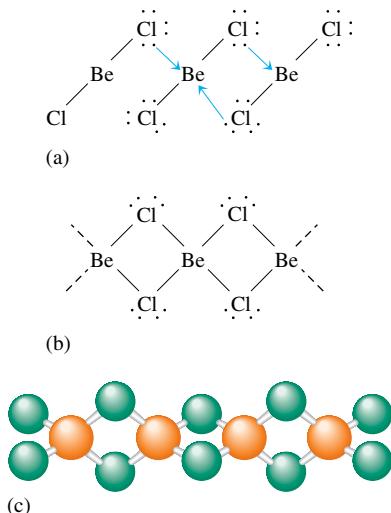




Calcium metal reacting with water to form bubbles of hydrogen gas.



**FIGURE 19.6**

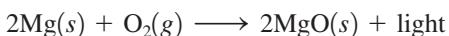
(a) Solid  $\text{BeCl}_2$  can be visualized as being formed from many  $\text{BeCl}_2$  molecules, where lone pairs on the chlorine atoms are used to bond to the beryllium atoms in adjacent  $\text{BeCl}_2$  molecules. (b) The extended structure of solid  $\text{BeCl}_2$ . (c) The ball-and-stick model of the extended structure.

As we saw in Section 19.1, the small size and relatively high electronegativity of the beryllium atom cause its bonds to be more covalent than is usual for a metal. For example, beryllium chloride with the Lewis structure



exists as a linear molecule, as predicted by the VSEPR model. The  $\text{Be}-\text{Cl}$  bonds are covalent, and beryllium is best described as being  $sp$  hybridized. As a solid,  $\text{BeCl}_2$  achieves an octet of electrons around each beryllium atom by forming an extended structure containing Be in a tetrahedral environment, as shown in Fig. 19.6. The lone pairs on the chlorine atoms are used to form  $\text{Be}-\text{Cl}$  bonds.

The alkaline earth metals have great practical importance. Calcium and magnesium ions are essential for human life. Calcium is found primarily in the structural minerals constituting bones and teeth; magnesium (as the  $\text{Mg}^{2+}$  ion) plays a vital role in metabolism and muscle functions. Also, magnesium was formerly used to produce the bright light for photographic flash bulbs from its reaction with oxygen:



Because magnesium metal has a relatively low density and moderate strength, it is a useful structural material, especially if alloyed with aluminum.

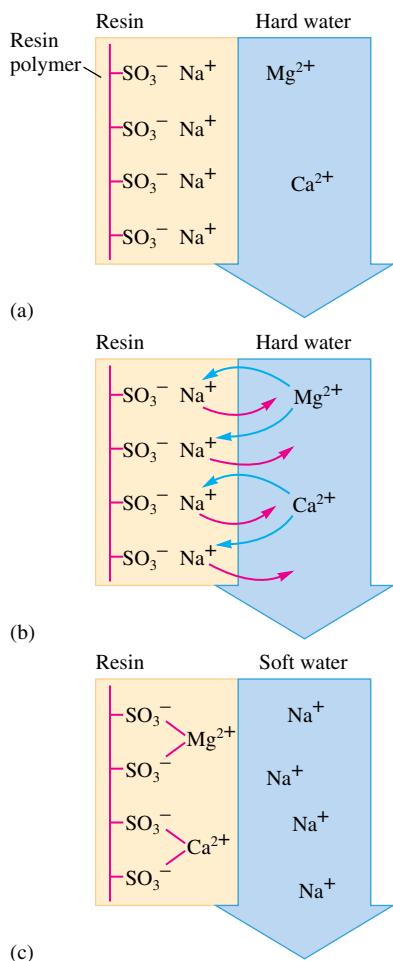
Table 19.8 summarizes some important reactions of the alkaline earth metals.



Bones contain large amounts of calcium.

**TABLE 19.8 Selected Reactions of the Group 2A Elements**

Reaction	Comment
$\text{M} + \text{X}_2 \rightarrow \text{MX}_2$	$\text{X}_2$ = any halogen molecule
$2\text{M} + \text{O}_2 \rightarrow 2\text{MO}$	$\text{Ba}$ gives $\text{BaO}_2$ as well
$\text{M} + \text{S} \rightarrow \text{MS}$	
$3\text{M} + \text{N}_2 \rightarrow \text{M}_3\text{N}_2$	High temperatures
$6\text{M} + \text{P}_4 \rightarrow 2\text{M}_3\text{P}_2$	High temperatures
$\text{M} + \text{H}_2 \rightarrow \text{MH}_2$	$\text{M} = \text{Ca}, \text{Sr}, \text{or Ba}$ ; high temperatures; $\text{Mg}$ at high pressure
$\text{M} + 2\text{H}_2\text{O} \rightarrow \text{M(OH)}_2 + \text{H}_2$	$\text{M} = \text{Ca}, \text{Sr}, \text{or Ba}$
$\text{M} + 2\text{H}^+ \rightarrow \text{M}^{2+} + \text{H}_2$	
$\text{Be} + 2\text{OH}^- + 2\text{H}_2\text{O} \rightarrow \text{Be(OH)}_4^{2-} + \text{H}_2$	

**FIGURE 19.7**

(a) A schematic representation of a typical cation-exchange resin. (b) and (c) When hard water is passed over the cation-exchange resin, the Ca<sup>2+</sup> and Mg<sup>2+</sup> bind to the resin.



The Dolomite mountains in Italy. Dolomite is a source of magnesium.

Relatively large concentrations of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions are often found in natural water supplies. These ions in this **hard water** interfere with the action of detergents and form precipitates with soap. In Section 14.6 we saw that Ca<sup>2+</sup> is often removed by precipitation as CaCO<sub>3</sub> in large-scale water softening. In individual homes Ca<sup>2+</sup>, Mg<sup>2+</sup>, and other cations are removed by **ion exchange**. An **ion-exchange resin** consists of large molecules (polymers) that have many ionic sites. A **cation-exchange resin** is represented schematically in Fig. 19.7(a), showing Na<sup>+</sup> ions bound ionically to the SO<sub>3</sub><sup>-</sup> groups that are covalently attached to the resin polymer. When hard water is passed over the resin, Ca<sup>2+</sup> and Mg<sup>2+</sup> bind to the resin in place of Na<sup>+</sup>, which is released into the solution [Fig. 19.7(b)]. Replacing Mg<sup>2+</sup> and Ca<sup>2+</sup> by Na<sup>+</sup> [Fig. 19.7(c)] “softens” the water because the sodium ions interfere much less with the action of soaps and detergents.

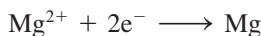
### Sample Exercise 19.2

### Electrolytic Production of Magnesium

Calculate the amount of time required to produce  $1.00 \times 10^3$  kg of magnesium metal by the electrolysis of molten MgCl<sub>2</sub> using a current of  $1.00 \times 10^2$  A.

#### Solution

The reaction for plating magnesium is



which means that 2 moles of electrons are required for each mole of Mg produced. The number of moles of magnesium in  $1.00 \times 10^3$  kg is

$$1.00 \times 10^3 \text{ kg} \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{1 \text{ mol Mg}}{24.31 \text{ g}} = 4.11 \times 10^4 \text{ mol Mg}$$

Thus

$$\frac{2 \text{ mol e}^-}{1 \text{ mol Mg}} \times 4.11 \times 10^4 \text{ mol Mg} = 8.22 \times 10^4 \text{ mol e}^-$$

Using the faraday ( $96,485 \text{ C/mol e}^-$ ), we can calculate the coulombs of charge:

$$8.22 \times 10^4 \text{ mol e}^- \times \frac{96,485 \text{ C}}{\text{mol e}^-} = 7.93 \times 10^9 \text{ C}$$

Since an ampere is a coulomb of charge per second, we can now calculate the time required:

$$\frac{7.93 \times 10^9 \text{ C}}{1.00 \times 10^2 \text{ C/s}} = 7.93 \times 10^7 \text{ s} \quad \text{or} \quad 918 \text{ days}$$

*See Exercises 19.29 and 19.30.*

## 19.5 The Group 3A Elements

3A	
B	
Al	
Ga	
In	
Tl	

The Group 3A elements (valence-electron configuration  $ns^2np^1$ ) generally show the increase in metallic character in going down the group that is characteristic of the representative elements. Some physical properties, sources, and methods of preparation for the Group 3A elements are summarized in Table 19.9.

*Boron* is a nonmetal, and most of its compounds are covalent. The most interesting compounds of boron are the covalent hydrides called **boranes**. We might expect  $\text{BH}_3$  to be the simplest hydride, since boron has three valence electrons to share with three hydrogen atoms. However, this compound is unstable, and the simplest known member of the series is diborane ( $\text{B}_2\text{H}_6$ ), with the structure shown in Fig. 19.8(a). In this molecule the terminal B—H bonds are normal covalent bonds, each involving one electron pair. The bridging bonds are three-center bonds using a single pair of electrons to bond all three atoms. Another interesting borane contains the square pyramidal  $\text{B}_5\text{H}_9$  molecule [Fig. 19.8(b)], which has four three-center bonds around the base of the pyramid. Because the boranes are extremely electron-deficient, they are highly reactive. The boranes react very exothermically with oxygen and were once evaluated as potential fuels for rockets in the U.S. space program.

*Aluminum*, the most abundant metal on earth, has metallic physical properties, such as high thermal and electrical conductivities and a lustrous appearance, but its bonds to nonmetals are significantly covalent. This covalency is responsible for the amphoteric

**TABLE 19.9 Selected Physical Properties, Sources, and Methods of Preparation for the Group 3A Elements**

Element	Radius of $\text{M}^{3+}$ (pm)	Ionization Energy (kJ/mol)	$\varnothing^\circ (\text{V})$ for $\text{M}^{3+} + 3\text{e}^- \rightarrow \text{M}$	Sources	Method of Preparation
Boron	20	798	—	Kernite, a form of borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ )	Reduction by $\text{Mg}$ or $\text{H}_2$
Aluminum	51	581	−1.71	Bauxite ( $\text{Al}_2\text{O}_3$ )	Electrolysis of $\text{Al}_2\text{O}_3$ in molten $\text{Na}_3\text{AlF}_6$
Gallium	62	577	−0.53	Traces in various minerals	Reduction with $\text{H}_2$ or electrolysis
Indium	81	556	−0.34	Traces in various minerals	Reduction with $\text{H}_2$ or electrolysis
Thallium	95	589	0.72	Traces in various minerals	Electrolysis



## CHEMICAL IMPACT

### Boost Your Boron

**E**veryone realizes that the body needs protein, carbohydrates, vitamins, and even fat. The importance of several trace elements in our diet, however, is often poorly understood. An example is the element boron. People in the United States have a relatively low intake of boron. For example, the U.S. population consumes a little more than 1 mg of boron per day, which is about 10% less than people living in Great Britain and Egypt and about 35% less than people in Germany and Mexico.

To study the importance of boron intake, Zuo-Fen Zhang and his colleagues in the School of Public Health at the University of California–Los Angeles examined nutrition data collected from thousands of men and women who filled out the National Health and Nutrition Examination Survey (NHANES). Zhang and his coworkers learned that

boron seems to protect against prostate cancer. Comparing the diets of men with prostate cancer to those without the disease indicated a strong correlation between boron consumption and the absence of the disease. The prostate cancer risk for men eating at least 1.8 mg boron per day was only one-third that of men who consumed less than 0.9 mg boron per day. The data show that boron offers no apparent protection for other types of cancer, just very specific protection for prostate cancer. Other studies involving animals indicate that boron consumption can furnish protection against autoimmune diseases such as rheumatoid arthritis.

Although boron intake in the neighborhood of 3.0 mg/day seems beneficial, large amounts of boron can be toxic. The best way to obtain extra boron in your diet is by consuming foods such as nuts and noncitrus fruits.



Gallium metal has such a low melting point (30°C) that it melts from the heat of a hand.

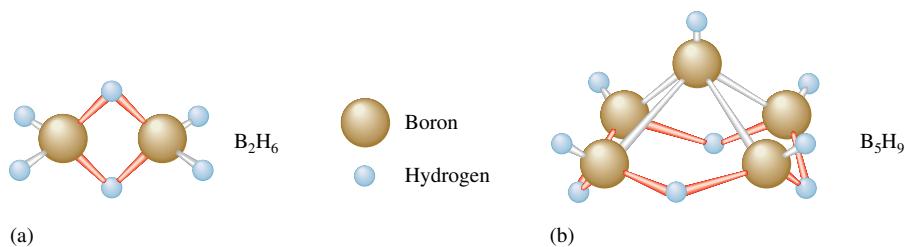
nature of  $\text{Al}_2\text{O}_3$ , which dissolves in acidic or basic solution, and for the acidity of  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  (see Section 14.8):



One especially interesting property of gallium is its unusually low melting point at 29.8°C, which is in contrast to the 660°C melting point of aluminum. Gallium's boiling point is approximately 2400°C. This gives gallium the largest liquid range of any metal, which makes it useful for thermometers, especially to measure high temperatures. Gallium, like water, expands when it freezes. The chemistry of gallium is quite similar to that of aluminum. For example,  $\text{Ga}_2\text{O}_3$  is amphoteric.

Table 19.10 summarizes some important reactions of the Group 3A elements.

The practical importance of the Group 3A elements centers on aluminum. Since the discovery of the electrolytic production process by Hall and Heroult (see Section 17.8), aluminum has become a highly important structural material in a wide variety of applications from aircraft bodies to bicycle components. Aluminum is especially valuable because it has a high strength-to-weight ratio and because it protects itself from corrosion by developing a tough, adherent oxide coating.



**FIGURE 19.8**

(a) The structure of  $\text{B}_2\text{H}_6$  with its two three-center B—H—B bridging bonds and four “normal” B—H bonds. (b) The structure of  $\text{B}_5\text{H}_9$ . There are five “normal” B—H bonds to terminal hydrogens and four three-center bridging bonds around the base.



Aluminum is used in airplane construction.

**TABLE 19.10 Selected Reactions of the Group 3A Elements**

Reaction	Comment
$2M + 3X_2 \rightarrow 2MX_3$	$X_2$ = any halogen molecule; Tl gives $TlX$ as well, but no $TlI_3$
$4M + 3O_2 \rightarrow 2M_2O_3$	High temperatures; Tl gives $Tl_2O$ as well
$2M + 3S \rightarrow M_2S_3$	High temperatures; Tl gives $Tl_2S$ as well
$2M + N_2 \rightarrow 2MN$	M = Al only
$2M + 6H^+ \rightarrow 2M^{3+} + 3H_2$	M = Al, Ga, or In; Tl gives $Tl^+$
$2M + 2OH^- + 6H_2O \rightarrow 2M(OH)_4^- + 3H_2$	M = Al or Ga

## 19.6 The Group 4A Elements

4A

C

Si

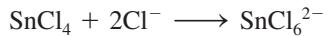
Ge

Sn

Pb

Group 4A (with the valence-electron configuration  $ns^2np^2$ ) contains two of the most important elements on earth: carbon, the fundamental constituent of the molecules necessary for life, and silicon, which forms the basis of the geologic world. The change from nonmetallic to metallic properties seen in Group 3A is also apparent in going down Group 4A from carbon, a typical nonmetal, to silicon and germanium, usually considered semimetals, to the metals tin and lead. Table 19.11 summarizes some physical properties, sources, and methods of preparation for the elements in this group.

All the Group 4A elements can form four covalent bonds to nonmetals—for example,  $CH_4$ ,  $SiF_4$ ,  $GeBr_4$ ,  $SnCl_4$ , and  $PbCl_4$ . In each of these tetrahedral molecules, the central atom is described as  $sp^3$  hybridized by the localized electron model. All these compounds, except those of carbon, can react with Lewis bases to form two additional covalent bonds. For example,  $SnCl_4$ , which is a fuming liquid ( $bp = 114^\circ C$ ), can add two chloride ions:



Carbon compounds cannot react in this way because of the small atomic size of carbon and because there are no  $d$  orbitals on carbon to accommodate the extra electrons, as there are on the other elements in the group.

**TABLE 19.11 Selected Physical Properties, Sources, and Methods of Preparation for the Group 4A Elements**

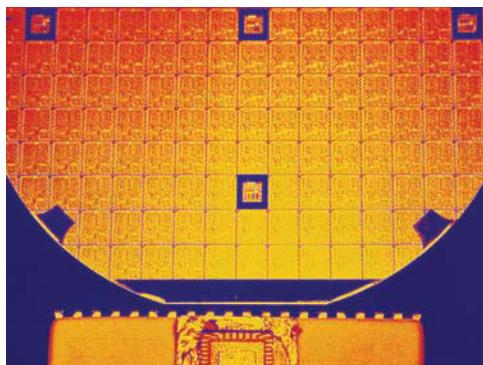
Element	Electronegativity	Melting Point (°C)	Boiling Point (°C)	Sources	Method of Preparation
Carbon	2.5	3727 (sublimes)	—	Graphite, diamond, petroleum, coal	—
Silicon	1.8	1410	2355	Silicate minerals, silica	Reduction of $K_2SiF_6$ with Al, or reduction of $SiO_2$ with Mg
Germanium	1.8	937	2830	Germanite (mixture of copper, iron, and germanium sulfides)	Reduction of $GeO_2$ with $H_2$ or C
Tin	1.8	232	2270	Cassiterite ( $SnO_2$ )	Reduction of $SnO_2$ with C
Lead	1.9	327	1740	Galena ( $PbS$ )	Roasting of $PbS$ with $O_2$ to form $PbO_2$ and then reduction with C

Although graphite is thermodynamically more stable than diamond, the transformation of diamond to graphite is not observed under normal conditions.

Fullerenes have been discovered recently by geologists in ancient rocks in Russia.

**TABLE 19.12 Strengths of C—C, Si—Si, and Si—O Bonds**

Bond	Bond Energy (kJ/mol)
C—C	347
Si—Si	340
Si—O	452

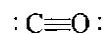


(top) A processed silicon wafer with (bottom) a silicon microchip.

We have seen that carbon also differs markedly from the other members of Group 4A in its ability to form  $\pi$  bonds. This accounts for the completely different structures and properties of  $CO_2$  and  $SiO_2$ . Note from Table 19.12 that C—C bonds and Si—O bonds are stronger than Si—Si bonds. This partly explains why the chemistry of carbon is dominated by C—C bonds, whereas that of silicon is dominated by Si—O bonds.

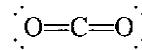
Carbon occurs in the earth's crust mainly in two allotropic forms—graphite and diamond. In addition, new forms of elemental carbon, including buckminsterfullerene ( $C_{60}$ ) and other related substances, have recently been characterized. The structures of graphite and diamond are given in Section 10.5.

