus. (Section 21.1)

potential energy The energy that an object possesses as a result of its composition or its position with respect to another object. (Section 5.1)

precipitate An insoluble substance that forms in, and separates from, a solution. (Section 4.2)

precipitation reaction A reaction that occurs between substances in solution in which one of the products is insoluble. (Section 4.2)

precision The closeness of agreement among several measurements of the same quantity; the reproducibility of a measurement. (Section 1.5)

pressure A measure of the force exerted on a unit area. In chemistry, pressure is often expressed in units of atmospheres (atm) or torr: 760 torr = 1 atm; in SI units pressure is expressed in pascals (Pa). (Section 10.2)

pressure–volume (*PV*) work Work performed by expansion of a gas against a resisting pressure. (Section 5.3)

primary structure The sequence of amino acids along a protein chain. (Section 24.7)

primitive lattice A crystal lattice in which the lattice points are located only at the corners of each unit cell. (Section 12.2)

probability density (ψ^2) A value that represents the probability that an electron will be found at a given point in space. Also called **electron density**. (Section 6.5)

product A substance produced in a chemical reaction; it appears to the right of the arrow in a chemical equation. (Section 3.1)

property A characteristic that gives a sample of matter its unique identity. (Section 1.1)

protein A biopolymer formed from amino acids. (Section 24.7)

protium The most common isotope of hydrogen. (Section 22.2)

proton A positively charged subatomic particle found in the nucleus of an atom. (Section 2.3)

pure substance Matter that has a fixed composition and distinct properties. (Section 1.2)

pyrometallurgy A process in which heat converts a mineral in an ore from one chemical form to another and eventually to the free metal. (Section 23.2)

qualitative analysis The determination of the presence or absence of a particular substance in a mixture. (Section 17.7)

quantitative analysis The determination of the amount of a given substance that is present in a sample. (Section 17.7)

quantum The smallest increment of radiant energy that may be absorbed or emitted; the magnitude of radiant energy is $h\nu$. (Section 6.2)

quaternary structure The structure of a protein resulting from the clustering of several individual protein chains into a final specific shape. (Section 24.7)

racemic mixture A mixture of equal amounts of the dextrorotatory and levorotatory forms of a chiral molecule. A racemic mixture will not rotate the plane of polarized light. (Section 23.4)

rad A measure of the energy absorbed from radiation by tissue or other biological material; 1 rad = transfer of 1×10^{-2} J of energy per kilogram of material. (Section 21.9)

radial probability function The probability that the electron will be found at a certain distance from the nucleus. (Section 6.6)

radioactive Possessing **radioactivity**, the spontaneous disintegration of an unstable atomic nucleus with accompanying emission of radiation. (Section 2.2; Chapter 21: Introduction)

radioactive series A series of nuclear reactions that begins with an unstable nucleus and terminates with a stable one. Also called **nuclear disintegration series**. (Section 21.2)

radioisotope An isotope that is radioactive; that is, it is undergoing nuclear changes with emission of radiation. (Section 21.1)

radionuclide A radioactive nuclide. (Section 21.1)

radiotracer A radioisotope that can be used to trace the path of an element in a chemical system. (Section 21.5)

Raoult's law A law stating that the partial pressure of a solvent over a solution, P_{solution}, is given by the vapor pressure of the pure solvent, $P^{\circ}_{\text{solvent}}$, times the mole fraction of a solvent in the solution, X_{solvent}: $P_{\text{solution}} = X_{\text{solvent}}P^{\circ}_{\text{solvent}}$. (Section 13.5)

rare earth element See **lanthanide element.** (Sections 6.8 and 6.9)

rate constant A constant of proportionality between the reaction rate and the concentrations of reactants that appear in the rate law. (Section 14.3)

rate-determining step The slowest elementary step in a reaction mechanism. (Section 14.6)

rate law An equation that relates the reaction rate to the concentrations of reactants (and sometimes of products also). (Section 14.3)

reactant A starting substance in a chemical reaction; it appears to the left of the arrow in a chemical equation. (Section 3.1)

reaction mechanism A detailed picture, or model, of how the reaction occurs; that is, the order in which bonds are broken and formed and the changes in relative positions of the atoms as the reaction proceeds. (Section 14.6)

reaction order The power to which the concentration of a reactant is raised in a rate law. (Section 14.3)