Carbon monoxide ( $CO$ ), one of three oxides of carbon, is an odorless, colorless, and toxic gas formed as a by-product of the combustion of carbon-containing compounds when there is a limited oxygen supply. Incidents of carbon monoxide poisoning are especially common in the winter in cold areas of the world when blocked furnace vents limit the availability of oxygen. The bonding in carbon monoxide, which has the Lewis structure

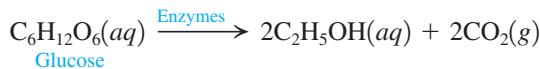


is described in terms of  $sp$  hybridized carbon and oxygen atoms that interact to form one  $\sigma$  and two  $\pi$  bonds.

Carbon dioxide, a linear molecule with the Lewis structure



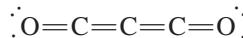
has an  $sp$  hybridized carbon atom, and is a product of human and animal respiration and of the combustion of fossil fuels. It is also produced by fermentation, a process by which the sugar in fruits and grains is changed to ethanol ( $C_2H_5OH$ ) and carbon dioxide (see Section 22.4):



Carbon dioxide dissolves in water to produce an acidic solution:



Carbon suboxide, the third carbon oxide, is a linear molecule with the Lewis structure



which contains  $sp$  hybridized carbon atoms.



## CHEMICAL IMPACT

### Concrete Learning

**C**oncrete has literally paved the way for civilization. Over the past 5000 years, tracing its roots to the ancient Egyptians. At a cost of about a penny per pound, concrete is ubiquitous in today's world—used in houses, factories, roads, dams, cooling towers, pipes, skyscrapers, and countless other places. In the United States alone there are an estimated \$6 trillion worth of concrete-based structures.

Most concretes are based on Portland cement, patented in 1824 by an English bricklayer named J. Aspdin and so named because it forms a product that resembles the natural limestone on the Isle of Portland in England. Portland cement is a powder containing a mixture of calcium silicates [ $\text{Ca}_2\text{SiO}_4$  (26%) and  $\text{Ca}_3\text{SiO}_5$  (51%)], calcium aluminate [ $\text{Ca}_3\text{Al}_2\text{O}_6$  (11%)], and calcium iron aluminate [ $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$  (1%)]. Portland cement is made from a mixture of limestone, sand, shale, clay, and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). When the cement is mixed with sand, gravel, and water, it turns into a muddy substance that eventually hardens into the familiar concrete that finds so many uses in our world. The hardening of concrete occurs not through drying but through hydration. The material becomes dry and hard as the water is consumed in building the complex silicate structures present in cured concrete. Although many of the details of this process are poorly understood, the main “glue” that holds the components of concrete together is calcium silicate hydrate, which forms a three-dimensional network mainly responsible for concrete's strength.

Despite its strength when newly produced, concrete contains pockets of air and water dispersed throughout,

making it porous and subject to deterioration. Thus, despite all the advantages of concrete, it cracks and deteriorates seriously over time.

Much research is now being carried out to improve the durability of concrete. Most of these efforts are directed toward lowering the porosity of concrete and making it less brittle. One group of additives aimed at solving this problem consists of molecules with carbon atom backbones that have sulfate groups attached. These so-called superplasticizers allow the formation of concrete using much less water, and these chemicals have doubled the strength of ready-mix concrete over the past 20 years.

Researchers also have found that the properties of concrete can be greatly improved by adding fibers of various kinds, including those made of steel, glass, and carbon-based polymers. One type of fiber concrete—called *slurry infiltrated fiber concrete* (SIFCON), which is tough enough to be used to make missile silos and can be formed into complex shapes—may be especially useful for structures in earthquake-prone areas.

Other efforts to improve concrete center on replacing Portland cement with other binders such as carbon-based polymers. Although these polymer-based concretes will burn and do lose their shapes at high temperatures, they are much more resistant to the effects of water, acids, and salts than those made with Portland cement.

Despite the fact that most concrete now used is very similar to that used by the Romans to build the Pantheon, progress is being made, and revolutionary improvements may be just around the corner.

*Silicon*, the second most abundant element in the earth's crust, is a semimetal found widely distributed in silica and silicates (see Section 10.5). Approximately 85% of the earth's crust is composed of these substances. Although silicon is found in some steel and aluminum alloys, its major use is in semiconductors for electronic devices (see the Chemical Impact in Section 10.5).

*Germanium*, a relatively rare element, is a semimetal used mainly in the manufacture of semiconductors for transistors and similar electronic devices.

*Tin* is a soft silvery metal that can be rolled into thin sheets (tin foil) and has been used for centuries in various alloys such as bronze (~20% Sn and ~80% Cu), solder (~33% Sn and ~67% Pb), and pewter (~85% Sn, ~7% Cu, ~6% Bi, and ~2% Sb). Tin exists as three allotropes: *white tin*, stable at normal temperatures; *gray tin*, stable at temperatures below 13.2°C; and *brittle tin*, found at temperatures above 161°C. When tin is exposed to low temperatures, it gradually changes to the powdery gray tin and crumbles away; this process is known as *tin disease*.

The compositions of these alloys vary significantly. For example, the tin content of bronze varies from 5% to 30%, and the tin content of pewter is often as high as 95%.



## CHEMICAL IMPACT

### Beethoven: Hair Is the Story

Ludwig van Beethoven, arguably the greatest composer who ever lived, led a troubled life fraught with sickness, deafness, and personality aberrations. Now we may know the source of these difficulties: lead poisoning. Scientists have recently reached this conclusion through analysis of Beethoven's hair. When Beethoven died in 1827 at age 56, many mourners took samples of the great man's hair. In fact, it was said at the time that he was practically bald by the time he was buried. The hair that was recently analyzed consisted of 582 strands—3 to 6 inches long—bought for the Center of Beethoven Studies for \$7300 in 1994 from Sotheby's auction house in London.

According to William Walsh of the Health Research Institute (HRI) in suburban Chicago, Beethoven's hair showed a lead concentration 100 times the normal levels. The scientists concluded that Beethoven's exposure to lead came as an adult, possibly from the mineral water he drank and swam in when he visited spas.

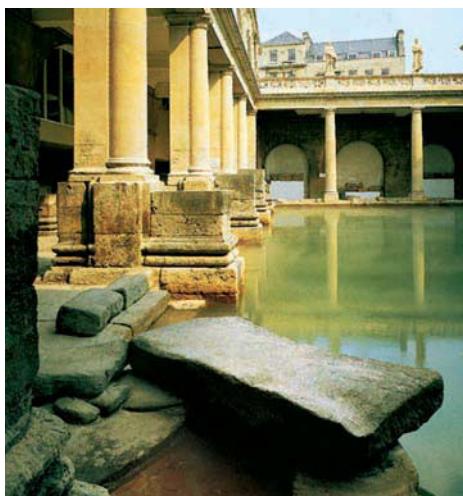
The lead poisoning may well explain Beethoven's volatile temper—the composer was subject to towering rages and sometimes had the look of a wild animal. In rare cases lead poisoning has been known to cause deafness, but the researchers remain unsure if this problem led to Beethoven's hearing loss.

According to Walsh, the scientists at HRI were originally looking for mercury, a common treatment for syphilis



Portrait of Beethoven by Josef Kari Stieler.

in the early nineteenth century, in Beethoven's hair. The absence of mercury supports the consensus of scholars that Beethoven did not have this disease. Not surprisingly, Beethoven himself wanted to know what made him so ill. In a letter to his brothers in 1802, he asked them to have doctors find the cause of his frequent abdominal pain after his death.



Roman baths such as these in Bath, England, used lead pipes for water.

The major current use for tin is as a protective coating for steel, especially for cans used as food containers. The thin layer of tin, applied electrolytically, forms a protective oxide coating that prevents further corrosion.

*Lead* is easily obtained from its ore, galena ( $PbS$ ). Because lead melts at such a low temperature, it may have been the first pure metal obtained from its ore. We know that lead was used as early as 3000 B.C. by the Egyptians and was later used by the Romans to make eating utensils, glazes on pottery, and even intricate plumbing systems. Lead is very toxic, however. In fact, the Romans had so much contact with lead that it may have contributed to the demise of their civilization. Analysis of bones from that era shows significant levels of lead.

Although lead poisoning has been known since at least the second century B.C., the incidences of this problem have been relatively isolated. However, the widespread use of tetraethyl lead,  $(C_2H_5)_4Pb$ , as an antiknock agent in gasoline increased the lead levels in our environment in the twentieth century. Concern about the effects of this lead pollution has caused the U.S. government to require the gradual replacement of the lead in gasoline with other antiknock agents. The largest commercial use of lead (about 1.3 million tons annually) is for electrodes in the lead storage batteries used in automobiles (see Section 17.5).

Table 19.13 summarizes some important reactions of the Group 4A elements.

Lead(II) oxide, known as *litharge*.**TABLE 19.13 Selected Reactions of the Group 4A Elements**

Reaction	Comment
$M + 2X_2 \rightarrow MX_4$	$X_2$ = any halogen molecule; $M$ = Ge or Sn; Pb gives $PbX_2$
$M + O_2 \rightarrow MO_2$	$M$ = Ge or Sn; high temperatures; Pb gives $PbO$ or $Pb_3O_4$
$M + 2H^+ \rightarrow M^{2+} + H_2$	$M$ = Sn or Pb

## Key Terms

### Section 19.1

representative elements  
transition metals  
lanthanides  
actinides  
metalloids (semimetals)  
metallurgy  
liquefaction

### Section 19.2

alkali metals  
superoxide

### Section 19.3

hydride  
ionic (saltlike) hydride  
covalent hydride  
metallic (interstitial) hydride

### Section 19.4

alkaline earth metals  
hard water  
ion exchange  
ion-exchange resin  
cation-exchange resin

### Section 19.5

boranes

## For Review

### Representative elements

- Chemical properties are determined by their *s* and *p* valence-electron configurations
- Metallic character increases going down the group
- The properties of the first element in a group usually differ most from the properties of the other elements in the group due to a significant difference in size
  - In Group 1A, hydrogen is a nonmetal and the other members of the group are active metals
  - The first member of a group forms the strongest  $\pi$  bonds, causing nitrogen and oxygen to exist as  $N_2$  and  $O_2$  molecules

### Elemental abundances on earth

- Oxygen is the most abundant element, followed by silicon
- The most abundant metals are aluminum and iron, which are found as ores

### Group 1A elements (alkali metals)

- Have valence configuration  $ns^1$
- Except for hydrogen, readily lose one electron to form  $M^+$  ions in their compounds with nonmetals
- React vigorously with water to form  $M^+$  and  $OH^-$  ions and hydrogen gas
- Form a series of oxides of the types  $M_2O$  (oxide),  $M_2O_2$  (peroxide), and  $MO_2$  (superoxide)
  - Not all metals form all types of oxide compounds
- Hydrogen forms covalent compounds with nonmetals
- With very active metals, hydrogen forms hydrides that contain the  $H^-$  ion

### Group 2A (alkaline earth metals)

- Have valence configuration  $ns^2$
- React less violently with water than alkali metals
- The heavier alkaline earths form nitrides and hydrides
- Hard water contains  $Ca^{2+}$  and  $Mg^{2+}$  ions
  - Form precipitates with soap
  - Usually removed by ion-exchange resins that replace the  $Ca^{2+}$  and  $Mg^{2+}$  ions with  $Na^+$

### Group 3A

- Have valence configuration  $ns^2np^1$
- Show increasing metallic character going down the group
- Boron is a nonmetal that forms many types of covalent compounds, including boranes, which are highly electron-deficient and thus are very reactive
- The metals aluminum, gallium, and indium show some covalent tendencies

**Group 4A**

- Have valence configuration  $ns^2np^2$
- Lighter members are nonmetals; heavier members are metals
  - All group members can form covalent bonds to nonmetals
- Carbon forms a huge variety of compounds, most of which are classified as organic compounds

**REVIEW QUESTIONS**

1. What are the two most abundant elements by mass in the earth's crust, oceans, and atmosphere? Does this make sense? Why? What are the four most abundant elements by mass in the human body? Does this make sense? Why?
2. What evidence supports putting hydrogen in Group 1A of the periodic table? In some periodic tables hydrogen is listed separately from any of the groups. In what ways is hydrogen unlike a typical Group 1A element?
3. What is the valence electron configuration for the alkali metals? List some common properties of alkali metals. How are the pure metals prepared? Predicting formulas for the compound formed when an alkali metal reacts with oxygen can be difficult. Why? What is the difference between an oxide, a peroxide, and a superoxide? Describe how potassium superoxide is used in a self-contained breathing apparatus. Predict the formulas of the compounds formed when an alkali metal reacts with F<sub>2</sub>, S, N<sub>2</sub>, H<sub>2</sub>, and H<sub>2</sub>O.
4. List two major industrial uses of hydrogen. Name the three types of hydrides. How do they differ from one another?
5. What is the valence electron configuration for alkaline earth metals? List some common properties of alkaline earth metals. How are alkaline earth metals prepared? What ions are found in hard water? What happens when water is "softened"?
6. Predict the formulas of the compounds formed when an alkaline earth metal reacts with F<sub>2</sub>, O<sub>2</sub>, S, N<sub>2</sub>, H<sub>2</sub>, and H<sub>2</sub>O.
7. What is the valence electron configuration for the Group 3A elements? How does metallic character change as one goes down this group? How are boron and aluminum different? Al<sub>2</sub>O<sub>3</sub> is amphoteric. What does this mean?
8. Predict the formulas of the compounds formed when aluminum reacts with F<sub>2</sub>, O<sub>2</sub>, S, and N<sub>2</sub>.
9. What is the valence electron configuration for Group 4A elements? Group 4A contains two of the most important elements on earth. What are they, and why are they so important? How does metallic character change as one goes down Group 4A? Why is the chemistry of carbon dominated by C—C bonds, whereas that of silicon is dominated by Si—O bonds? What are the two allotropic forms of carbon?
10. List some properties of germanium, tin, and lead. Predict the formulas of the compounds formed when Ge reacts with F<sub>2</sub> and O<sub>2</sub>.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

**Questions**

1. Although the earth was formed from the same interstellar material as the sun, there is little elemental hydrogen (H<sub>2</sub>) in the earth's atmosphere. Explain.
2. Many lithium salts are hygroscopic (absorb water), whereas the corresponding salts of the other alkali metals are not. Explain.
3. How do the acidities of the aqueous solutions of the alkaline earth metal ions ( $M^{2+}$ ) change in going down the group?
4. What are three-centered bonds?
5. Why is graphite a good lubricant? What advantages does it have over grease- or oil-based lubricants?
6. What are some of the structural differences between quartz and amorphous SiO<sub>2</sub>?

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7. What type of semiconductor is formed when a Group 3A element is added as an impurity to Si or Ge?
8. Diagonal relationships in the periodic table exist as well as the vertical relationships. For example, Be and Al are similar in some of their properties as are B and Si. Rationalize why these diagonal relationships hold for properties such as size, ionization energy, and electron affinity.
9. Atomic size seems to play an important role in explaining some of the differences between the first element in a group and the subsequent group elements. Explain.
10. What will be the atomic number of the next alkali metal to be discovered? How would you expect the physical properties of the next alkali metal to compare with the properties of the other alkali metals summarized in Table 19.4?
11. In most compounds, the solid phase is denser than the liquid phase. Why isn't this true for water?
12. Beryllium shows some covalent characteristics in some of its compounds, unlike the other alkaline earth halides. Give a possible explanation for this phenomenon.

### Exercises

In this section similar exercises are paired.

#### Group 1A Elements

13. Hydrogen is produced commercially by the reaction of methane with steam:
$$\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + 3\text{H}_2(g)$$

  - a. Calculate  $\Delta H^\circ$  and  $\Delta S^\circ$  for this reaction (use the data in Appendix 4).
  - b. What temperatures will favor product formation at standard conditions? Assume  $\Delta H^\circ$  and  $\Delta S^\circ$  do not depend on temperature.

14. The major industrial use of hydrogen is in the production of ammonia by the Haber process:
$$3\text{H}_2(g) + \text{N}_2(g) \rightarrow 2\text{NH}_3(g)$$

  - a. Using data from Appendix 4, calculate  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  for the Haber process reaction.
  - b. Is the reaction spontaneous at standard conditions?
  - c. At what temperatures is the reaction spontaneous at standard conditions? Assume  $\Delta H^\circ$  and  $\Delta S^\circ$  do not depend on temperature.

15. Name each of the following compounds.

- a. Li<sub>2</sub>O    b. KO<sub>2</sub>    c. Na<sub>2</sub>O<sub>2</sub>
16. Write the formula for each of the following compounds.

- a. lithium nitride    c. rubidium hydroxide
- b. potassium carbonate    d. sodium hydride

17. Complete and balance the following reactions.

- a. Li<sub>2</sub>O(s) + H<sub>2</sub>O(l) →
- b. Na<sub>2</sub>O<sub>2</sub>(s) + H<sub>2</sub>O(l) →
- c. LiH(s) + H<sub>2</sub>O(l) →
- d. KO<sub>2</sub>(s) + H<sub>2</sub>O(l) →

18. Write balanced equations describing the reaction of lithium metal with each of the following: O<sub>2</sub>, S<sub>8</sub>, Cl<sub>2</sub>, P<sub>4</sub>, H<sub>2</sub>, H<sub>2</sub>O, and HCl.

19. Lithium reacts with acetylene in liquid ammonia to produce LiC<sub>2</sub>H (lithium acetylide, LiC≡CH) and hydrogen gas. Write a balanced equation for this reaction. What type of reaction is this?

20. The electrolysis of aqueous sodium chloride (brine) is an important industrial process for the production of chlorine and sodium hydroxide. In fact, this process is the second largest consumer of electricity in the United States, after the production of aluminum. Write a balanced equation for the electrolysis of aqueous sodium chloride (hydrogen gas is also produced).

#### Group 2A Elements

21. Name each of the following compounds.

  - a. MgCO<sub>3</sub>    b. BaSO<sub>4</sub>    c. Sr(OH)<sub>2</sub>

22. Write the formula for each of the following compounds.

  - a. calcium nitride    b. beryllium chloride    c. barium hydride

23. One harmful effect of acid rain is the deterioration of structures and statues made of marble or limestone, both of which are essentially calcium carbonate. The reaction of calcium carbonate with sulfuric acid yields carbon dioxide, water, and calcium sulfate. Because calcium sulfate is marginally soluble in water, part of the object is washed away by the rain. Write a balanced chemical equation for the reaction of sulfuric acid with calcium carbonate.
24. Write balanced equations describing the reaction of Sr with each of the following: O<sub>2</sub>, S<sub>8</sub>, Cl<sub>2</sub>, P<sub>4</sub>, H<sub>2</sub>, H<sub>2</sub>O, and HCl.
25. Predict the structure of BeF<sub>2</sub> in the gas phase. What structure would you predict for BeF<sub>2</sub>(s)?
26. The beryllium atom in BeCl<sub>2</sub> is electron-deficient (only four valence electrons surround it), which makes it very reactive toward electron-pair donors such as ammonia. Draw a Lewis structure for the expected product when BeCl<sub>2</sub> reacts with excess ammonia.
27. The U.S. Public Health Service recommends the fluoridation of water as a means for preventing tooth decay. The recommended concentration is 1 mg F<sup>-</sup> per liter. The presence of calcium ions in hard water can precipitate the added fluoride. What is the maximum molarity of calcium ions in hard water if the fluoride concentration is at the USPHS recommended level? ( $K_{sp}$  for CaF<sub>2</sub> =  $4.0 \times 10^{-11}$ )
28. Slaked lime, Ca(OH)<sub>2</sub>, is used to soften hard water by removing calcium ions from hard water through the reaction



Although CaCO<sub>3</sub>(s) is considered insoluble, some of it does dissolve in aqueous solutions. Calculate the molar solubility of CaCO<sub>3</sub> in water ( $K_{sp}$  =  $8.7 \times 10^{-9}$ ).

29. What mass of barium is produced when molten BaCl<sub>2</sub> is electrolyzed by a current of  $2.50 \times 10^5$  A for 6.00 h?
30. Electrolysis of an alkaline earth metal chloride using a current of 5.00 A for 748 s deposits 0.471 g of metal at the cathode. What is the identity of the alkaline earth metal chloride?

#### Group 3A Elements

31. Write the formula for each of the following compounds.

  - a. aluminum nitride    b. gallium fluoride    c. gallium sulfide

32. Thallium and indium form +1 and +3 oxidation states when in compounds. Predict the formulas of the possible compounds between thallium and oxygen and between indium and chlorine. Name the compounds.

- 33.** Boron hydrides were once evaluated for possible use as rocket fuels. Complete and balance the following equation for the combustion of diborane.



- 34.** Elemental boron is produced by reduction of boron oxide with magnesium to give boron and magnesium oxide. Write a balanced equation for this reaction.

- 35.**  $\text{Ga}_2\text{O}_3$  is an amphoteric oxide, and  $\text{In}_2\text{O}_3$  is a basic oxide. Write equations for the reactions that illustrate these properties.

- 36.** Aluminum hydroxide is amphoteric and will dissolve in both acidic and basic solutions. Write balanced chemical equations representing each process.

- 37.** Write equations describing the reactions of Ga with each of the following:  $\text{F}_2$ ,  $\text{O}_2$ ,  $\text{S}_8$ ,  $\text{N}_2$ , and  $\text{HCl}$ .

- 38.** Write a balanced equation describing the reaction of aluminum metal with concentrated aqueous sodium hydroxide.

### Group 4A Elements

- 39.** Draw Lewis structures for  $\text{CF}_4$ ,  $\text{GeF}_4$ , and  $\text{GeF}_6^{2-}$ . Predict the molecular structure (including bond angles), and give the expected hybridization of the central atom in these three substances. Explain why  $\text{CF}_6^{2-}$  does not form.

- 40.** Carbon and sulfur form compounds with the formulas  $\text{CS}_2$  and  $\text{C}_3\text{S}_2$ . Draw Lewis structures and predict the shapes of these two compounds.

- 41.** Silicon is produced for the chemical and electronics industries by the following reactions. Give the balanced equation for each reaction.

- $\text{SiO}_2(s) + \text{C}(s) \rightarrow \text{Si}(s) + \text{CO}(g)$
- Silicon tetrachloride is reacted with very pure magnesium, producing silicon and magnesium chloride.
- $\text{Na}_2\text{SiF}_6(s) + \text{Na}(s) \rightarrow \text{Si}(s) + \text{NaF}(s)$

- 42.** Write equations describing the reactions of Sn with each of the following:  $\text{Cl}_2$ ,  $\text{O}_2$ , and  $\text{HCl}$ .

- 43.** Why are people advised not to drink hot tap water if their plumbing contains lead solder?

- 44.** Calculate the solubility of  $\text{Pb}(\text{OH})_2$  ( $K_{\text{sp}} = 1.2 \times 10^{-15}$ ) in water. Is  $\text{Pb}(\text{OH})_2$  more or less soluble in acidic solutions? Explain.

- 45.** The fermentation of glucose produces ethanol and carbon dioxide. Write a balanced equation for this reaction.

- 46.** Tin forms compounds in the +2 and +4 oxidation states. Therefore, when tin reacts with fluorine, two products are possible. Write balanced equations for the production of the two tin halide compounds and name them.

- 47.** The resistivity (a measure of electrical resistance) of graphite is  $(0.4 \text{ to } 5.0) \times 10^{-4} \text{ ohm} \cdot \text{cm}$  in the basal plane. (The basal plane is the plane of the six-membered rings of carbon atoms.) The resistivity is 0.2 to 1.0  $\text{ohm} \cdot \text{cm}$  along the axis perpendicular to the plane. The resistivity of diamond is  $10^{14}$  to  $10^{16} \text{ ohm} \cdot \text{cm}$  and is independent of direction. How can you account for this behavior in terms of the structures of graphite and diamond?

- 48.** Silicon carbide ( $\text{SiC}$ ) is an extremely hard substance. Propose a structure for  $\text{SiC}$ .

## Additional Exercises

- 49.** A 0.250-g chunk of sodium metal is cautiously dropped into a mixture of 50.0 g of water and 50.0 g of ice, both at 0°C. The reaction is



Will the ice melt? Assuming the final mixture has a specific heat capacity of  $4.18 \text{ J/g} \cdot ^\circ\text{C}$ , calculate the final temperature. The enthalpy of fusion for ice is 6.02 kJ/mol.

- 50.** One of the chemical controversies of the nineteenth century concerned the element beryllium (Be). Berzelius originally claimed that beryllium was a trivalent element (forming  $\text{Be}^{3+}$  ions) and that it gave an oxide with the formula  $\text{Be}_2\text{O}_3$ . This resulted in a calculated atomic mass of 13.5 for beryllium. In formulating his periodic table, Mendeleev proposed that beryllium was divalent (forming  $\text{Be}^{2+}$  ions) and that it gave an oxide with the formula  $\text{BeO}$ . This assumption gives an atomic mass of 9.0. In 1894, A. Combes (*Comptes Rendus* 1894, p. 1221) reacted beryllium with the anion  $\text{C}_5\text{H}_7\text{O}_2^-$  and measured the density of the gaseous product. Combes's data for two different experiments are as follows:

	I	II
Mass	0.2022 g	0.2224 g
Volume	$22.6 \text{ cm}^3$	$26.0 \text{ cm}^3$
Temperature	$13^\circ\text{C}$	$17^\circ\text{C}$
Pressure	765.2 mm Hg	764.6 mm

If beryllium is a divalent metal, the molecular formula of the product will be  $\text{Be}(\text{C}_5\text{H}_7\text{O}_2)_2$ ; if it is trivalent, the formula will be  $\text{Be}(\text{C}_5\text{H}_7\text{O}_2)_3$ . Show how Combes's data help to confirm that beryllium is a divalent metal.

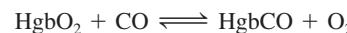
- 51.** It takes 15 kWh (kilowatt-hours) of electrical energy to produce 1.0 kg of aluminum metal from aluminum oxide by the Hall–Heroult process. Compare this to the amount of energy necessary to melt 1.0 kg of aluminum metal. Why is it economically feasible to recycle aluminum cans? (The enthalpy of fusion for aluminum metal is 10.7 kJ/mol [1 watt = 1 J/s].)

- 52.** Borazine ( $\text{B}_3\text{N}_3\text{H}_6$ ) has often been called “inorganic” benzene. Write Lewis structures for borazine. Borazine contains a six-membered ring of alternating boron and nitrogen atoms with one hydrogen bonded to each boron and nitrogen.

- 53.** Carbon monoxide is toxic because it bonds much more strongly to the iron in hemoglobin (Hgb) than does  $\text{O}_2$ . Consider the following reactions and approximate standard free energy changes:



Using these data, estimate the equilibrium constant value at  $25^\circ\text{C}$  for the following reaction:



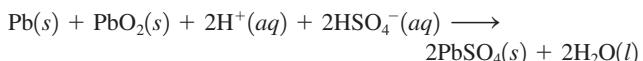
- 54.** The three most stable oxides of carbon are carbon monoxide ( $\text{CO}$ ), carbon dioxide ( $\text{CO}_2$ ), and carbon suboxide ( $\text{C}_3\text{O}_2$ ). The space-filling models for these three compounds are



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For each oxide, draw the Lewis structure, predict the molecular structure, and describe the bonding (in terms of the hybrid orbitals for the carbon atoms).

55. The overall reaction in the lead storage battery is



Calculate  $\mathcal{E}$  at 25°C for this battery when  $[\text{H}_2\text{SO}_4] = 4.5\text{ M}$ , that is,  $[\text{H}^+] = [\text{HSO}_4^-] = 4.5\text{ M}$ . At 25°C,  $\mathcal{E}^\circ = 2.04\text{ V}$  for the lead storage battery.

56. The bright yellow light emitted by a sodium vapor lamp consists of two emission lines at 589.0 and 589.6 nm. What are the frequency and the energy of a photon of light at each of these wavelengths? What are the energies in kJ/mol?

57. In the 1950s and 1960s, several nations conducted tests of nuclear warheads in the atmosphere. It was customary following each test to monitor the concentration of strontium-90 (a radioactive isotope of strontium) in milk. Why would strontium-90 tend to accumulate in milk?

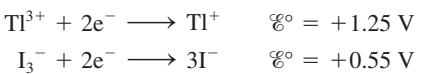
58. The compound  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  cannot be dehydrated easily by heating. It dissolves in water to give an acidic solution. Explain these observations.

59. The inert-pair effect is sometimes used to explain the tendency of heavier members of group 3A to exhibit +1 and +3 oxidation states. What does the inert-pair effect reference? Hint: Consider the valence electron configuration for group 3A elements.

60. Assume that element 113 is produced. What is the expected electron configuration for element 113?

61. Calculate the pH of a 0.050 M  $\text{Al}(\text{NO}_3)_3$  solution. The  $K_a$  value for  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  is  $1.4 \times 10^{-5}$ .

62. The compound with the formula  $\text{TlI}_3$  is a black solid. Given the following standard reduction potentials:



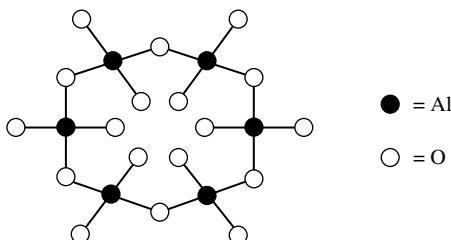
would you formulate this compound as thallium(III) iodide or thallium(I) triiodide?

63. How could you determine experimentally whether the compound  $\text{Ga}_2\text{Cl}_4$  contains two gallium(II) ions or one gallium(I) and one gallium(III) ion? Hint: Consider the electron configurations of the three possible ions.)

64. Tricalcium aluminate, an important component of Portland cement, is 44.4% calcium and 20.0% aluminum by mass. The remainder is oxygen.

a. Calculate the empirical formula of tricalcium aluminate.

b. The structure of tricalcium aluminate was not determined until 1975. The aluminate anion ( $\text{Al}_6\text{O}_{18}^{18-}$ ) has the following structure:



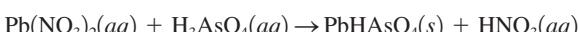
What is the molecular formula of tricalcium aluminate?

- c. How would you describe the bonding in the  $\text{Al}_6\text{O}_{18}^{18-}$  anion?

65. In Exercise 107 in Chapter 5, the pressure of  $\text{CO}_2$  in a bottle of sparkling wine was calculated assuming that the  $\text{CO}_2$  was insoluble in water. This was a bad assumption. Redo this problem by assuming  $\text{CO}_2$  obeys Henry's law. Use the data given in that problem to calculate the partial pressure of  $\text{CO}_2$  in the gas phase and the solubility of  $\text{CO}_2$  in the wine at 25°C. The Henry's law constant for  $\text{CO}_2$  is  $3.1 \times 10^{-2}\text{ mol/L} \cdot \text{atm}$  at 25°C with Henry's law in the form  $C = kP$ , where  $C$  is the concentration of the gas in mol/L.

66. The compound  $\text{Pb}_3\text{O}_4$  (red lead) contains a mixture of lead(II) and lead(IV) oxidation states. What is the mole ratio of lead(II) to lead(IV) in  $\text{Pb}_3\text{O}_4$ ?

67. Lead hydrogen arsenate, an inorganic insecticide used against the potato beetle, is produced by the following reaction:



Balance this equation.

### Challenge Problems

68. Provide a reasonable estimate for the number of atoms in an average adult human. Explain your answer. Use the information given in Table 19.2.

69. Suppose 10.00 g of an alkaline earth metal reacts with 10.0 L of water to produce 6.10 L of hydrogen gas at 1.00 atm and 25°C. Identify the metal and determine the pH of the solution.

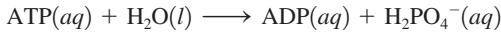
70. Gallium arsenide,  $\text{GaAs}$ , has gained widespread use in semiconductor devices that convert light and electrical signals in fiber-optic communications systems. Gallium consists of 60%  $^{69}\text{Ga}$  and 40%  $^{71}\text{Ga}$ . Arsenic has only one naturally occurring isotope,  $^{75}\text{As}$ . Gallium arsenide is a polymeric material, but its mass spectrum shows fragments with the formulas  $\text{GaAs}$  and  $\text{Ga}_2\text{As}_2$ . What would the distribution of peaks look like for these two fragments?

71. Consider dissolving 0.50 mol of  $\text{CO}_2(g)$  to enough water to make a 1.0-L solution. Determine the pH of this solution, and  $[\text{CO}_3^{2-}]$ . Use data from Appendix 5, Table 5.2.

72. a. Many biochemical reactions that occur in cells require relatively high concentrations of potassium ion ( $\text{K}^+$ ). The concentration of  $\text{K}^+$  in muscle cells is about 0.15 M. The concentration of  $\text{K}^+$  in blood plasma is about 0.0050 M. The high internal concentration in cells is maintained by pumping  $\text{K}^+$  from the plasma. How much work must be done to transport 1.0 mol of  $\text{K}^+$  from the blood to the inside of a muscle cell at 37°C (normal body temperature)?

b. When 1.0 mol of  $\text{K}^+$  is transferred from blood to the cells, do any other ions have to be transported? Why or why not?

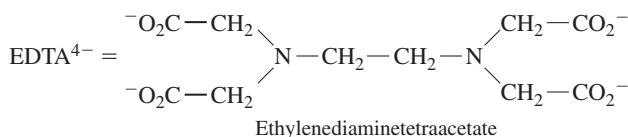
c. Cells use the hydrolysis of adenosine triphosphate, abbreviated ATP, as a source of energy. Symbolically, this reaction can be represented as



where ADP represents adenosine diphosphate. For this reaction at 37°C,  $K = 1.7 \times 10^5$ . How many moles of ATP must be hydrolyzed to provide the energy for the transport of 1.0 mol of  $\text{K}^+$ ? Assume standard conditions for the ATP hydrolysis reaction.

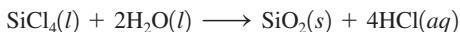
73. EDTA is used as a complexing agent in chemical analysis. Solutions of EDTA, usually containing the disodium salt  $\text{Na}_2\text{H}_2\text{EDTA}$ , are also used to treat heavy metal poisoning. The equilibrium constant for the following reaction is  $1.0 \times 10^{23}$ :





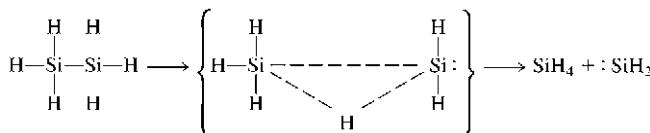
Calculate  $[\text{Pb}^{2+}]$  at equilibrium in a solution originally  $0.0010\text{ M}$  in  $\text{Pb}^{2+}$ ,  $0.050\text{ M}$  in  $\text{H}_2\text{EDTA}^{2-}$ , and buffered at  $\text{pH} = 6.00$ .

74. The compounds  $\text{CCl}_4$  and  $\text{H}_2\text{O}$  do not react with each other. On the other hand, silicon tetrachloride reacts with water according to the equation



Discuss the importance of thermodynamics and kinetics in the reactivity of water with  $\text{SiCl}_4$  as compared with its lack of reactivity with  $\text{CCl}_4$ .

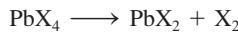
75. One reason suggested to account for the instability of long chains of silicon atoms is that the decomposition involves the transition state shown below:



The activation energy for such a process is  $210\text{ kJ/mol}$ , which is less than either the  $\text{Si}-\text{Si}$  or  $\text{Si}-\text{H}$  energy. Why would a similar mechanism not be expected to be very important in the decomposition of long carbon chains?

76. From the information on the temperature stability of white and gray tin given in this chapter, which form would you expect to have the more ordered structure?

77. Lead forms compounds in the  $+2$  and  $+4$  oxidation states. All lead(II) halides are known (and are known to be ionic). Only  $\text{PbF}_4$  and  $\text{PbCl}_4$  are known among the possible lead(IV) halides. Presumably lead(IV) oxidizes bromide and iodide ions, producing the lead(II) halide and the free halogen:



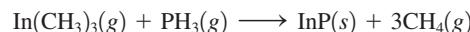
Suppose  $25.00\text{ g}$  of a lead(IV) halide reacts to form  $16.12\text{ g}$  of a lead(II) halide and the free halogen. Identify the halogen.

## Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

78. The heaviest member of the alkaline earth metals is radium (Ra), a naturally radioactive element discovered by Pierre and Marie Curie in 1898. Radium was initially isolated from the uranium ore pitchblende, in which it is present as approximately  $1.0\text{ g}$  per  $7.0\text{ metric tons}$  of pitchblende. How many atoms of radium can be isolated from  $1.75 \times 10^8\text{ g}$  of pitchblende ( $1\text{ metric ton} = 1000\text{ kg}$ )? One of the early uses of radium was as an additive to paint so that watch dials coated with this paint would glow in the dark. The longest-lived isotope of radium has a half-life of  $1.60 \times 10^3$  years. If an antique watch, manufactured in 1925, contains  $15.0\text{ mg}$  of radium, how many atoms of radium will remain in 2025?
79. Indium(III) phosphide is a semiconducting material that has been frequently used in lasers, light-emitting diodes (LED) and

fiber-optic devices. This material can be synthesized at  $900\text{ K}$  according to the following reaction:



- a. If  $2.56\text{ L}$  of  $\text{In}(\text{CH}_3)_3$  at  $2.00\text{ atm}$  is allowed to react with  $1.38\text{ L}$  of  $\text{PH}_3$  at  $3.00\text{ atm}$ , what mass of  $\text{InP}(s)$  will be produced assuming the reaction is  $87\%$  efficient?
- b. When an electric current is passed through an optoelectronic device containing InP, the light emitted has an energy of  $2.03 \times 10^{-19}\text{ J}$ . What is the wavelength of this light and is it visible to the human eye?
- c. The semiconducting properties of InP can be altered by doping. If a small number of phosphorus atoms are replaced by atoms with an electron configuration of  $[\text{Kr}]5s^24d^{10}5p^4$ , is this n-type or p-type doping?
80. The chemistry of tin(II) fluoride is particularly complex and demonstrates a wide range of reactivities. For example, in aqueous solutions of tin(II) fluoride containing sodium fluoride, the predominant species is  $\text{SnF}_3^-$ .
- a. What is the molecular geometry of  $\text{SnF}_3^-$  and the hybridization of the tin atom?
- b. When tin(II) fluoride is crystallized from aqueous solutions containing sodium fluoride, one of the products is the polyatomic cluster  $\text{Na}_4\text{Sn}_3\text{F}_{10}$ . Write a balanced chemical reaction for the formation of  $\text{Na}_4\text{Sn}_3\text{F}_{10}$  from tin(II) fluoride and NaF.
- c. Assuming complete conversion, what mass of  $\text{Na}_4\text{Sn}_3\text{F}_{10}$  can be prepared by mixing  $15.5\text{ mL}$  of  $1.48\text{ M}$  tin(II) fluoride with  $35.0\text{ mL}$  of  $1.25\text{ M}$  NaF?