reaction quotient (Q) The value that is obtained when concentrations of reactants and products are inserted into the equilibrium expression. If the concentrations are equilibrium concentrations, $Q = K$; otherwise, $Q \neq K$. (Section 15.6)

reaction rate A measure of the decrease in concentration of a reactant or the increase in concentration of a product with time. (Section 14.2)

redox (oxidation-reduction) reaction A reaction in which certain atoms undergo changes in oxidation states. The substance increasing in oxidation state is oxidized; the substance decreasing in oxidation state is reduced. (Section 4.4; Chapter 20: Introduction)

reducing agent, or reductant The substance that is oxidized and thereby causes the reduction of some other substance in an oxidation-reduction reaction. (Section 20.1)

reduction A process in which a substance gains one or more electrons. (Section 4.4)

rem A measure of the biological damage caused by radiation; rems = rads × RBE. (Section 21.9)

renewable energy sources Energy such as solar energy, wind energy, and hydroelectric energy derived from essentially inexhaustible sources. (Section 5.8)

representative (main-group) element An element from within the *s* and *p* blocks of the periodic table (Figure 6.29). (Section 6.9)

resonance structures (resonance forms) Individual Lewis structures in cases where two or more Lewis structures are equally good descriptions of a single molecule. The resonance structures in such an instance are "averaged" to give a more accurate description of the real molecule. (Section 8.6)

reverse osmosis The process by which water molecules move under high pressure through a semipermeable membrane from the more concentrated to the less concentrated solution. (Section 18.4)

reversible process A process that can go back and forth between states along exactly the same path; a system at equilibrium is reversible if equilibrium can be shifted by an infinitesimal modification of a variable such as temperature. (Section 19.1)

ribonucleic acid (RNA) A polynucleotide in which ribose is the sugar component. (Section 24.10)

root-mean-square (rms) speed (μ) The square root of the average of the squared speeds of the gas molecules in a gas sample. (Section 10.7)

rotational motion Movement of a molecule as though it is spinning like a top. (Section 19.3)

salinity A measure of the salt content of seawater, brine, or brackish water. It is equal to the mass in grams of dissolved salts present in 1 kg of seawater. (Section 18.3)

salt An ionic compound formed by replacing one or more hydrogens of an acid by other cations. (Section 4.3)

saponification Hydrolysis of an ester in the presence of a base. (Section 24.4)

saturated solution A solution in which undissolved solute and dissolved solute are in equilibrium. (Section 13.2)

scientific law A concise verbal statement or a mathematical equation that summarizes a wide range of observations and experiences. (Section 1.3)

scientific method The general process of advancing scientific knowledge by making experimental observations and by formulating hypotheses, theories, and laws. (Section 1.3)

secondary structure The manner in which a protein is coiled or stretched. (Section 24.7)

second law of thermodynamics A statement of our experience that there is a direction to the way events occur in nature. When a process occurs spontaneously in one direction, it is nonspontaneous in the reverse direction. It is possible to state the second law in many different forms, but they all relate back to the same idea about spontaneity. One of the most common statements found in chemical contexts is that in any spontaneous process the entropy of the universe increases. (Section 19.2)

second-order reaction A reaction in which the overall reaction order (the sum of the concentration-term exponents) in the rate law is 2. (Section 14.4)

sigma (σ) bond A covalent bond in which electron density is concentrated along the internuclear axis. (Section 9.6)

sigma (σ) molecular orbital A molecular orbital that centers the electron density about an imaginary line passing through two nuclei. (Section 9.7)

significant figures The digits that indicate the precision with which a measurement is made; all digits of a measured quantity are significant, including the last digit, which is uncertain. (Section 1.5)

silica Common name for silicon dioxide. (Section 22.4)

silicates Compounds containing silicon and oxygen, structurally based on SiO_4 tetrahedra. (Section 22.10)

single bond A covalent bond involving one electron pair. (Section 8.3)