## Marathon Problem

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

81. Use the symbols of the elements described in the following clues to fill in the blanks that spell out the name of a famous American scientist. Although this scientist was better known as a physicist than as a chemist, the Philadelphia institute that bears his name does include a biochemistry research facility.

(1) (2) (3) (4) (5) (6) (7)

- (1) The oxide of this alkaline earth metal is amphoteric.  
 (2) You might be surprised to learn that a binary compound of sodium with this element has the formula  $\text{NaX}_3$ , a compound used in airbags.  
 (3) This alkali metal is radioactive.  
 (4) This element is the alkali metal with the least negative standard reduction potential. Write its symbol in reverse order.  
 (5) Potash is an oxide of this alkali metal.  
 (6) This is the only alkali metal that reacts directly with nitrogen to make a binary compound with formula  $\text{M}_3\text{N}$ .  
 (7) This element is the first in Group 3A for which the  $+1$  oxidation state is exhibited in stable compounds. Use only the second letter of its symbol.



Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at [college.hmco.com/PIC/zumdahl7e](http://college.hmco.com/PIC/zumdahl7e).

# 20 The Representative Elements: Groups 5A Through 8A

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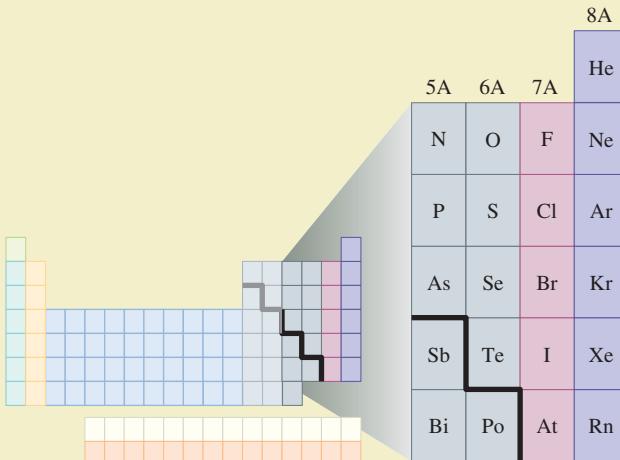


*The carnivorous pitcher plant “eats” insects to utilize the nitrogen held in the insect tissue.*

In Chapter 19 we saw that vertical groups of elements tend to show similar chemical characteristics because they have identical valence-electron configurations. Generally, metallic character increases going down a group, as the valence electrons are found farther from the nucleus. Also, recall that the most dramatic change in properties occurs after the first group member, mainly because the most dramatic change in size occurs between the first and second group members.

As we proceed from Group 1A to Group 7A, the elements change from active metals (electron donors) to strong nonmetals (electron acceptors). Thus it is not surprising that the middle groups show the most varied chemistry: Some group members behave principally as metals, others behave mainly as nonmetals, and some show both tendencies. The elements in Groups 5A and 6A show great chemical variety and form many compounds of considerable practical value. The halogens (Group 7A) are nonmetals that are also found in many everyday substances such as household bleach, photographic films, and “automatic” sunglasses. The elements in Group 8A (the noble gases) are most useful in their elemental forms, but their ability to form compounds, discovered only within the past 40 years, has provided important tests for the theories of chemical bonding.

In this chapter we give an overview of the elements in Groups 5A through 8A, concentrating on the chemistry of the most important elements in these groups: nitrogen, phosphorus, oxygen, sulfur, and the halogens.



## 20.1 The Group 5A Elements

The Group 5A elements (with the valence-electron configuration  $ns^2np^3$ ) are prepared as shown in Table 20.1, and they show remarkably varied chemical properties. As usual, metallic character increases going down the group, as is apparent from the electronegativity values (Table 20.1). *Nitrogen* and *phosphorus* are nonmetals that can gain three electrons to form 3<sup>-</sup> anions in salts with active metals—for example, magnesium nitride ( $Mg_3N_2$ ) and beryllium phosphide ( $Be_3P_2$ ). The chemistry of these two important elements is discussed in the next two sections.

5A
N
P
As
Sb
Bi

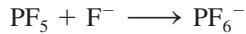
**TABLE 20.1 Selected Physical Properties, Sources, and Methods of Preparation for the Group 5A Elements**

Element	Electro-negativity	Sources	Method of Preparation
Nitrogen	3.0	Air	Liquefaction of air
Phosphorus	2.1	Phosphate rock (Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ) Fluorapatite (Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F)	2Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> + 6SiO <sub>2</sub> → 6CaSiO <sub>3</sub> + P <sub>4</sub> O <sub>10</sub>
			P <sub>4</sub> O <sub>10</sub> + 10C → 4P + 10CO
Arsenic	2.0	Arsenopyrite (Fe <sub>3</sub> As <sub>2</sub> , FeS)	Heating arsenopyrite in the absence of air
Antimony	1.9	Stibnite (Sb <sub>2</sub> S <sub>3</sub> )	Roasting Sb <sub>2</sub> S <sub>3</sub> in air to form Sb <sub>2</sub> O <sub>3</sub> and then reduction with carbon
Bismuth	1.9	Bismite (Bi <sub>2</sub> O <sub>3</sub> ), bismuth glance (Bi <sub>2</sub> S <sub>3</sub> )	Roasting Bi <sub>2</sub> S <sub>3</sub> in air to form Bi <sub>2</sub> O <sub>3</sub> and then reduction with carbon

*Bismuth* and *antimony* tend to be metallic, readily losing electrons to form cations. Although these elements have five valence electrons, so much energy is required to remove all five that no ionic compounds containing Bi<sup>5+</sup> or Sb<sup>5+</sup> ions are known. Three pentahalides (BiF<sub>5</sub>, SbCl<sub>5</sub>, and SbF<sub>5</sub>) are known, but these are molecular rather than ionic compounds.

The Group 5A elements can form molecules or ions that involve three, five, or six covalent bonds to the Group 5A atom. Examples involving three single bonds are NH<sub>3</sub>, PH<sub>3</sub>, NF<sub>3</sub>, and AsCl<sub>3</sub>. Each of these molecules has a lone pair of electrons (and thus can behave as a Lewis base) and a pyramidal shape as predicted by the VSEPR model (see Fig. 20.1).

All the Group 5A elements except nitrogen can form molecules with five covalent bonds (of general formula MX<sub>5</sub>). Nitrogen cannot form such molecules because of its small size and lack of available *d* orbitals. The MX<sub>5</sub> molecules have a trigonal bipyramidal shape (see Fig. 20.1) as predicted by the VSEPR model, and the central atom is described as *dsp*<sup>3</sup> hybridized. The MX<sub>5</sub> molecules can accept an additional electron pair to form ionic species containing six covalent bonds. An example is



where the PF<sub>6</sub><sup>-</sup> anion has an octahedral shape (see Fig. 20.1) and the phosphorus atom is described as *d*<sup>2</sup>*sp*<sup>3</sup> hybridized.

Although the MX<sub>5</sub> molecules have a trigonal bipyramidal structure in the gas phase, the solids of many of these compounds contain the ions MX<sub>4</sub><sup>+</sup> and MX<sub>6</sub><sup>-</sup> (Fig. 20.2), where the MX<sub>4</sub><sup>+</sup> cation is tetrahedral (the atom represented by M is described as *sp*<sup>3</sup> hybridized) and the MX<sub>6</sub><sup>-</sup> anion is octahedral (the atom represented by M is described as *d*<sup>2</sup>*sp*<sup>3</sup> hybridized). Examples are PCl<sub>5</sub>, which in the solid state contains PCl<sub>4</sub><sup>+</sup> and PCl<sub>6</sub><sup>-</sup>, and AsF<sub>3</sub>Cl<sub>2</sub>, which in the solid state contains AsCl<sub>4</sub><sup>+</sup> and AsF<sub>6</sub><sup>-</sup>.

As discussed in Section 19.1, the ability of the Group 5A elements to form  $\pi$  bonds decreases dramatically after nitrogen. This explains why elemental nitrogen exists as N<sub>2</sub> molecules, whereas the other elements in the group exist as larger aggregates containing single bonds. For example, in the gas phase, the elements phosphorus, arsenic, and antimony consist of P<sub>4</sub>, As<sub>4</sub>, and Sb<sub>4</sub> molecules, respectively.

**FIGURE 20.1**

The molecules of the types  $\text{MX}_3$ ,  $\text{MX}_5$ , and  $\text{MX}_6$  formed by Group 5A elements.

Molecule Type	Molecular structure	Hybridization of M
$\text{MX}_3$		 $sp^3$
$\text{MX}_5$		 $dsp^3$
$\text{MX}_6$		 $d^2sp^3$

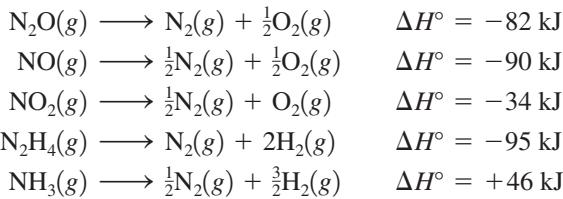
**FIGURE 20.2**

The structures of the tetrahedral  $\text{MX}_4^+$  and octahedral  $\text{MX}_6^-$  ions.

## 20.2 The Chemistry of Nitrogen

At the earth's surface, virtually all elemental nitrogen exists as the  $\text{N}_2$  molecule with its very strong triple bond (941 kJ/mol). Because of this high bond strength, the  $\text{N}_2$  molecule is so unreactive that it can coexist with most other elements under normal conditions without undergoing any appreciable reaction. This property makes nitrogen gas very useful as a medium for experiments involving substances that react with oxygen or water. Such experiments can be done using an inert-atmosphere box of the type shown in Fig. 20.3.

The strength of the triple bond in the  $\text{N}_2$  molecule is important both thermodynamically and kinetically. Thermodynamically, the great stability of the  $\text{N}\equiv\text{N}$  bond means that most binary compounds containing nitrogen decompose exothermically to the elements. For example:



Of these compounds, only ammonia is thermodynamically more stable than its component elements. That is, only for ammonia is energy required (endothermic process, positive

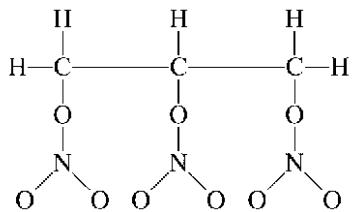


At the Centers for Disease Control and Prevention in Atlanta, Georgia, a worker checks samples stored in a liquid nitrogen tank.

value of  $\Delta H^\circ$ ) to decompose the molecule to its elements. For the remaining molecules, energy is released when decomposition to the elements occurs as a result of the great stability of  $N_2$ .

The importance of the thermodynamic stability of  $N_2$  can be seen clearly in the power of nitrogen-based explosives, such as nitroglycerin ( $C_3H_5N_3O_9$ ), which has the structure

The decomposition of nitroglycerin is a complex process that occurs in many steps. This equation only summarizes the stoichiometry of the reaction.



**FIGURE 20.3**

An inert-atmosphere box used when working with oxygen- or water-sensitive materials. The box is filled with an inert gas such as nitrogen, and work is done through the ports fitted with large rubber gloves.

When ignited or subjected to sudden impact, nitroglycerin decomposes very rapidly and exothermically:



An explosion occurs; that is, large volumes of gas are produced in a fast, highly exothermic reaction. Note that 4 moles of liquid nitroglycerin produce 29 ( $6 + 12 + 10 + 1$ ) moles of gaseous products. This alone produces a large increase in volume. However, also note that the products, including  $\text{N}_2$ , are very stable molecules with strong bonds. Their formation is therefore accompanied by the release of large quantities of energy as heat, which increases the gaseous volume. The hot, rapidly expanding gases produce a pressure surge and damaging shock wave.

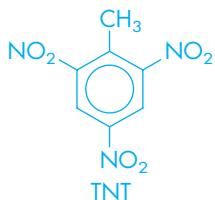
Pure nitroglycerin is quite dangerous because it explodes with little provocation. However, in 1867 the Swedish inventor Alfred Nobel found that if nitroglycerin is absorbed in porous silica, it can be handled quite safely. This tremendously important explosive (see Fig. 20.4), which he called *dynamite*, earned Nobel a great fortune, which he subsequently used to establish the Nobel Prizes.

Most high explosives are organic compounds that, like nitroglycerin, contain nitro ( $-\text{NO}_2$ ) groups and produce nitrogen and other gases as products. Another example is *trinitrotoluene*, or TNT, a solid at normal temperatures, which decomposes as follows:



Note that 2 moles of solid TNT produce 20 moles of gaseous products plus energy.

FÉUEWH



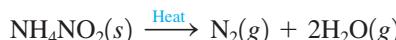
### Sample Exercise 20.1

### Decomposition of $\text{NH}_4\text{NO}_2$

When ammonium nitrite is heated, it decomposes to nitrogen gas and water. Calculate the volume of  $\text{N}_2$  gas produced from 1.00 g of solid  $\text{NH}_4\text{NO}_2$  at  $250^\circ\text{C}$  and 1.00 atm.

#### Solution

The decomposition reaction is



Using the molar mass of  $\text{NH}_4\text{NO}_2$  (64.05 g/mol), we first calculate the moles of  $\text{NH}_4\text{NO}_2$ :

$$1.00 \text{ g } \text{NH}_4\text{NO}_2 \times \frac{1 \text{ mol } \text{NH}_4\text{NO}_2}{64.05 \text{ g } \text{NH}_4\text{NO}_2} = 1.56 \times 10^{-2} \text{ mol } \text{NH}_4\text{NO}_2$$

Since 1 mol  $\text{N}_2$  is produced for each mole of  $\text{NH}_4\text{NO}_2$ ,  $1.56 \times 10^{-2}$  mol  $\text{N}_2$  will be produced in the given experiment. We can calculate the volume of  $\text{N}_2$  from the ideal gas law:

$$PV = nRT$$

In this case we have

$$P = 1.00 \text{ atm}$$

$$n = 1.56 \times 10^{-2} \text{ mol}$$

$$R = 0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol}$$

$$T = 250 + 273 = 523 \text{ K}$$

and the volume of  $\text{N}_2$  is

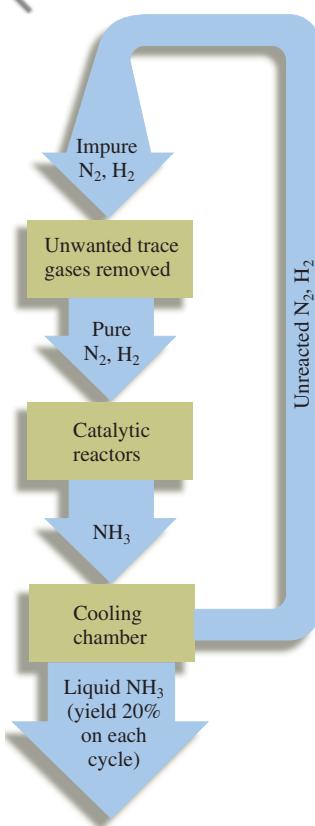
$$V = \frac{nRT}{P} = \frac{(1.56 \times 10^{-2} \text{ mol}) \left( 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \right) (523 \text{ K})}{1.00 \text{ atm}} \\ = 0.670 \text{ L}$$



**FIGURE 20.4**

Chemical explosives are used to demolish a building in Miami, Florida.

*See Exercises 20.17 and 20.18.*

**FIGURE 20.5**

A schematic diagram of the Haber process for the manufacture of ammonia.



Nodules on the roots of pea plants contain nitrogen-fixing bacteria.

The effect of bond strength on the kinetics of reactions involving the N<sub>2</sub> molecule is illustrated by the synthesis of ammonia from nitrogen and hydrogen, a reaction we have discussed many times before. Because a large quantity of energy is required to disrupt the N≡N bond, the ammonia synthesis reaction has a negligible rate at room temperature, even though the equilibrium constant is very large ( $K \approx 10^6$ ) at 25°C. Of course, the most direct way to increase the rate is to raise the temperature, but since the reaction is very exothermic, that is,



the value of  $K$  decreases significantly with a temperature increase (at 500°C,  $K \approx 10^{-2}$ ).

Obviously, the kinetics and the thermodynamics of this reaction are in opposition. A compromise must be reached: high pressure to force the equilibrium to the right and high temperature to produce a reasonable rate. The **Haber process** for manufacturing ammonia illustrates this compromise (see Fig. 20.5). The process is carried out at a pressure of about 250 atm and a temperature of approximately 400°C. Even higher temperatures would be required except that a catalyst, consisting of a solid iron oxide mixed with small amounts of potassium oxide and aluminum oxide, is used to facilitate the reaction.

Nitrogen is essential to living systems. The problem with nitrogen is not one of supply—we are surrounded by it—but of changing it from inert N<sub>2</sub> molecules to a form usable by plants and animals. The process of transforming N<sub>2</sub> to other nitrogen-containing compounds is called **nitrogen fixation**. The Haber process is one example of nitrogen fixation. The ammonia produced can be applied to the soil as a fertilizer, since plants can readily employ the nitrogen in ammonia to make the nitrogen-containing biomolecules essential for their growth.

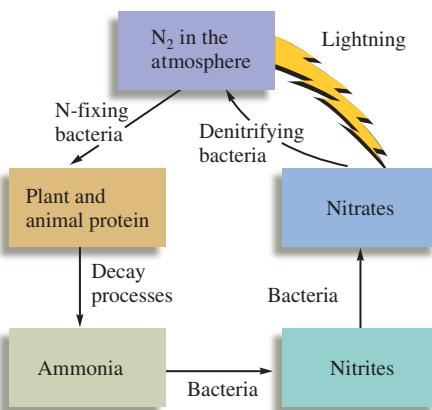
Nitrogen fixation also results from the high-temperature combustion process in automobile engines. The nitrogen in the air drawn into the engine reacts at a significant rate with oxygen to form nitric oxide (NO), which further reacts with oxygen from the air to form nitrogen dioxide (NO<sub>2</sub>). This nitrogen dioxide, which is an important contributor to photochemical smog in many urban areas (see Section 12.8), eventually reacts with moisture in the air and reaches the soil to form nitrate salts, which are plant nutrients.

Nitrogen fixation also occurs naturally. For example, lightning provides the energy to disrupt N<sub>2</sub> and O<sub>2</sub> molecules in the air, producing highly reactive nitrogen and oxygen atoms that attack other N<sub>2</sub> and O<sub>2</sub> molecules to form nitrogen oxides that eventually become nitrates. Although lightning traditionally has been credited with forming about 10% of the total fixed nitrogen, recent studies indicate that lightning may account for as much as half the fixed nitrogen available on earth. Another natural nitrogen fixation process is provided by bacteria that reside in the root nodules of plants such as beans, peas, and alfalfa. These **nitrogen-fixing bacteria** readily allow the conversion of nitrogen to ammonia and other nitrogen-containing compounds useful to plants. The efficiency of these bacteria is intriguing: They produce ammonia at soil temperature and 1 atm of pressure, whereas the Haber process requires severe conditions of 400°C and 250 atm. For obvious reasons, researchers are studying these bacteria intensively.

When plants and animals die, they decompose, and the elements they consist of are returned to the environment. In the case of nitrogen, the return of the element to the atmosphere as nitrogen gas, called **denitrification**, is carried out by bacteria that change nitrates to nitrogen. The complex **nitrogen cycle** is summarized in Fig. 20.6. It has been estimated that as much as 10 million tons per year more nitrogen is currently being fixed by natural and human processes than is being returned to the atmosphere. This fixed nitrogen is accumulating in the soil, lakes, rivers, and oceans, where it can promote the growth of algae and other undesirable organisms.

## Nitrogen Hydrides

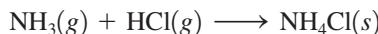
By far the most important hydride of nitrogen is **ammonia** (NH<sub>3</sub>). A toxic, colorless gas with a pungent odor, ammonia is manufactured in huge quantities (~30 billion pounds per year), mainly for use in fertilizers.

**FIGURE 20.6**

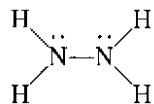
The nitrogen cycle. To be used by plants and animals, nitrogen must be converted from N<sub>2</sub> to nitrogen-containing compounds, such as nitrates, ammonia, and proteins. The nitrogen is returned to the atmosphere by natural decay processes.

The pyramidal ammonia molecule (see Fig. 20.1) has a lone pair of electrons on the nitrogen atom and polar N—H bonds. This structure leads to a high degree of intermolecular interaction by hydrogen bonding in the liquid state and produces an unusually high boiling point ( $-33.4^{\circ}\text{C}$ ) for a substance of such low molar mass. Note, however, that the hydrogen bonding in liquid ammonia is clearly not as important as that in liquid water, which has about the same molar mass but a much higher boiling point. The water molecule has two polar bonds involving hydrogen and two lone pairs—the right combination for optimal hydrogen bonding—in contrast to the one lone pair and three polar bonds of the ammonia molecule.

As we saw in Chapter 14, ammonia behaves as a base and reacts with acids to produce ammonium salts. For example,



A second nitrogen hydride of major importance is **hydrazine** (N<sub>2</sub>H<sub>4</sub>). The Lewis structure of hydrazine is

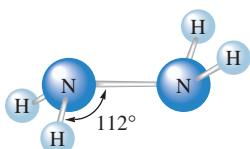


indicating that each nitrogen atom should be *sp*<sup>3</sup> hybridized with bond angles close to 109.5 degrees (the tetrahedral angle), since the nitrogen atom is surrounded by four electron pairs. The observed structure with bond angles of 112 degrees (see Fig. 20.7) agrees reasonably well with these predictions. Hydrazine, a colorless liquid with an ammonia-like odor, freezes at 2°C and boils at 113.5°C. This boiling point is quite high for a compound with a molar mass of 32 g/mol; this suggests that considerable hydrogen bonding must occur among the polar hydrazine molecules.

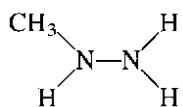
Hydrazine is a powerful reducing agent that has been used widely as a rocket propellant. For example, its reaction with oxygen is highly exothermic:



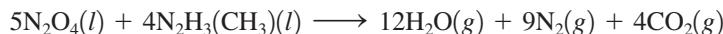
Since hydrazine also reacts vigorously with the halogens, fluorine is often used instead of oxygen as the oxidizer in rocket engines. Substituted hydrazines, where one or more of the hydrogen atoms are replaced by other groups, are also useful rocket fuels. For example, monomethylhydrazine,

**FIGURE 20.7**

The molecular structure of hydrazine (N<sub>2</sub>H<sub>4</sub>). This arrangement minimizes the repulsion between the lone pairs on the nitrogen atoms by placing them on opposite sides.



is used with the oxidizer dinitrogen tetroxide ( $\text{N}_2\text{O}_4$ ) to power the U.S. space shuttle orbiter. The reaction is

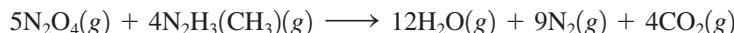


Because of the large number of gaseous molecules produced and the exothermic nature of this reaction, a very high thrust per mass of fuel is achieved. The reaction is also self-starting—it begins immediately when the fuels are mixed—which is a useful property for rocket engines that must be started and stopped frequently.

### Sample Exercise 20.2

### Heats of Reaction from Bond Energies

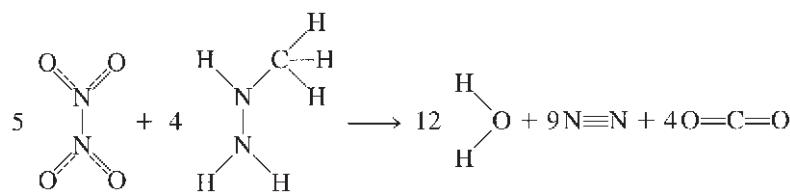
Using the bond energies in Table 8.4, calculate the approximate value of  $\Delta H$  for the reaction between gaseous monomethylhydrazine and dinitrogen tetroxide:



The bonding in  $\text{N}_2\text{O}_4$  is described by resonance structures that predict that the N—O bonds are intermediate in strength between single and double bonds (assume an average N—O bond energy of 440 kJ/mol).

#### Solution

To calculate  $\Delta H$  for this reaction, we must compare the energy necessary to break the bonds of the reactants and the energy released by formation of the bonds in the products:



Breaking bonds requires energy (positive sign), and forming bonds releases energy (negative sign). As summarized in the following table,

$$\Delta H = (21.1 \times 10^3 \text{ kJ}) - (26.1 \times 10^3 \text{ kJ}) = -5.0 \times 10^3 \text{ kJ}$$

The reaction is highly exothermic.

Bonds Broken	Energy Required (kJ/mol)	Bonds Formed	Energy Released (kJ/mol)
$5 \times 4 = 20 \text{ N}=\text{O}$	$20 \times 440 = 8.8 \times 10^3$	$12 \times 2 = 24 \text{ O—H}$	$24 \times 467 = 1.12 \times 10^4$
$5 + 4 = 9 \text{ N—N}$	$9 \times 160 = 1.4 \times 10^3$	$9 \text{ N}\equiv\text{N}$	$9 \times 941 = 8.5 \times 10^3$
$4 \times 3 = 12 \text{ N—H}$	$12 \times 391 = 4.7 \times 10^3$	$4 \times 2 = 8 \text{ C}=\text{O}$	$8 \times 799 = 6.4 \times 10^3$
$4 \times 3 = 12 \text{ C—H}$	$12 \times 413 = 5.0 \times 10^3$		
$4 \times 1 = 4 \text{ C—N}$	$4 \times 305 = 1.2 \times 10^3$		
Total	$21.1 \times 10^3$		Total $26.1 \times 10^3$

*See Exercise 20.19.*

The use of hydrazine as a rocket propellant is a rather specialized application. The main industrial use of hydrazine is as a “blowing” agent in the manufacture of plastics. Hydrazine decomposes to form nitrogen gas, which causes foaming in the liquid plastic, which results in a porous texture. Another major use of hydrazine is in the production of



Blowing agents such as hydrazine, which forms nitrogen gas on decomposition, are used to produce porous plastics like these styrofoam products.

agricultural pesticides. Of the many hundreds of hydrazine derivatives (substituted hydrazines) that have been tested, 40 are used as fungicides, herbicides, insecticides, and plant growth regulators.

The manufacture of hydrazine involves the oxidation of ammonia by the hypochlorite ion in basic solution:



Although this reaction looks straightforward, the actual process involves many steps and requires high pressure, high temperature, and catalysis to optimize the yield of hydrazine in the face of many competing reactions.

## Nitrogen Oxides

Nitrogen forms a series of oxides in which it has an oxidation state from +1 to +5, as shown in Table 20.2.

*Dinitrogen monoxide* ( $\text{N}_2\text{O}$ ), more commonly called *nitrous oxide* or “laughing gas,” has an inebriating effect and has been used as a mild anesthetic by dentists. Because of its high solubility in fats, nitrous oxide is used widely as a propellant in aerosol cans of whipped cream. It is dissolved in the liquid in the can at high pressure and forms bubbles that produce foaming as the liquid is released from the can. A significant amount of  $\text{N}_2\text{O}$  exists in the atmosphere, mostly produced by soil microorganisms, and its concentration

**TABLE 20.2 Some Common Nitrogen Compounds**

Oxidation State of Nitrogen	Compound	Formula	Lewis Structure*
-3	Ammonia	$\text{NH}_3$	$\begin{array}{c} \cdot\ddot{\text{N}}\cdot\text{H} \\   \\ \text{H} \end{array}$
-2	Hydrazine	$\text{N}_2\text{H}_4$	$\begin{array}{c} \cdot\ddot{\text{N}}\cdot\text{N}\cdots\text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$
-1	Hydroxylamine	$\text{NH}_2\text{OH}$	$\begin{array}{c} \cdot\ddot{\text{N}}\cdot\text{O}\cdots\text{H} \\   \\ \text{H} \end{array}$
0	Nitrogen	$\text{N}_2$	$:\text{N}\equiv\text{N}:$
+1	Dinitrogen monoxide (nitrous oxide)	$\text{N}_2\text{O}$	$:\ddot{\text{N}}=\text{N}=\ddot{\text{O}}:$
+2	Nitrogen monoxide (nitric oxide)	$\text{NO}$	$:\ddot{\text{N}}=\text{O}:$
+3	Dinitrogen trioxide	$\text{N}_2\text{O}_3$	$\begin{array}{c} \text{O} \quad \cdot\ddot{\text{N}}\cdots\text{N}=\text{O} \\    \quad \cdot\ddot{\text{O}} \end{array}$
+4	Nitrogen dioxide	$\text{NO}_2$	$:\ddot{\text{O}}-\text{N}=\text{O}:$
+5	Nitric acid	$\text{HNO}_3$	$:\ddot{\text{O}}-\text{N}(\text{O}-\text{H})=\text{O}:$

\*In some cases, additional resonance structures are needed to fully describe the electron distribution.

appears to be gradually increasing. Because it can strongly absorb infrared radiation, nitrous oxide plays a small but probably significant role in controlling the earth's temperature in the same way that atmospheric carbon dioxide and water vapor do (see the discussion of the greenhouse effect in Section 6.5). Some scientists fear that the rapid decrease of tropical rain forests resulting from development in countries such as Brazil will significantly affect the rate of production of  $\text{N}_2\text{O}$  by soil organisms and thus will have important effects on the earth's temperature.

In the laboratory, nitrous oxide is prepared by the thermal decomposition of ammonium nitrate:



**Do not attempt this experiment unless you have the proper safety equipment.**

*This experiment must be done carefully because ammonium nitrate can explode.* In fact, one of the greatest industrial disasters in U.S. history occurred in 1947 in Texas, when a ship loaded with ammonium nitrate for use as fertilizer exploded and killed nearly 600 people.

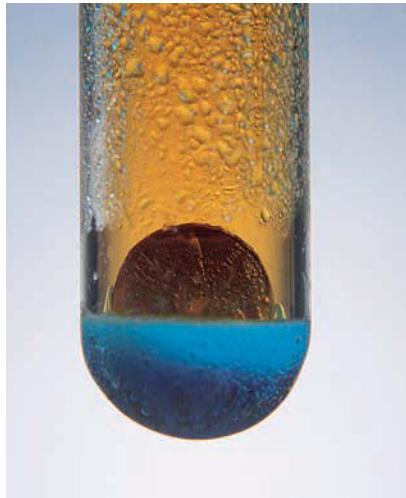
Nitrogen monoxide ( $\text{NO}$ ), commonly called *nitric oxide*, is a colorless gas under normal conditions that can be produced in the laboratory by reaction of 6 M nitric acid with copper metal:



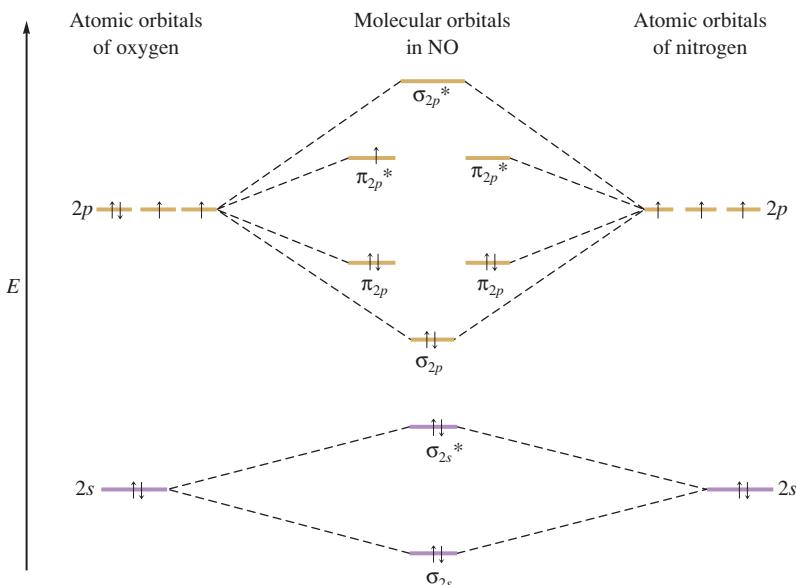
When this reaction is run in the air, the nitric oxide is immediately oxidized to brown nitrogen dioxide ( $\text{NO}_2$ ).

Although nitric oxide is toxic when inhaled, it has been shown to be produced in certain tissues of the human body, where it behaves as a neurotransmitter. Current research indicates that nitric oxide plays a role in regulating blood pressure, blood clotting, and the muscle changes that allow erection of the penis in males.

Since the NO molecule has an odd number of electrons, it is most conveniently described in terms of the molecular orbital model. The molecular orbital energy-level diagram is shown in Fig. 20.8. Note that the NO molecule is paramagnetic and should have a bond order of 2.5, a prediction that is supported by experimental observations. Since the NO molecule has one high-energy electron, it is not surprising that it can be rather easily oxidized to form  $\text{NO}^+$ , the *nitrosyl ion*. Because an antibonding electron is removed in going from NO to  $\text{NO}^+$ , the ion should have a stronger bond (the predicted bond order is 3) than the molecule. This is borne out by experiment. The bond lengths and bond



A copper penny reacts with nitric acid to produce NO gas, which is immediately oxidized in air to brown  $\text{NO}_2$ .



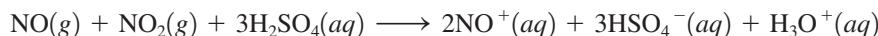
**FIGURE 20.8**

The molecular orbital energy-level diagram for nitric oxide ( $\text{NO}$ ). The bond order is 2.5, or  $(8 - 3)/2$ .

**TABLE 20.3 Comparison of the Bond Lengths and Bond Energies for Nitric Oxide and the Nitrosyl Ion**

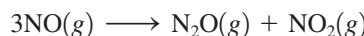
	NO	NO <sup>+</sup>
Bond length (pm)	115	109
Bond energy (kJ/mol)	630	1020
Bond order (predicted by MO model)	2.5	3

energies for nitric oxide and the nitrosyl ion are shown in Table 20.3. The nitrosyl ion is formed when nitric oxide and nitrogen dioxide are dissolved in concentrated sulfuric acid:



The ionic compound NO<sup>+</sup>HSO<sub>4</sub><sup>-</sup> can be isolated from this solution.

Nitric oxide is thermodynamically unstable and decomposes to nitrous oxide and nitrogen dioxide:



Nitrogen dioxide (NO<sub>2</sub>) is also an odd-electron molecule and has a V-shaped structure. The brown, paramagnetic NO<sub>2</sub> molecule readily dimerizes to form dinitrogen tetroxide,



which is diamagnetic and colorless. The value of the equilibrium constant is  $\sim 1$  for this process at 55°C, and since the dimerization is exothermic,  $K$  decreases as the temperature increases.

### Sample Exercise 20.3

### Molecular Orbital Description of NO<sup>-</sup>

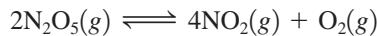
Use the molecular orbital model to predict the bond order and magnetism of the NO<sup>-</sup> ion.

#### Solution

Using the energy-level diagram for the NO molecule in Fig. 20.8, we can see that NO<sup>-</sup> has one more antibonding electron than NO. Thus there will be unpaired electrons in the two  $\pi_{2p}^*$  orbitals, and NO<sup>-</sup> will be paramagnetic with a bond order of  $(8 - 4)/2$ , or 2. Note that the bond in the NO<sup>-</sup> ion is weaker than that in the NO molecule.

*See Exercises 20.23 and 20.24.*

The least common of the nitrogen oxides are *dinitrogen trioxide* (N<sub>2</sub>O<sub>3</sub>), a blue liquid that readily dissociates into gaseous nitric oxide and nitrogen dioxide, and *dinitrogen pentoxide* (N<sub>2</sub>O<sub>5</sub>), which under normal conditions is a solid that is best viewed as a mixture of NO<sub>2</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> ions. Although N<sub>2</sub>O<sub>5</sub> molecules do exist in the gas phase, they readily dissociate to nitrogen dioxide and oxygen:



This reaction follows first-order kinetics, as was discussed in Section 12.4.

### Oxyacids of Nitrogen

**Nitric acid** is an important industrial chemical (almost 10 million tons is produced annually) used in the manufacture of many products, such as nitrogen-based explosives and ammonium nitrate for use as fertilizer.

Production of NO<sub>2</sub> by power plants and automobiles leads to smog (see Section 12.8).