SI units The preferred metric units for use in science. (Section 1.4)

smectic liquid crystalline phase A liquid crystal in which the molecules are aligned along their long axes and arranged in sheets, with the ends of the molecules aligned. There are several different kinds of smectic phases. (Section 12.8)

solid Matter that has both a definite shape and a definite volume. (Section 1.2)

solubility The amount of a substance that dissolves in a given quantity of solvent at a given temperature to form a saturated solution. (Sections 4.2 and 13.2)

solubility-product constant (solubility product) (K_{sp}) An equilibrium constant related to the equilibrium between a solid salt and its ions in solution. It provides a quantitative measure of the solubility of a slightly soluble salt. (Section 17.4)

solute A substance dissolved in a solvent to form a solution; it is normally the component of a solution present in the smaller amount. (Section 4.1)

solution A mixture of substances that has a uniform composition; a homogeneous mixture. (Section 1.2)

solution alloy A homogeneous alloy, where two or more elements are distributed randomly and uniformly throughout the solid. (Section 12.3)

solvation The clustering of solvent molecules around a solute particle. (Section 13.1)

solvent The dissolving medium of a solution; it is normally the component of a solution present in the greater amount. (Section 4.1)

specific heat (C_s) The heat capacity of 1 g of a substance; the heat required to raise the temperature of 1 g of a substance by 1 °C. (Section 5.5)

spectator ions Ions that go through a reaction unchanged and that appear on both sides of the complete ionic equation. (Section 4.2)

spectrochemical series A list of ligands arranged in order of their abilities to split the *d*-orbital energies (using the terminology of the crystal-field model). (Section 23.6)

spectrum The distribution among various wavelengths of the radiant energy emitted or absorbed by an object. (Section 6.3)

spin magnetic quantum number (m_s) A quantum number associated with the electron spin; it may have values of $+\frac{1}{2}$ or $-\frac{1}{2}$. (Section 6.7)

spin-pairing energy The energy required to pair an electron with another electron occupying an orbital. (Section 23.6)

spontaneous process A process that is capable of proceeding in a given direction, as written or described, without needing to be driven by an outside source of energy. A process may be spontaneous even though it is very slow. (Section 19.1)

standard atmospheric pressure Defined as 760 torr or, in SI units, 101.325 kPa. (Section 10.2)

standard emf, also called the standard cell potential ($E°$) The emf of a cell when all reagents are at standard conditions. (Section 20.4)

standard enthalpy change ($\Delta H°$) The change in enthalpy in a process when all reactants and products are in their stable forms at 1 atm pressure and a specified temperature, commonly 25 °C. (Section 5.7)

standard enthalpy of formation ($\Delta H_f°$) The change in enthalpy that accompanies the formation of one mole of a substance from its elements, with all substances in their standard states. (Section 5.7)

standard free energy of formation ($\Delta G_f°$) The change in free energy associated with the formation of a substance from its elements under standard conditions. (Section 19.5)

standard hydrogen electrode (SHE) An electrode based on the half-reaction $2\,H^+(1\,M) + 2\,e^- \longrightarrow H_2(1\text{ atm})$. The standard electrode potential of the standard hydrogen electrode is defined as 0 V. (Section 20.4)

standard molar entropy ($S°$) The entropy value for a mole of a substance in its standard state. (Section 19.4)

standard reduction potential ($E°_{red}$) The potential of a reduction half-reaction under standard conditions, measured relative to the standard hydrogen electrode. A standard reduction potential is also called a **standard electrode potential**. (Section 20.4)

standard solution A solution of known concentration. (Section 4.6)

standard temperature and pressure (STP) Defined as 0 °C and 1 atm pressure; frequently used as reference conditions for a gas. (Section 10.4)

starch The general name given to a group of polysaccharides that acts as energy-storage substances in plants. (Section 24.8)

state function A property of a system that is determined by its state or condition and not by how it got to that state; its value is fixed when temperature, pressure, composition, and physical form are specified; *P*, *V*, *T*, *E*, and *H* are state functions. (Section 5.2)

states of matter The three forms that matter can assume: solid, liquid, and gas. (Section 1.2)

stereoisomers Compounds possessing the same formula and bonding arrangement but differing in the spatial arrangements of the atoms. (Section 23.4)

stoichiometry The relationships among the quantities of reactants and products involved in chemical reactions. (Chapter 3: Introduction)

stratosphere The region of the atmosphere directly above the troposphere. (Section 18.1)

strong acid An acid that ionizes completely in water. (Section 4.3)

strong base A base that ionizes completely in water. (Section 4.3)

strong electrolyte A substance (strong acids, strong bases, and most salts) that is completely ionized in solution. (Section 4.1)

structural formula A formula that shows not only the number and kinds of atoms in the molecule but also the arrangement (connections) of the atoms. (Section 2.6)