## CHEMICAL IMPACT

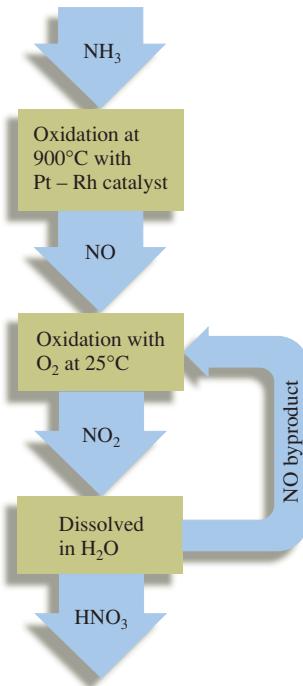
### Nitrous Oxide: Laughing Gas That Propels Whipped Cream and Cars

**N**itrous oxide ( $\text{N}_2\text{O}$ ), more properly called *dinitrogen monoxide*, is a compound with many interesting uses. It was discovered in 1772 by Joseph Priestley (who is also given credit for discovering oxygen gas), and its intoxicating effects were noted almost immediately. In 1798, the 20-year-old Humphry Davy became director of the Pneumatic Institute, which was set up to investigate the medical effects of various gases. Davy tested the effects of  $\text{N}_2\text{O}$  on himself, reporting that after inhaling 16 quarts of the gas in 7 minutes, he became “absolutely intoxicated.”

Over the next century “laughing gas,” as nitrous oxide became known, was developed as an anesthetic, particularly for dental procedures. Nitrous oxide is still used as an anesthetic, although it has been largely replaced by more modern drugs.

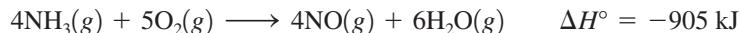
One major use of nitrous oxide today is as the propellant in cans of “instant” whipped cream. The high solubility of  $\text{N}_2\text{O}$  in the whipped cream mixture makes it an excellent candidate for pressurizing the cans of whipped cream.

Another current use of nitrous oxide is to produce “instant horsepower” for hot rods and street racers. Because the reaction of  $\text{N}_2\text{O}$  with  $\text{O}_2$  to form NO actually absorbs heat, this reaction has a cooling effect when placed in the fuel mixture in an automobile engine. This cooling effect lowers combustion temperatures, thus allowing the fuel–air mixture to be significantly more dense (the density of a gas is inversely proportional to temperature). This effect can produce a burst of additional power in excess of 200 horsepower. Because engines are not designed to run steadily at such high power levels, the nitrous oxide is injected from a tank when extra power is desired.



**FIGURE 20.9**  
The Ostwald process.

Nitric acid is produced commercially by the oxidation of ammonia in the **Ostwald process** (see Fig. 20.9). In the first step of this process, ammonia is oxidized to nitric oxide:



Although this reaction is highly exothermic, it is very slow at  $25^\circ\text{C}$ . There is also a side reaction between nitric oxide and ammonia:



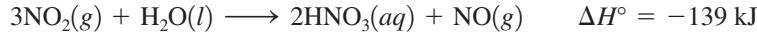
which is particularly undesirable because it traps the nitrogen as very unreactive  $\text{N}_2$  molecules. To speed up the desired reaction and minimize the effects of the competing reaction, the ammonia oxidation is carried out using a catalyst of a platinum–rhodium alloy heated to  $900^\circ\text{C}$ . Under these conditions, there is a 97% conversion of the ammonia to nitric oxide.

In the second step, nitric oxide reacts with oxygen to produce nitrogen dioxide:

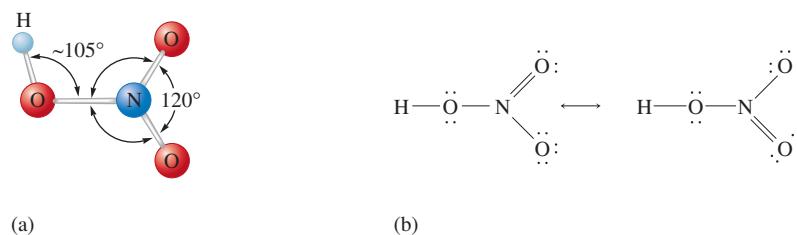


This oxidation reaction has a rate that *decreases* with increasing temperature. Because of this very unusual behavior, the reaction is carried out at  $\sim 25^\circ\text{C}$  and is kept at this temperature by cooling with water.

The third step in the Ostwald process is the absorption of nitrogen dioxide by water:



The gaseous NO produced in this reaction is recycled to be oxidized to  $\text{NO}_2$ . The aqueous nitric acid from this process is about 50%  $\text{HNO}_3$  by mass, which can be increased to 68% by distillation to remove some of the water. The maximum concentration attainable this way is 68% because nitric acid and water form an *azeotrope* at this concentration. The solution



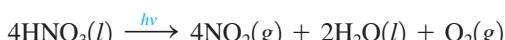
## FIGURE 20.10

- (a) The molecular structure of  $\text{HNO}_3$ .  
 (b) The resonance structures of  $\text{HNO}_3$ .

An *azeotrope* is a solution that, like a pure liquid, distills at a constant temperature without a change in composition.

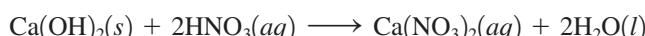
can be further concentrated to 95%  $\text{HNO}_3$  by treatment with concentrated sulfuric acid, which strongly absorbs water;  $\text{H}_2\text{SO}_4$  is often used as a dehydrating (water-removing) agent.

Nitric acid is a colorless, fuming liquid ( $\text{bp} = 83^\circ\text{C}$ ) with a pungent odor; it decomposes in sunlight via the following reaction:



As a result, nitric acid turns yellow as it ages because of the dissolved nitrogen dioxide. The common laboratory reagent known as concentrated nitric acid is 15.9 M  $\text{HNO}_3$  (70.4%  $\text{HNO}_3$  by mass) and is a very strong oxidizing agent. The resonance structures and molecular structure of  $\text{HNO}_3$  are shown in Fig. 20.10. Note that the hydrogen is bound to an oxygen atom rather than to nitrogen, as the formula suggests.

Nitric acid reacts with metal oxides, hydroxides, and carbonates and with other ionic compounds containing basic anions to form nitrate salts. For example,



Nitrate salts are generally very soluble in water.

*Nitrous acid ( $\text{HNO}_2$ ) is a weak acid.*



that forms pale yellow nitrite ( $\text{NO}_2^-$ ) salts. In contrast to nitrates, which are often used as explosives, nitrites are quite stable even at high temperatures. Nitrites are usually prepared by bubbling equal numbers of moles of nitric oxide and nitrogen dioxide into the appropriate aqueous solution of a metal hydroxide. For example,



## 20.3 The Chemistry of Phosphorus

Although phosphorus lies directly below nitrogen in Group 5A of the periodic table, its chemical properties are significantly different from those of nitrogen. The differences arise mainly from four factors: nitrogen's ability to form much stronger  $\pi$  bonds, the greater electronegativity of nitrogen, the larger size of the phosphorus atom, and the availability of empty valence  $d$  orbitals on phosphorus.

The chemical differences are apparent in the elemental forms of nitrogen and phosphorus. In contrast to the diatomic form of elemental nitrogen, which is stabilized by strong  $\pi$  bonds, there are several solid forms of phosphorus, all containing aggregates of atoms. *White phosphorus*, which contains discrete tetrahedral  $P_4$  molecules [see Fig. 20.11(a)], is very reactive and bursts into flames on contact with air (it is said to be *pyrophoric*). To prevent this, white phosphorus is commonly stored under water. White phosphorus is quite toxic, and the  $P_4$  molecules are very damaging to tissue, particularly the cartilage and bones of the nose and jaw. The much less reactive forms known as *black phosphorus* and *red phosphorus* are network solids (see Section 10.5). Black phosphorus has a regular crystalline structure [Fig. 20.11(b)], but red phosphorus is amorphous and is thought to consist of chains of  $P_4$  units [Fig. 20.11(c)]. Red phosphorus can be obtained



## Visualization: Barking Dogs: Reaction of Phosphorus



## CHEMICAL IMPACT

### Phosphorus: An Illuminating Element

The elemental form of phosphorus was discovered by accident in 1669 by German alchemist Henning Brand when he heated dried urine with sand (alchemists often investigated the chemistry of body fluids in an attempt to better understand the “stuff of life”). When Brand passed the resulting vapors through water, he was able to isolate the form of elemental phosphorus known as *white phosphorus* (contains  $P_4$  molecules). The name *phosphorus* is derived from the Latin *phos*, meaning “light,” and *phorus*, meaning “bearing.” It seems that when Brand stored the solid white phosphorus in a sealed bottle, it glowed in the dark! This effect—a glow that persists even after the light source has been removed—came to be called *phosphorescence*. Interestingly, the term phosphorescence is derived from the name of an element that really does not phosphoresce. The glow that Brand saw actually was the result of a reaction of oxygen from the air on the surface of white phosphorus. If isolated

completely from air, phosphorus does not glow in the dark after being irradiated.

After its discovery, phosphorus became quite a novelty in the seventeenth century. People would deposit a film of phosphorus on their faces and hands so that they would glow in the dark.\* This fascination was short-lived—painful, slow-healing burns result from the spontaneous reaction of phosphorus with oxygen from the air.

The greatest consumer use of phosphorus compounds concerns the chemistry of matches. Two kinds of matches are currently available—strike-anywhere matches and safety

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\*An interesting reference to white phosphorus can be found in the Sherlock Holmes mystery, *The Hound of the Baskervilles*, where a large dog was coated with white phosphorus to scare Baskerville family members to death.

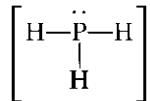
by heating white phosphorus in the absence of oxygen at 1 atm. Black phosphorus is obtained from either white or red phosphorus by heating at high pressures.

Even though phosphorus has a lower electronegativity than nitrogen, it will form phosphides (ionic substances containing the  $P^{3-}$  anion) such as  $Na_3P$  and  $Ca_3P_2$ . Phosphide salts react vigorously with water to produce *phosphine* ( $PH_3$ ), a toxic, colorless gas:

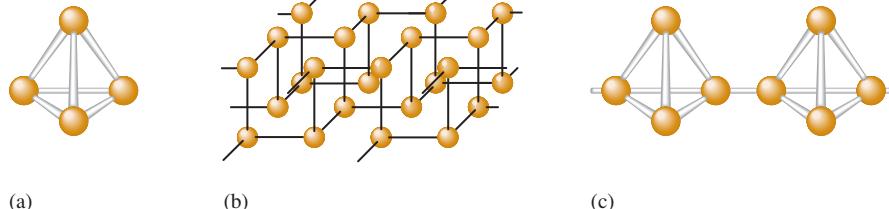


Phosphine is analogous to ammonia, although it is a much weaker base ( $K_b \approx 10^{-26}$ ) and much less soluble in water. Because phosphine has a relatively small affinity for protons, phosphonium ( $PH_4^+$ ) salts are very uncommon and not very stable—only  $PH_4I$ ,  $PH_4Cl$ , and  $PH_4Br$  are known.

Phosphine has the Lewis structure



and a pyramidal molecular structure, as we would predict from the VSEPR model. However, it has bond angles of 94 degrees, rather than 107 degrees, as found in the ammonia



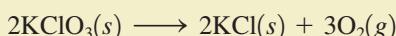
**FIGURE 20.11**

(a) The  $P_4$  molecule found in white phosphorus. (b) The crystalline network structure of black phosphorus. (c) The chain structure of red phosphorus.

matches. Both types of matches use phosphorus (in different forms) to help initiate a flame at the match head. The chemistry of matches is quite interesting. The tip of a strike-anywhere match is made from a mixture of powdered glass, binder, and tetraphosphorus trisulfide ( $P_4S_3$ ). When the match is struck, friction ignites the combustion reaction of  $P_4S_3$ :



The heat from this reaction causes an oxidizing agent such as potassium chlorate to decompose:



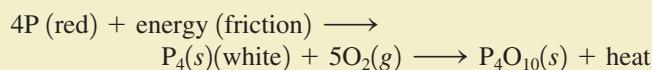
which in turn causes solid sulfur to melt and react with oxygen, producing sulfur dioxide and more heat. This then ignites a paraffin wax that helps to “light” the wooden stem of the match.

The chemistry of a safety match is quite similar, but the location of the reactants is different. The phosphorus needed to initiate all the reactions is found on the striking surface of the box. Thus, in theory, a safety match is able to ignite



The phosphorus in safety matches helps ignite the flame in the match.

only when used with the box. For a safety match, the striking surface contains red phosphorus, which is easily converted to white phosphorus by the friction of the match head on the striking surface. White phosphorus ignites spontaneously in air and generates enough heat to initiate all the other reactions to ignite the match stem.

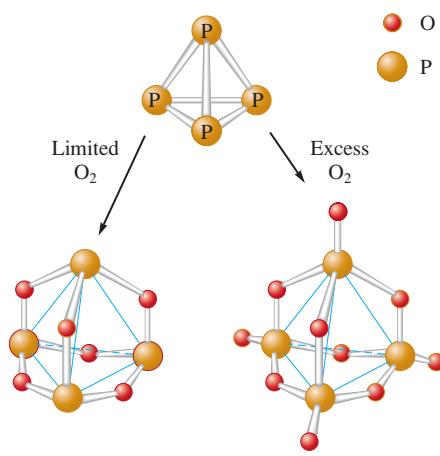


molecule. The reasons for this are complex, and we will simply regard phosphine as an exception to the simple version of the VSEPR model that we use.

## Phosphorus Oxides and Oxyacids

Phosphorus reacts with oxygen to form oxides in which it has oxidation states of +5 and +3. The oxide  $P_4O_6$  is formed when elemental phosphorus is burned in a limited supply of oxygen, and  $P_4O_{10}$  is produced when the oxygen is in excess. These oxides, as shown in Fig. 20.12, can be pictured as being constructed by adding oxygen atoms to the fundamental  $P_4$  structure. The intermediate states,  $P_4O_7$ ,  $P_4O_8$ , and  $P_4O_9$ , which contain one, two, and three terminal oxygen atoms, respectively, are also known.

The terminal oxygens are the nonbridging oxygen atoms.

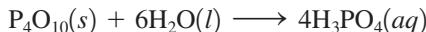


**FIGURE 20.12**

The structures of  $P_4O_6$  and  $P_4O_{10}$ .

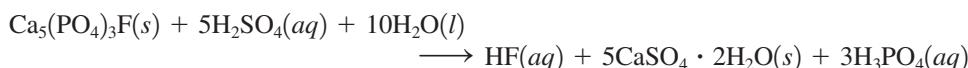
Tetraphosphorus decoxide ( $P_4O_{10}$ ), which was formerly represented as  $P_2O_5$ , has a great affinity for water and thus is a powerful dehydrating agent. For example, it can be used to convert  $HNO_3$  and  $H_2SO_4$  to their parent oxides,  $N_2O_5$  and  $SO_3$ , respectively.

When tetraphosphorus decoxide dissolves in water, **phosphoric acid** ( $H_3PO_4$ ), also called **orthophosphoric acid**, is produced:



Pure phosphoric acid is a white solid that melts at  $42^\circ C$ . Aqueous phosphoric acid is a much weaker acid ( $K_{a_1} \approx 10^{-2}$ ) than nitric acid or sulfuric acid and is a poor oxidizing agent.

Phosphate minerals are the main source of phosphoric acid. Unlike nitrogen, phosphorus is found in nature exclusively in a combined state, principally as the  $PO_4^{3-}$  ion in phosphate rock, which is mainly calcium phosphate,  $Ca_3(PO_4)_2$ , and fluorapatite,  $Ca_5(PO_4)_3F$ . Fluorapatite can be converted to phosphoric acid by grinding up the phosphate rock and forming a slurry with sulfuric acid:



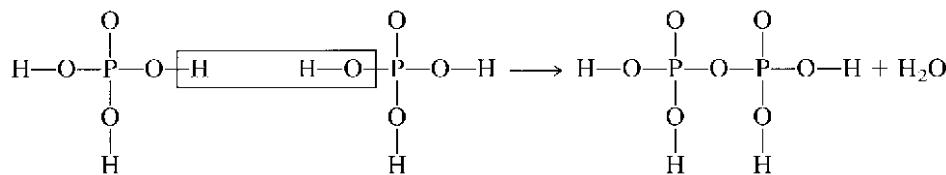
(A similar reaction can be written for the conversion of calcium phosphate.) The solid product  $CaSO_4 \cdot 2H_2O$ , called *gypsum*, is used to manufacture wallboard for the construction of buildings.

The process just described, called the *wet process*, produces only impure phosphoric acid. In another procedure, phosphate rock, sand ( $SiO_2$ ), and coke are heated in an electric furnace to form white phosphorus:

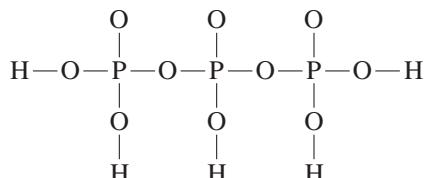


The white phosphorus obtained is burned in air to form tetraphosphorus decoxide, which is then combined with water to give phosphoric acid.

Phosphoric acid easily undergoes **condensation reactions**, where a molecule of water is eliminated in the joining of two molecules of acid:



The product ( $H_4P_2O_7$ ) is called *pyrophosphoric acid*. Further heating produces polymers, such as *tripolyphosphoric acid* ( $H_5P_3O_{10}$ ), which has the structure

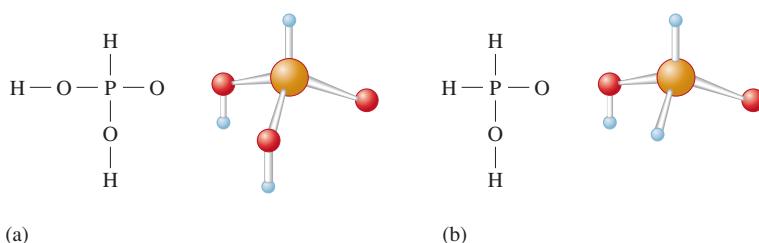


The sodium salt of tripolyphosphoric acid is widely used in detergents because the  $P_3O_{10}^{5-}$  anion can form complexes with metal ions such as  $Mg^{2+}$  and  $Ca^{2+}$ , which would otherwise interfere with detergent action.

#### Sample Exercise 20.4

#### Structure of Phosphoric Acid

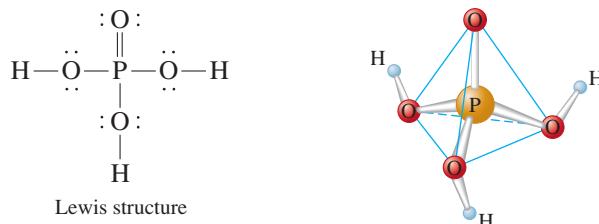
What are the molecular structure and the hybridization of the central atom of the phosphoric acid molecule?