structural isomers Compounds possessing the same formula but differing in the bonding arrangements of the atoms. (Sections 23.4 and 24.2)

subatomic particles Particles such as protons, neutrons, and electrons that are smaller than an atom. (Section 2.2)

subshell One or more orbitals with the same set of quantum numbers n and l. For example, we speak of the $2p$ subshell ($n = 2$, $l = 1$), which is composed of three orbitals ($2p_x$, $2p_y$, and $2p_z$). (Section 6.5)

substitutional alloy A homogeneous (solution) alloy in which atoms of different elements randomly occupy sites in the lattice. (Section 23.6)

substitution reactions Reactions in which one atom (or group of atoms) replaces another atom (or group) within a molecule; substitution reactions are typical for alkanes and aromatic hydrocarbons. (Section 24.3)

substrate A substance that undergoes a reaction at the active site in an enzyme. (Section 14.7)

supercritical mass An amount of fissionable material larger than the critical mass. (Section 21.7)

supersaturated solution A solution containing more solute than an equivalent saturated solution. (Section 13.2)

surface tension The intermolecular, cohesive attraction that causes a liquid to minimize its surface area. (Section 11.3)

surroundings In thermodynamics, everything that lies outside the system that we study. (Section 5.1)

system In thermodynamics, the portion of the universe that we single out for study. We must be careful to state exactly what the system contains and what transfers of energy it may have with its surroundings. (Section 5.1)

termolecular reaction An elementary reaction that involves three molecules. Termolecular reactions are rare. (Section 14.6)

tertiary structure The overall shape of a large protein, specifically, the manner in which sections of the protein fold back upon themselves or intertwine. (Section 24.7)

theoretical yield The quantity of product that is calculated to form when all of the limiting reagent reacts. (Section 3.7)

theory A tested model or explanation that satisfactorily accounts for a certain set of phenomena. (Section 1.3)

thermochemistry The relationship between chemical reactions and energy changes. (Chapter 5: Introduction)

thermodynamics The study of energy and its transformation. (Chapter 5: Introduction)

thermonuclear reaction Another name for fusion reactions; reactions in which two light nuclei are joined to form a more massive one. (Section 21.8)

thermoplastic A polymeric material that can be readily reshaped by application of heat and pressure. (Section 12.8)

thermosetting plastic A plastic that, once formed in a particular mold, is not readily reshaped by application of heat and pressure. (Section 12.8)

third law of thermodynamics A law stating that the entropy of a pure, crystalline solid at absolute zero temperature is zero: $S(0\text{ K}) = 0$. (Section 19.3)

titration The process of reacting a solution of unknown concentration with one of known concentration (a standard solution). (Section 4.6)

torr A unit of pressure ($1\text{ torr} = 1\text{ mm Hg}$). (Section 10.2)

transition elements (transition metals) Elements in which the d orbitals are partially occupied. (Section 6.8)

transition state (activated complex) The particular arrangement of reactant and product molecules at the point of maximum energy in the rate-determining step of a reaction. (Section 14.5)

translational motion Movement in which an entire molecule moves in a definite direction. (Section 19.3)

transuranium elements Elements that follow uranium in the periodic table. (Section 21.3)

triple bond A covalent bond involving three electron pairs. (Section 8.3)

triple point The temperature at which solid, liquid, and gas phases coexist in equilibrium. (Section 11.6)

tritium The isotope of hydrogen whose nucleus contains a proton and two neutrons. (Section 22.2)

troposphere The region of Earth's atmosphere extending from the surface to about 12 km altitude. (Section 18.1)

Tyndall effect The scattering of a beam of visible light by the particles in a colloidal dispersion. (Section 13.6)

uncertainty principle A principle stating there is an inherent uncertainty in the precision with which we can simultaneously specify the position and momentum of a particle. This uncertainty is significant only for particles of extremely small mass, such as electrons. (Section 6.4)

unimolecular reaction An elementary reaction that involves a single molecule. (Section 14.6)

unit cell The smallest portion of a crystal that reproduces the structure of the entire crystal when repeated in different directions in space. It is the repeating unit or building block of the crystal lattice. (Section 12.2)

unsaturated solution A solution containing less solute than a saturated solution. (Section 13.2)

valence band A band of closely spaced molecular orbitals that is essentially fully occupied by electrons. (Section 12.7)

valence-bond theory A model of chemical bonding in which an electron-pair bond is formed between two atoms by the overlap of orbitals on the two atoms. (Section 9.4)

valence electrons The outermost electrons of an atom; those that occupy orbitals not occupied in the nearest noble-gas element of lower atomic number. The valence electrons are the ones the atom uses in bonding. (Section 6.8)

valence orbitals Orbitals that contain the outer-shell electrons of an atom. (Chapter 7: Introduction)

valence-shell electron-pair repulsion (VSEPR) model A model that accounts for the geometric arrangements of shared and unshared electron pairs around a central atom in terms of the repulsions between electron pairs. (Section 9.2)

van der Waals equation An equation of state for nonideal gases that is based on adding corrections to the ideal-gas equation. The correction terms account for intermolecular forces of attraction and for the volumes occupied by the gas molecules themselves. (Section 10.9)

vapor Gaseous state of any substance that normally exists as a liquid or solid. (Section 10.1)

vapor pressure The pressure exerted by a vapor in equilibrium with its liquid or solid phase. (Section 11.5)

vibrational motion Movement of the atoms within a molecule in which they move periodically toward and away from one another. (Section 19.3)

viscosity A measure of the resistance of fluids to flow. (Section 11.3)

volatile Tending to evaporate readily. (Section 11.5)

voltaic (galvanic) cell A device in which a spontaneous oxidation-reduction reaction occurs with the passage of electrons through an external circuit. (Section 20.3)

vulcanization The process of cross-linking polymer chains in rubber. (Section 12.6)

watt A unit of power; $1\text{ W} = 1\text{ J/s}$. (Section 20.5)

wave function A mathematical description of an allowed energy state (an orbital) for an electron in the quantum mechanical model of the atom; it is usually symbolized by the Greek letter ψ. (Section 6.5)

wavelength The distance between identical points on successive waves. (Section 6.1)

weak acid An acid that only partly ionizes in water. (Section 4.3)

weak base A base that only partly ionizes in water. (Section 4.3)

weak electrolyte A substance that only partly ionizes in solution. (Section 4.1)

work The movement of an object against some force. (Section 5.1)

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INDEX

Common Ions

Positive Ions (Cations)

1 +

ammonium (NH_4^+)
cesium (Cs^+)
copper(I) or cuprous (Cu^+)
hydrogen (H^+)
lithium (Li^+)
potassium (K^+)
silver (Ag^+)
sodium (Na^+)

2 +

barium (Ba^{2+})
cadmium (Cd^{2+})
calcium (Ca^{2+})
chromium(II) or chromous (Cr^{2+})
cobalt(II) or cobaltous (Co^{2+})
copper(II) or cupric (Cu^{2+})
iron(II) or ferrous (Fe^{2+})
lead(II) or plumbous (Pb^{2+})
magnesium (Mg^{2+})
manganese(II) or manganous (Mn^{2+})
mercury(I) or mercurous (Hg_2^{2+})
mercury(II) or mercuric (Hg^{2+})
strontium (Sr^{2+})
nickel(II) (Ni^{2+})
tin(II) or stannous (Sn^{2+})
zinc (Zn^{2+})

3 +

aluminum (Al^{3+})
chromium(III) or chromic (Cr^{3+})
iron(III) or ferric (Fe^{3+})

Negative Ions (Anions)

1 −

acetate (CH_3COO^- or $C_2H_3O_2^-$)
bromide (Br^-)
chlorate (ClO_3^-)
chloride (Cl^-)
cyanide (CN^-)
dihydrogen phosphate ($H_2PO_4^-$)
fluoride (F^-)
hydride (H^-)
hydrogen carbonate or bicarbonate (HCO_3^-)
hydrogen sulfite or bisulfite (HSO_3^-)
hydroxide (OH^-)
iodide (I^-)
nitrate (NO_3^-)
nitrite (NO_2^-)
perchlorate (ClO_4^-)
permanganate (MnO_4^-)
thiocyanate (SCN^-)

2 −

carbonate (CO_3^{2-})
chromate (CrO_4^{2-})
dichromate ($Cr_2O_7^{2-}$)
hydrogen phosphate (HPO_4^{2-})
oxide (O^{2-})
peroxide (O_2^{2-})
sulfate (SO_4^{2-})
sulfide (S^{2-})
sulfite (SO_3^{2-})

3 −

arsenate (AsO_4^{3-})
phosphate (PO_4^{3-})