**FIGURE 20.13**

(a) The structure of phosphorous acid (H<sub>3</sub>PO<sub>3</sub>). (b) The structure of hypophosphorous acid (H<sub>3</sub>PO<sub>2</sub>).

### Solution

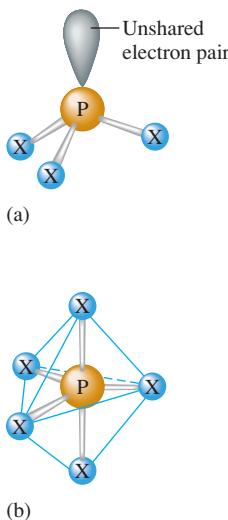
In the phosphoric acid molecule, the hydrogen atoms are attached to oxygens, and the Lewis structure is as shown below. Thus the phosphorus atom is surrounded by four effective pairs, which are arranged tetrahedrally. The atom is described as *sp*<sup>3</sup> hybridized.



*See Exercises 20.27 and 20.28.*

When P<sub>4</sub>O<sub>6</sub> is placed in water, **phosphorous acid** (H<sub>3</sub>PO<sub>3</sub>) is formed [Fig. 20.13(a)]. Although the formula suggests a triprotic acid, phosphorous acid is a *diprotic* acid. The hydrogen atom bonded directly to the phosphorus atom is not acidic in aqueous solution; only those hydrogen atoms bonded to the oxygen atoms in H<sub>3</sub>PO<sub>3</sub> can be released as protons.

A third oxyacid of phosphorus is *hypophosphorous acid* (H<sub>3</sub>PO<sub>2</sub>) [Fig. 20.13(b)], which is a monoprotic acid.

**FIGURE 20.14**

Structures of the phosphorus halides.  
(a) The PX<sub>3</sub> compounds have pyramidal molecules. (b) The gaseous and liquid phases of the PX<sub>5</sub> compounds are composed of trigonal bipyramidal molecules.

### Phosphorus in Fertilizers

Phosphorus is essential for plant growth. Although most soil contains large amounts of phosphorus, it is often present as insoluble minerals, which makes it inaccessible to plants. Soluble phosphate fertilizers are manufactured by treating phosphate rock with sulfuric acid to make **superphosphate of lime**, a mixture of CaSO<sub>4</sub> · 2H<sub>2</sub>O and Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> · H<sub>2</sub>O. If phosphate rock is treated with phosphoric acid, Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>, or *triple phosphate*, is produced. The reaction of ammonia and phosphoric acid gives *ammonium dihydrogen phosphate* (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>), a very efficient fertilizer because it furnishes both phosphorus and nitrogen.

### Phosphorus Halides

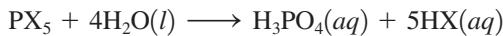
Phosphorus forms all possible halides of the general formulas PX<sub>3</sub> and PX<sub>5</sub>, with the exception of PI<sub>5</sub>. The PX<sub>3</sub> molecule has the expected pyramidal structure [Fig. 20.14(a)]. Under normal conditions of temperature and pressure, PF<sub>3</sub> is a colorless gas, PCl<sub>3</sub> is a liquid (bp = 74°C), PBr<sub>3</sub> is a liquid (bp = 175°C), and PI<sub>3</sub> is an unstable red solid (mp = 61°C). All the PX<sub>3</sub> compounds react with water to produce phosphorous acid:



In the gaseous and liquid states, the PX<sub>5</sub> compounds have molecules with a trigonal bipyramidal structure [Fig. 20.14(b)]. However, PCl<sub>5</sub> and PBr<sub>5</sub> form ionic solids: Solid

$\text{PCl}_5$  contains a mixture of octahedral  $\text{PCl}_6^-$  ions and tetrahedral  $\text{PCl}_4^+$  ions, and solid  $\text{PBr}_5$  appears to consist of  $\text{PBr}_4^+$  and  $\text{Br}^-$  ions.

The  $\text{PX}_5$  compounds react with water to form phosphoric acid:



## 20.4 The Group 6A Elements

6A
O
S
Se
Te
Po

Although in Group 6A (Table 20.4) there is the usual tendency for metallic properties to increase going down the group, none of the Group 6A elements (valence-electron configuration  $n^2np^4$ ) behaves as a typical metal. The most common chemical behavior of a Group 6A atom is to achieve a noble gas electron configuration by adding two electrons to become a 2 $-$  anion in ionic compounds with metals. In fact, for most metals, the oxides and sulfides constitute the most common minerals.

The Group 6A elements can form covalent bonds with other nonmetals. For example, they combine with hydrogen to form a series of covalent hydrides of the general formula  $\text{H}_2\text{X}$ . Those members of the group that have valence *d* orbitals available (all except oxygen) commonly form molecules in which they are surrounded by more than eight electrons. Examples are  $\text{SF}_4$ ,  $\text{SF}_6$ ,  $\text{TeI}_4$ , and  $\text{SeBr}_4$ .

In recent years there has been a growing interest in the chemistry of selenium, an element found throughout the environment in trace amounts. Selenium's toxicity has long been known, but recent medical studies have shown an *inverse* relationship between the incidence of cancer and the selenium levels in soil. It has been suggested that the resulting greater dietary intake of selenium by people living in areas of relatively high levels of selenium somehow furnishes protection from cancer. These studies are only preliminary, but selenium is known to be physiologically important (it is involved in the activity of vitamin E and certain enzymes) and selenium deficiency has been shown to be connected to the occurrence of congestive heart failure. Also of importance is the fact that selenium (along with tellurium) is a semiconductor and therefore finds some application in the electronics industry.

Polonium was discovered in 1898 by Marie and Pierre Curie in their search for the sources of radioactivity in pitchblende. Polonium has 27 isotopes and is highly toxic and very radioactive. It has been suggested that the isotope  $^{210}\text{Po}$ , a natural contaminant of tobacco and an  $\alpha$ -particle emitter (see Section 18.1), might be at least partly responsible for the incidence of cancer in smokers.

**TABLE 20.4 Selected Physical Properties, Sources, and Methods of Preparation for the Group 6A Elements**

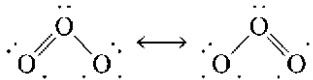
Element	Electro-negativity	Radius of $\text{X}^{2-}$ (pm)	Source	Method of Preparation
Oxygen	3.5	140	Air	Distillation from liquid air
Sulfur	2.5	184	Sulfur deposits	Melted with hot water and pumped to the surface
Selenium	2.4	198	Impurity in sulfide ores	Reduction of $\text{H}_2\text{SeO}_4$ with $\text{SO}_2$
Tellurium	2.1	221	Nagyagite (mixed sulfide and telluride)	Reduction of ore with $\text{SO}_2$
Polonium	2.0	230	Pitchblende	

## 20.5 The Chemistry of Oxygen

It is hard to overstate the importance of oxygen, the most abundant element in and near the earth's crust. Oxygen is present in the atmosphere in oxygen gas and ozone; in soil and rocks in oxide, silicate, and carbonate minerals; in the oceans in water; and in our bodies in water and in a myriad of molecules. In addition, most of the energy we need to live and to run our civilization comes from the exothermic reactions of oxygen and carbon-containing molecules.

The most common elemental form of oxygen ( $O_2$ ) constitutes 21% of the volume of the earth's atmosphere. Since nitrogen has a lower boiling point than oxygen, nitrogen can be boiled away from liquid air, leaving oxygen and small amounts of argon, another component of air. Liquid oxygen is a pale blue liquid that freezes at  $-219^{\circ}\text{C}$  and boils at  $-183^{\circ}\text{C}$ . The paramagnetism of the  $O_2$  molecule can be demonstrated by pouring liquid oxygen between the poles of a strong magnet, where it "sticks" as it boils away (see Fig. 9.40). The paramagnetism of the  $O_2$  molecule can be accounted for by the molecular orbital model (see Fig. 9.39), which also explains its bond strength.

The other form of elemental oxygen is **ozone** ( $O_3$ ), a molecule that can be represented by the resonance structures



The bond angle in the  $O_3$  molecule is 117 degrees, in reasonable agreement with the prediction of the VSEPR model (three effective pairs require a trigonal planar arrangement). That the bond angle is slightly less than 120 degrees can be explained by concluding that more space is required for the lone pair than for the bonding pairs.

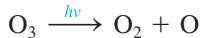
Ozone can be prepared by passing an electric discharge through pure oxygen gas. The electrical energy disrupts the bonds in some  $O_2$  molecules to give oxygen atoms, which react with other  $O_2$  molecules to form  $O_3$ . Ozone is much less stable than oxygen at  $25^{\circ}\text{C}$  and 1 atm. For example,  $K \approx 10^{-57}$  for the equilibrium



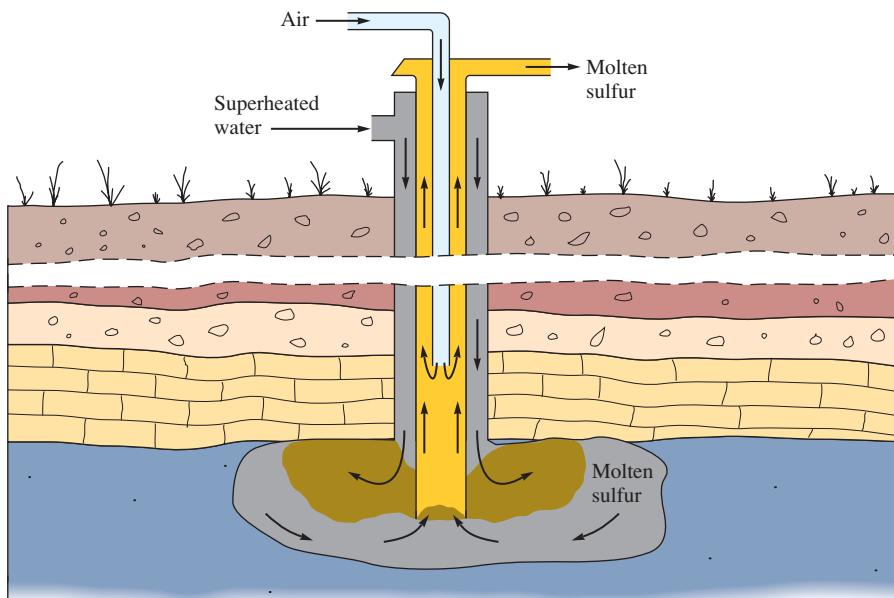
A pale blue, highly toxic gas, ozone is a much more powerful oxidizing agent than oxygen. Because of its oxidizing ability, ozone is being considered as a replacement for chlorine in municipal water purification. Chlorine leaves residues of chloro compounds, such as chloroform ( $\text{CHCl}_3$ ), which may cause cancer after long-term exposure. Although ozone effectively kills the bacteria in water, one problem with **ozonation** is that the water supply is not protected against recontamination, since virtually no ozone remains after the initial treatment. In contrast, for chlorination, significant residual chlorine remains after treatment.

The oxidizing ability of ozone can be highly detrimental, especially when it is formed in the pollution from automobile exhausts (see Section 5.10).

Ozone exists naturally in the upper atmosphere of the earth. The *ozone layer* is especially important because it absorbs ultraviolet light and thus acts as a screen to prevent this radiation, which can cause skin cancer, from penetrating to the earth's surface. When an ozone molecule absorbs this energy, it splits into an oxygen molecule and an oxygen atom:



If the oxygen molecule and atom collide, they will not stay together as ozone unless a "third body," such as a nitrogen molecule, is present to help absorb the energy released in the bond formation. The third body absorbs the energy as kinetic energy; its temperature is increased. Therefore, the energy originally absorbed as ultraviolet radiation is eventually changed to thermal energy. Thus the ozone prevents the harmful high-energy ultraviolet light from reaching the earth.

**FIGURE 20.15**

The Frasch process for recovering sulfur from underground deposits.

The scrubbing of sulfur dioxide from exhaust gases was discussed in Section 5.10.

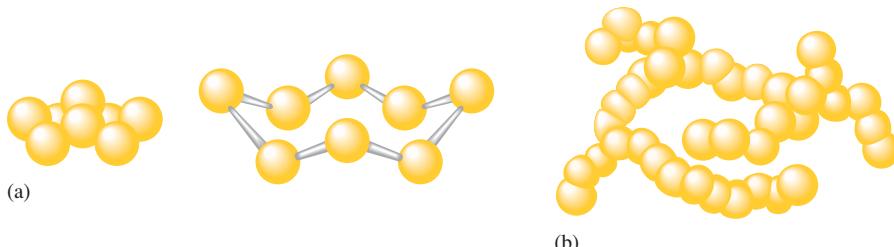
## 20.6 The Chemistry of Sulfur

Sulfur is found in nature both in large deposits of the free element and in widely distributed ores, such as galena ( $\text{PbS}$ ), cinnabar ( $\text{HgS}$ ), pyrite ( $\text{FeS}_2$ ), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), and glauberite ( $\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$ ).

About 60% of the sulfur produced in the United States comes from the underground deposits of elemental sulfur found in Texas and Louisiana. This sulfur is recovered using the **Frasch process** developed by Herman Frasch in the 1890s. Superheated water is pumped into the deposit to melt the sulfur ( $\text{mp} = 113^\circ\text{C}$ ), which is then forced to the surface by air pressure (see Fig. 20.15). The remaining 40% of sulfur produced in the United States is either a by-product of the purification of fossil fuels before combustion to prevent pollution or comes from the sulfur dioxide ( $\text{SO}_2$ ) scrubbed from the exhaust gases when sulfur-containing fuels are burned.

In contrast to oxygen, elemental sulfur exists as  $\text{S}_2$  molecules only in the gas phase at high temperatures. Because sulfur atoms form much stronger  $\sigma$  bonds than  $\pi$  bonds,  $\text{S}_2$  is less stable at  $25^\circ\text{C}$  than larger aggregates such as  $\text{S}_6$  and  $\text{S}_8$  rings and  $\text{S}_n$  chains (Fig. 20.16). The most stable form of sulfur at  $25^\circ\text{C}$  and 1 atm is called *rhombic sulfur* [see Fig. 20.17(a)], which contains stacked  $\text{S}_8$  rings. If rhombic sulfur is melted and heated to  $120^\circ\text{C}$ , it forms *monoclinic sulfur* as it cools slowly [Fig. 20.17(b)]. This form also contains  $\text{S}_8$  rings, but the rings are stacked differently than they are in rhombic sulfur.

As sulfur is heated beyond its melting point, a relatively nonviscous liquid containing  $\text{S}_8$  rings forms initially. With continued heating, the liquid becomes highly viscous as the rings first break and then link up to form long chains. Further heating lowers the viscosity

**FIGURE 20.16**

(a) The  $\text{S}_8$  molecule. (b) Chains of sulfur atoms in viscous liquid sulfur. The chains may contain as many as 10,000 atoms.



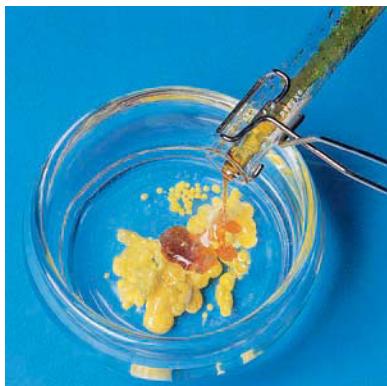
(a)



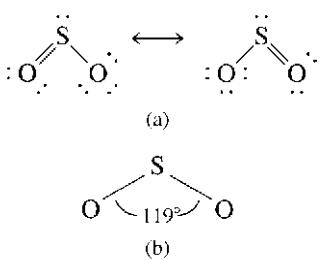
(b)

**FIGURE 20.17**

(a) Crystals of rhombic sulfur. (b) Crystals of monoclinic sulfur.



Pouring liquid sulfur into water to produce plastic sulfur.

**FIGURE 20.18**(a) Two of the resonance structures for  $\text{SO}_2$ . (b)  $\text{SO}_2$  is a bent molecule with a 119-degree bond angle, as predicted by the VSEPR model.**FIGURE 20.19**(a) Three of the resonance structures of  $\text{SO}_3$ . (b) A resonance structure with three double bonds. (c)  $\text{SO}_3$  is a planar molecule with 120-degree bond angles.

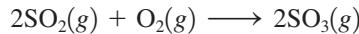
because the long chains are broken down as the energetic sulfur atoms break loose. If the liquid is suddenly cooled, a substance called *plastic sulfur*, which contains  $\text{S}_n$  chains and has rubberlike qualities, is formed. Eventually, this form reverts back to the more stable  $\text{S}_8$  rings.

### Sulfur Oxides

From its position below oxygen in the periodic table, we might expect the simplest stable oxide of sulfur to have the formula  $\text{SO}$ . However, *sulfur monoxide*, which can be produced in small amounts when gaseous sulfur dioxide ( $\text{SO}_2$ ) is subjected to an electrical discharge, is very unstable. The difference in the stabilities of the  $\text{O}_2$  and  $\text{SO}$  molecules probably reflects the stronger  $\pi$  bonding between oxygen atoms than between sulfur and oxygen atoms.

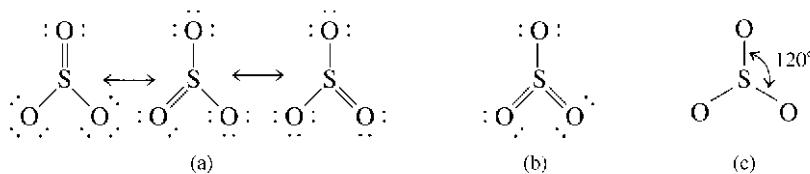
Sulfur burns in air with a bright blue flame to give *sulfur dioxide* ( $\text{SO}_2$ ), a colorless gas with a pungent odor, which condenses to a liquid at  $-10^\circ\text{C}$  and 1 atm. Sulfur dioxide is a very effective antibacterial agent and is often used to preserve stored fruit. Its structure is given in Fig. 20.18.

Sulfur dioxide reacts with oxygen to produce *sulfur trioxide* ( $\text{SO}_3$ ):



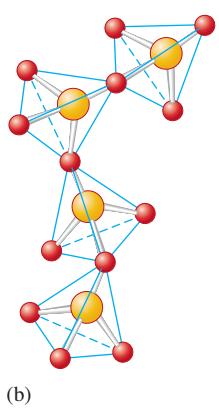
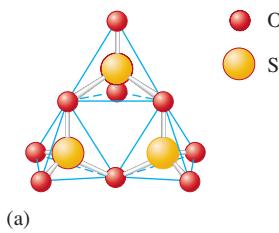
However, this reaction is very slow in the absence of a catalyst. One of the mysteries during early research on air pollution was how the sulfur dioxide produced from the combustion of sulfur-containing fuels is so rapidly converted to sulfur trioxide. It is now known that dust and other particles can act as heterogeneous catalysts for this process (see Section 12.8). In the preparation of sulfur trioxide for the manufacture of sulfuric acid, a platinum or vanadium(V) oxide ( $\text{V}_2\text{O}_5$ ) catalyst is used, and the reaction is carried out at  $\sim 500^\circ\text{C}$ , even though this temperature decreases the value of the equilibrium constant for this exothermic reaction.