Fundamental Constants*

Atomic mass unit	1 amu	$= 1.660538782 \times 10^{-27}$ kg
	1 g	$= 6.02214179 \times 10^{23}$ amu
Avogadro's number	N_A	$= 6.02214179 \times 10^{23}$/mol
Boltzmann's constant	k	$= 1.3806504 \times 10^{-23}$ J/K
Electron charge	e	$= 1.602176487 \times 10^{-19}$ C
Faraday's constant	F	$= 9.64853399 \times 10^{4}$ C/mol
Gas constant	R	= 0.082058205 L-atm/mol-K
		= 8.314472 J/mol-K
Mass of electron	m_e	$= 5.48579909 \times 10^{-4}$ amu
		$= 9.10938215 \times 10^{-31}$ kg
Mass of neutron	m_n	= 1.008664916 amu
		$= 1.674927211 \times 10^{-27}$ kg
Mass of proton	m_p	= 1.007276467 amu
		$= 1.672621637 \times 10^{-27}$ kg
Pi	π	= 3.1415927
Planck's constant	h	$= 6.62606896 \times 10^{-34}$ J-s
Speed of light in vacuum	c	$= 2.99792458 \times 10^{8}$ m/s

*Fundamental constants are listed at the National Institute of Standards and Technology Web site: http://www.nist.gov/physlab/data/physicalconst.cfm

Useful Conversion Factors and Relationships

Length

SI unit: meter (m)

1 km = 0.62137 mi
1 mi = 5280 ft
= 1.6093 km
1 m = 1.0936 yd
1 in. = 2.54 cm (exactly)
1 cm = 0.39370 in.
1 Å = 10^{-10} m

Mass

SI unit: kilogram (kg)

1 kg = 2.2046 lb
1 lb = 453.59 g
= 16 oz
1 amu = $1.660538782 \times 10^{-24}$ g

Temperature

SI unit: Kelvin (K)

0 K = −273.15 °C
= −459.67 °F
K = °C + 273.15
°C = $\frac{5}{9}$(°F − 32°)
°F = $\frac{9}{5}$°C + 32°

Energy (derived)

SI unit: Joule (J)

1 J = 1 kg-m^2/s^2
= 0.2390 cal
= 1 C-V
1 cal = 4.184 J
1 eV = 1.602×10^{-19} J

Pressure (derived)

SI unit: Pascal (Pa)

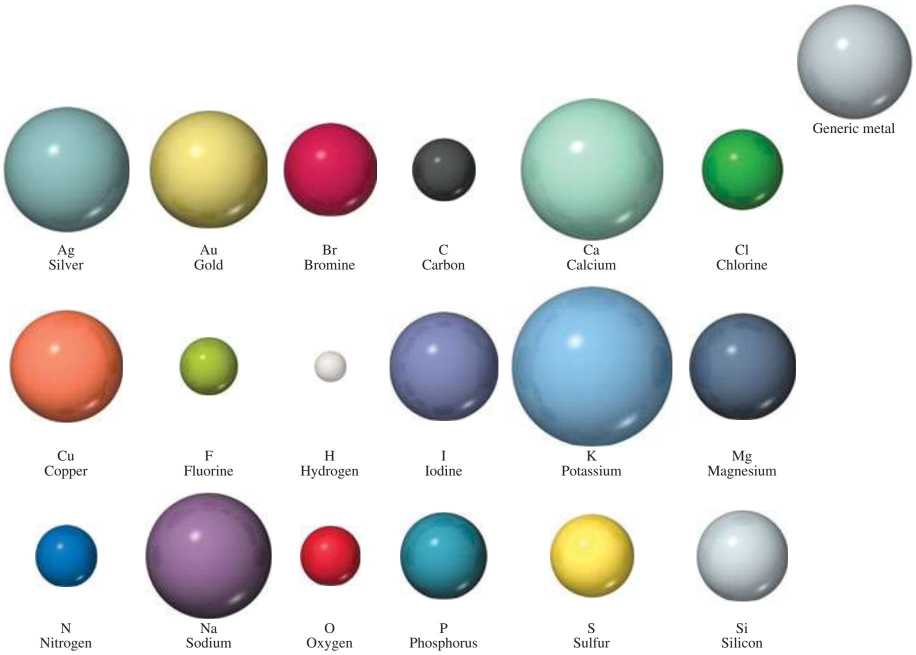
1 Pa = 1 N/m^2
= 1 kg/m-s^2
1 atm = 1.01325×10^5 Pa
= 760 torr
= 14.70 lb/in^2
1 bar = 10^5 Pa
1 torr = 1 mm Hg

Volume (derived)

SI unit: cubic meter (m^3)

1 L = 10^{-3} m^3
= 1 dm^3
= 10^3 cm^3
= 1.0567 qt
1 gal = 4 qt
= 3.7854 L
1 cm^3 = 1 mL
1 in^3 = 16.4 cm^3

Color Chart for Common Elements



Periodic Table of the Elements

Main Group Representative Elements (groups 1A–2A)

Transition metals (groups 3B–2B)

Main Group Representative Elements (groups 3A–8A)

Metals

Metalloids

Nonmetals

	1A[a]	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A	8A
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 **H** 1.00794																	2 **He** 4.002602
2	3 **Li** 6.941	4 **Be** 9.012182											5 **B** 10.811	6 **C** 12.0107	7 **N** 14.0067	8 **O** 15.9994	9 **F** 18.998403	10 **Ne** 20.1797
3	11 **Na** 22.989770	12 **Mg** 24.3050											13 **Al** 26.981538	14 **Si** 28.0855	15 **P** 30.973761	16 **S** 32.065	17 **Cl** 35.453	18 **Ar** 39.948
4	19 **K** 39.0983	20 **Ca** 40.078	21 **Sc** 44.955910	22 **Ti** 47.867	23 **V** 50.9415	24 **Cr** 51.9961	25 **Mn** 54.938049	26 **Fe** 55.845	27 **Co** 58.933200	28 **Ni** 58.6934	29 **Cu** 63.546	30 **Zn** 65.39	31 **Ga** 69.723	32 **Ge** 72.64	33 **As** 74.92160	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.80
5	37 **Rb** 85.4678	38 **Sr** 87.62	39 **Y** 88.90585	40 **Zr** 91.224	41 **Nb** 92.90638	42 **Mo** 95.94	43 **Tc** [98]	44 **Ru** 101.07	45 **Rh** 102.90550	46 **Pd** 106.42	47 **Ag** 107.8682	48 **Cd** 112.411	49 **In** 114.818	50 **Sn** 118.710	51 **Sb** 121.760	52 **Te** 127.60	53 **I** 126.90447	54 **Xe** 131.293
6	55 **Cs** 132.90545	56 **Ba** 137.327	71 **Lu** 174.967	72 **Hf** 178.49	73 **Ta** 180.9479	74 **W** 183.84	75 **Re** 186.207	76 **Os** 190.23	77 **Ir** 192.217	78 **Pt** 195.078	79 **Au** 196.96655	80 **Hg** 200.59	81 **Tl** 204.3833	82 **Pb** 207.2	83 **Bi** 208.98038	84 **Po** [208.98]	85 **At** [209.99]	86 **Rn** [222.02]
7	87 **Fr** [223.02]	88 **Ra** [226.03]	103 **Lr** [262.11]	104 **Rf** [261.11]	105 **Db** [262.11]	106 **Sg** [266.12]	107 **Bh** [264.12]	108 **Hs** [269.13]	109 **Mt** [268.14]	110 **Ds** [281.15]	111 **Rg** [272.15]	112 **Cn** [285]	113 [284]	114 [289]	115 [288]	116 [292]	117 ** [294]	118 [294]

Lanthanide series	57 **La** 138.9055	58 **Ce** 140.116	59 **Pr** 140.90765	60 **Nd** 144.24	61 **Pm** [145]	62 **Sm** 150.36	63 **Eu** 151.964	64 **Gd** 157.25	65 **Tb** 158.92534	66 **Dy** 162.50	67 **Ho** 164.93032	68 **Er** 167.259	69 **Tm** 168.93421	70 **Yb** 173.04
Actinide series	89 **Ac** [227.03]	90 **Th** 232.0381	91 **Pa** 231.03588	92 **U** 238.02891	93 **Np** [237.05]	94 **Pu** [244.06]	95 **Am** [243.06]	96 **Cm** [247.07]	97 **Bk** [247.07]	98 **Cf** [251.08]	99 **Es** [252.08]	100 **Fm** [257.10]	101 **Md** [258.10]	102 **No** [259.10]

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

The names and symbols for elements 113 and above have not yet been decided.

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

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

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

List of Elements with Their Symbols and Atomic Weights

Element	Symbol	Atomic Number	Atomic Weight
Actinium	Ac	89	227.03[a]
Aluminum	Al	13	26.981538
Americium	Am	95	243.06[a]
Antimony	Sb	51	121.760
Argon	Ar	18	39.948
Arsenic	As	33	74.92160
Astatine	At	85	209.99[a]
Barium	Ba	56	137.327
Berkelium	Bk	97	247.07[a]
Beryllium	Be	4	9.012182
Bismuth	Bi	83	208.98038
Bohrium	Bh	107	264.12[a]
Boron	B	5	10.811
Bromine	Br	35	79.904
Cadmium	Cd	48	112.411
Calcium	Ca	20	40.078
Californium	Cf	98	251.08[a]
Carbon	C	6	12.0107
Cerium	Ce	58	140.116
Cesium	Cs	55	132.90545
Chlorine	Cl	17	35.453
Chromium	Cr	24	51.9961
Cobalt	Co	27	58.933200
Copernicium	Cn	112	285
Copper	Cu	29	63.546
Curium	Cm	96	247.07[a]
Darmstadtium	Ds	110	281.15[a]
Dubnium	Db	105	262.11[a]
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	252.08[a]
Erbium	Er	68	167.259
Europium	Eu	63	151.964
Fermium	Fm	100	257.10[a]
Fluorine	F	9	18.9984032
Francium	Fr	87	223.02[a]
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.723
Germanium	Ge	32	72.64
Gold	Au	79	196.96655
Hafnium	Hf	72	178.49
Hassium	Hs	108	269.13[a]
Helium	He	2	4.002602[a]
Holmium	Ho	67	164.93032
Hydrogen	H	1	1.00794
Indium	In	49	114.818
Iodine	I	53	126.90447
Iridium	Ir	77	192.217
Iron	Fe	26	55.845
Krypton	Kr	36	83.80
Lanthanum	La	57	138.9055
Lawrencium	Lr	103	262.11[a]
Lead	Pb	82	207.2
Lithium	Li	3	6.941
Lutetium	Lu	71	174.967
Magnesium	Mg	12	24.3050
Manganese	Mn	25	54.938049
Meitnerium	Mt	109	268.14[a]
Mendelevium	Md	101	258.10[a]
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.1797
Neptunium	Np	93	237.05[a]
Nickel	Ni	28	58.6934
Niobium	Nb	41	92.90638
Nitrogen	N	7	14.0067
Nobelium	No	102	259.10[a]
Osmium	Os	76	190.23
Oxygen	O	8	15.9994
Palladium	Pd	46	106.42
Phosphorus	P	15	30.973761
Platinum	Pt	78	195.078
Plutonium	Pu	94	244.06[a]
Polonium	Po	84	208.98[a]
Potassium	K	19	39.0983
Praseodymium	Pr	59	140.90765
Promethium	Pm	61	145[a]
Protactinium	Pa	91	231.03588
Radium	Ra	88	226.03[a]
Radon	Rn	86	222.02[a]
Rhenium	Re	75	186.207[a]
Rhodium	Rh	45	102.90550
Roentgenium	Rg	111	272.15[a]
Rubidium	Rb	37	85.4678
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	261.11[a]
Samarium	Sm	62	150.36
Scandium	Sc	21	44.955910
Seaborgium	Sg	106	266[a]
Selenium	Se	34	78.96
Silicon	Si	14	28.0855
Silver	Ag	47	107.8682
Sodium	Na	11	22.989770
Strontium	Sr	38	87.62
Sulfur	S	16	32.065
Tantalum	Ta	73	180.9479
Technetium	Tc	43	98[a]
Tellurium	Te	52	127.60
Terbium	Tb	65	158.92534
Thallium	Tl	81	204.3833
Thorium	Th	90	232.0381
Thulium	Tm	69	168.93421
Tin	Sn	50	118.710
Titanium	Ti	22	47.867
Tungsten	W	74	183.84
Uranium	U	92	238.02891
Vanadium	V	23	50.9415
Xenon	Xe	54	131.293
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.90585
Zinc	Zn	30	65.39
Zirconium	Zr	40	91.224
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*[b]		117	294[a]
*[b]		118	294[a]

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

[b] The names of elements 113 and above have not yet been decided.