The bonding in the  $\text{SO}_3$  molecule is usually described in terms of the resonance structures shown in Fig. 20.19. The molecule is trigonal planar, as predicted by the VSEPR





(left) A sulfur deposit. (right) Melted sulfur obtained from underground deposits by the Frasch process.



**FIGURE 20.20**

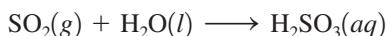
Different structures for solid  $\text{SO}_3$ . (a)  $\text{S}_3\text{O}_9$  rings. (b)  $(\text{SO}_3)_x$  chains. In both cases the sulfur atoms are surrounded by a tetrahedral arrangement of oxygen atoms.

model. Sulfur trioxide is a corrosive gas with a choking odor that forms white fumes of sulfuric acid when it reacts with moisture in the air. Thus sulfur trioxide and nitrogen dioxide, which reacts with water to form a mixture of nitrous and nitric acids, are the major culprits in the formation of acid rain.

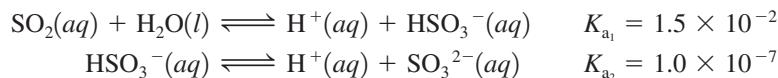
Sulfur trioxide condenses to a colorless liquid at  $44.5^\circ\text{C}$  and freezes at  $16.8^\circ\text{C}$  to give three solid forms, one containing  $\text{S}_3\text{O}_9$  rings and the other two containing  $(\text{SO}_3)_x$  chains (Fig. 20.20).

### Oxyacids of Sulfur

Sulfur dioxide dissolves in water to form an acidic solution. The reaction is often represented as

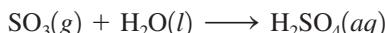


where  $\text{H}_2\text{SO}_3$  is called *sulfurous acid*. However, very little  $\text{H}_2\text{SO}_3$  actually exists in the solution. The major form of sulfur dioxide in water is  $\text{SO}_2$ , and the acid dissociation equilibria are best represented as



This situation is analogous to the behavior of carbon dioxide in water (see Section 14.7). Although  $\text{H}_2\text{SO}_3$  cannot be isolated, salts of  $\text{SO}_3^{2-}$  (*sulfites*) and  $\text{HSO}_3^-$  (*hydrogen sulfites*) are well known.

Sulfur trioxide reacts violently with water to produce the diprotic acid **sulfuric acid**:



Manufactured in greater amounts than any other chemical, sulfuric acid is usually produced by the *contact process*, which is described at the end of Chapter 3. About 60% of the sulfuric acid manufactured in the United States is used to produce fertilizers from phosphate rock (see Section 20.3). The other 40% is used in lead storage batteries and in petroleum refining, in steel manufacturing, and for various purposes in most of the chemical industries.

Because sulfuric acid has a high affinity for water, it is often used as a dehydrating agent. Gases that do not react with sulfuric acid, such as oxygen, nitrogen, and carbon dioxide, are often dried by bubbling them through concentrated solutions of the acid.



(a)



(b)

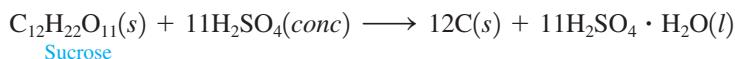


(c)

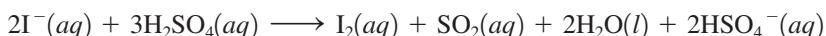
**FIGURE 20.21**

(a) A beaker of sucrose (table sugar). (b) Concentrated sulfuric acid reacts with the sucrose to produce a column of carbon (c), accompanied by an intense burnt-sugar odor.

Sulfuric acid is such a powerful dehydrating agent that it will remove hydrogen and oxygen from a substance in a 2:1 ratio even when the substance contains no molecular water. For example, concentrated sulfuric acid reacts vigorously with common table sugar (sucrose), leaving a charred mass of carbon (see Fig. 20.21):



Sulfuric acid is a moderately strong oxidizing agent, especially at high temperatures. Hot concentrated sulfuric acid oxidizes bromide or iodide ions to elemental bromine or iodine. For example,



Hot sulfuric acid attacks copper metal:



The cold acid does not react with copper.

### Other Compounds of Sulfur

Sulfur reacts with both metals and nonmetals to form a wide variety of compounds in which it has a +6, +4, +2, 0, or -2 oxidation state (see Table 20.5). The -2 oxidation state occurs in the metal sulfides and in *hydrogen sulfide* ( $\text{H}_2\text{S}$ ), a toxic, foul-smelling gas that acts as a diprotic acid when dissolved in water. Hydrogen sulfide is a strong reducing agent in aqueous solution, producing a milky-looking suspension of finely divided sulfur as one of the products. For example, hydrogen sulfide reacts with chlorine in aqueous solution as follows:



↑  
Milky suspension of sulfur

The acidic properties of sulfuric acid solutions are discussed in Section 14.7.

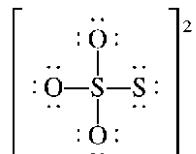
**TABLE 20.5 Common Compounds of Sulfur with Various Oxidation States**

Oxidation State of Sulfur	Compounds
+6	$\text{SO}_3$ , $\text{H}_2\text{SO}_4$ , $\text{SO}_4^{2-}$ , $\text{SF}_6$
+4	$\text{SO}_2$ , $\text{HSO}_3^-$ , $\text{SO}_3^{2-}$ , $\text{SF}_4$
+2	$\text{SCl}_2$
0	$\text{S}_8$ and all other forms of elemental sulfur
-2	$\text{H}_2\text{S}$ , $\text{S}^{2-}$

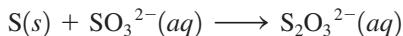
The preparation of sulfur trioxide provides an example of the compromise that often must be made between thermodynamics and kinetics.

The prefix *thio* means “sulfur.”

Sulfur also forms the **thiosulfate ion** ( $\text{S}_2\text{O}_3^{2-}$ ), which has the Lewis structure



Note that this anion can be viewed as a sulfate ion in which one of the oxygen atoms has been replaced by sulfur, which is reflected in the name *thiosulfate*. The thiosulfate ion can be formed by heating sulfur with a sulfite salt in aqueous solution:



One important use of thiosulfate ion is in photography, where  $\text{S}_2\text{O}_3^{2-}$  dissolves solid silver bromide by forming a complex with the  $\text{Ag}^+$  ion (see the Chemical Impact in Section 20.7). Thiosulfate ion is also a good reducing agent and is often used to analyze for iodine:



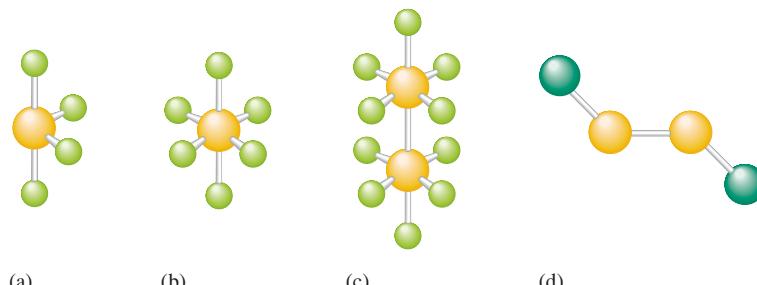
where  $\text{S}_4\text{O}_6^{2-}$  is called the *tetrathionate ion*.

Sulfur reacts with the halogens to form a variety of compounds, such as  $\text{S}_2\text{Cl}_2$ ,  $\text{SF}_4$ ,  $\text{SF}_6$ , and  $\text{S}_2\text{F}_{10}$ . The structures of these molecules are shown in Fig. 20.22.

## 20.7 The Group 7A Elements

7A
F
Cl
Br
I
At

In our coverage of the representative elements, we have progressed from groups of metallic elements (Groups 1A and 2A), through groups in which the lighter members are nonmetals and the heavier members are metals (Groups 3A, 4A, and 5A), to a group of all nonmetals (Group 6A—although some might prefer to call polonium a metal). The



**FIGURE 20.22**

The structures of (a)  $\text{SF}_4$ , (b)  $\text{SF}_6$ , (c)  $\text{S}_2\text{F}_{10}$ , and (d)  $\text{S}_2\text{Cl}_2$ .

**TABLE 20.6 Trends in Selected Physical Properties of the Group 7A Elements**

Element	Electro-negativity	Radius of $X^-$ (pm)	$\mathcal{E}^\circ$ (V) for $X_2 + 2e \rightarrow 2X^-$	Bond Energy of $X_2$ (kJ/mol)
Fluorine	4.0	136	2.87	154
Chlorine	3.0	181	1.36	239
Bromine	2.8	185	1.09	193
Iodine	2.5	216	0.54	149
Astatine	2.2	—	—	—

Group 7A elements, the **halogens** (with the valence-electron configuration  $ns^2np^5$ ), are also all nonmetals whose properties generally vary smoothly going down the group. The only notable exceptions are the unexpectedly low values for the electron affinity of fluorine and the bond energy of the  $F_2$  molecule (see Section 19.1). Table 20.6 summarizes the trends in some physical properties of the halogens.

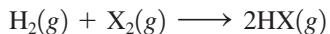
Because of their high reactivities, the halogens are not found as the free elements in nature. Instead, they are found as halide ions ( $X^-$ ) in various minerals and in seawater (see Table 20.7).

Although astatine is a member of Group 7A, its chemistry is of no practical importance because all its known isotopes are radioactive. The longest-lived isotope,  $^{210}\text{At}$ , has a half-life of only 8.3 hours.

The halogens, particularly fluorine, have very high electronegativity values (Table 20.6). They tend to form polar covalent bonds with other nonmetals and ionic bonds with metals in their lower oxidation states. When a metal ion is in a higher oxidation state, such as +3 or +4, the metal–halogen bonds are polar covalent ones. For example,  $\text{TiCl}_4$  and  $\text{SnCl}_4$  are both covalent compounds that are liquids under normal conditions.

## Hydrogen Halides

The hydrogen halides can be prepared by a reaction of the elements:



This reaction occurs with explosive vigor when fluorine and hydrogen are mixed. On the other hand, hydrogen and chlorine can coexist with little apparent reaction for relatively



Chlorine, bromine, and iodine.

**TABLE 20.7 Some Physical Properties, Sources, and Methods of Preparation for the Group 7A Elements**

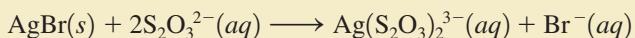
Element	Color and State	Percentage of Earth's Crust	Melting Point (°C)	Boiling Point (°C)	Sources	Method of Preparation
Fluorine	Pale yellow gas	0.07	-220	-188	Fluorospar ( $\text{CaF}_2$ ), cryolite ( $\text{Na}_3\text{AlF}_6$ ), fluorapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ )	Electrolysis of molten $\text{KHF}_2$
Chlorine	Yellow-green gas	0.14	-101	-34	Rock salt ( $\text{NaCl}$ ), halite ( $\text{NaCl}$ ), sylvite ( $\text{KCl}$ )	Electrolysis of aqueous $\text{NaCl}$
Bromine	Red-brown liquid	$2.5 \times 10^{-4}$	-7.3	59	Seawater, brine wells	Oxidation of $\text{Br}^-$ by $\text{Cl}_2$
Iodine	Violet-black solid	$3 \times 10^{-5}$	113	184	Seaweed, brine wells	Oxidation of $\text{I}^-$ by electrolysis or $\text{MnO}_2$



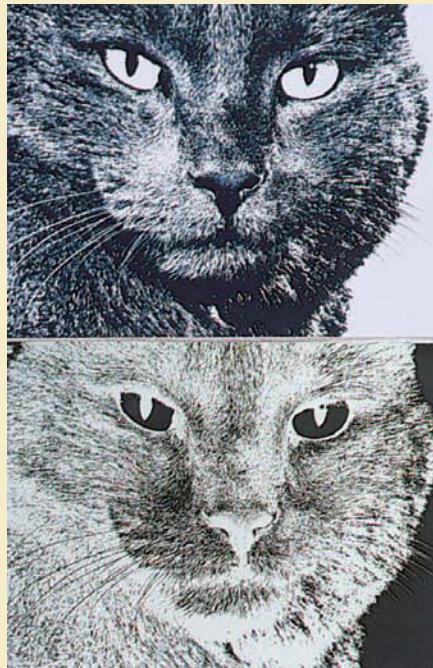
## CHEMICAL IMPACT

### Photography

In black-and-white photography, light from an object is focused onto a special paper containing an emulsion of solid silver bromide. Silver salts turn dark when exposed to light because the radiant energy stimulates the transfer of an electron to the  $\text{Ag}^+$  ion, forming an atom of elemental silver. When photographic paper (film) is exposed to light, the areas exposed to the brightest light form the most silver atoms. The next step is the application of a chemical reducing agent to the film, a process called *developing*. The real advantage of silver-based films is that the silver atoms already present from exposure to light catalyze the reduction of millions of  $\text{Ag}^+$  ions in the immediate vicinity in the developing process. Thus the effect of exposure to light is greatly intensified in this chemical reduction process. Once the image has been developed, the unchanged solid silver bromide must be removed so that the film is no longer light-sensitive and the image is fixed. A solution of sodium thiosulfate (called *hypo*) is used in this *fixing process*:



After the excess silver bromide is dissolved and washed away, the fixed image (the *negative*) is ready to produce the positive print. By shining light through the negative onto a fresh sheet of film and repeating the developing and fixing processes, a black-and-white photograph can be produced.



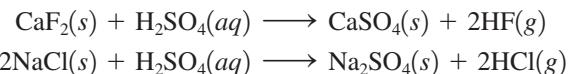
Positive and negative images.



A candle burning in an atmosphere of  $\text{Cl}_2(g)$ . The exothermic reaction, which involves breaking C—C and C—H bonds in the wax and forming C—Cl bonds in their places, produces enough heat to make the gases in the region incandescent (a flame results).

long periods in the dark. However, ultraviolet light causes an explosively fast reaction, and this is the basis of a popular lecture demonstration, the “hydrogen–chlorine cannon.” Bromine and iodine also react with hydrogen, but more slowly.

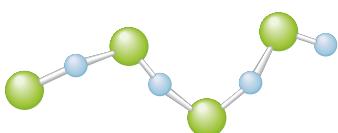
The hydrogen halides also can be prepared by treating halide salts with acid. For example, hydrogen fluoride and hydrogen chloride can be prepared as follows:



Sulfuric acid is capable of oxidizing  $\text{Br}^-$  to  $\text{Br}_2$  and  $\text{I}^-$  to  $\text{I}_2$  and so cannot be used to prepare hydrogen bromide and hydrogen iodide. However, phosphoric acid, a nonoxidizing acid, can be used to treat bromides and iodides to form the corresponding hydrogen halides.

Some physical properties of the hydrogen halides are listed in Table 20.8. Note the very high boiling point for hydrogen fluoride, which results from extensive hydrogen bonding among the very polar HF molecules (Fig. 20.23). Fluoride ion has such a high affinity for protons that in concentrated aqueous solutions of hydrogen fluoride, the ion  $[\text{F}—\text{H}—\text{F}]^-$  exists, in which an  $\text{H}^+$  ion is centered between two  $\text{F}^-$  ions.

When dissolved in water, the hydrogen halides behave as acids, and all except hydrogen fluoride are completely dissociated. Because water is a much stronger base than



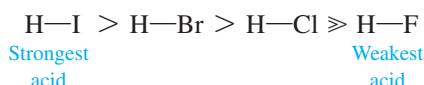
**FIGURE 20.23**

The hydrogen bonding among HF molecules in liquid hydrogen fluoride.

**TABLE 20.8 Some Physical Properties of the Hydrogen Halides**

HX	Melting Point (°C)	Boiling Point (°C)	H—X Bond Energy (kJ/mol)
HF	-83	20	565
HCl	-114	-85	427
HBr	-87	-67	363
HI	-51	-35	295

$\text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{I}^-$  ion, the acid strengths of  $\text{HCl}$ ,  $\text{HBr}$ , and  $\text{HI}$  cannot be differentiated in water. However, in a less basic solvent, such as glacial (pure) acetic acid, the acids show different strengths of the order



To see why hydrogen fluoride is the only weak acid in water among the HX molecules, let's consider the dissociation equilibrium



where

$$K_a = \frac{[H^+][X^-]}{[HX]}$$

from a thermodynamic point of view. Recall that acid strength is reflected by the magnitude of  $K_a$ —a small  $K_a$  value means a weak acid. Also recall that the value of an equilibrium constant depends on the standard free energy change for the reaction as follows:

$$\Delta G^\circ = -RT \ln(K)$$

As  $\Delta G^\circ$  becomes more negative,  $K$  becomes larger; a *decrease* in free energy favors a given reaction. As we saw in Chapter 16, free energy depends on enthalpy, entropy, and temperature. For a process at constant temperature,

$$\Delta G^\circ \equiv \Delta H^\circ - T\Delta S^\circ$$

Thus, to explain the various acid strengths of the hydrogen halides, we must focus on the factors that determine  $\Delta H^\circ$  and  $\Delta S^\circ$  for the acid dissociation reaction.

What energy terms are important in determining  $\Delta H^\circ$  for the dissociation of HX in water? (Keep in mind that large positive contributions to the value of  $\Delta H^\circ$  will tend to make  $\Delta G^\circ$  more highly positive,  $K_a$  smaller, and the acid weaker.) One important factor is certainly the H—X bond strength. Note from Table 20.8 that the H—F bond is much stronger than the other H—X bonds. This factor tends to make HF a weaker acid than the others.

Another important contribution to  $\Delta H^\circ$  is the enthalpy of hydration (see Section 11.2) of  $X^-$  (see Table 20.9). As we would expect, the smallest of the halide ions,  $F^-$ , has the most negative value—its hydration is the most exothermic. This term favors the dissociation of HF into its ions more so than it does for the other  $HX$  molecules.

So far we have two conflicting factors: The large HF bond energy tends to make HF a weaker acid than the other hydrogen halides, but the enthalpy of hydration favors the dissociation of HF more than that of the others. In comparing data for HF and HCl, the difference in bond energy (138 kJ/mol) is slightly smaller than the difference in the enthalpies of hydration for the anions (144 kJ/mol). If these were the *only* important factors, HF should be a stronger acid than HCl because the large enthalpy of hydration of F<sup>-</sup> more than makes up for the large HF bond strength.

When  $\text{H}_2\text{O}$  molecules cluster around an ion, an ordering effect occurs, and  $\Delta S_{\text{hyd}}^\circ$  is negative.

**TABLE 20.9 The Enthalpies and Entropies of Hydration for the Halide Ions**

$X^- (g)$	$\xrightarrow{H_2O} X^- (aq)$	
$X^-$	$\Delta H^\circ (\text{kJ/mol})$	$\Delta S^\circ (\text{J/K} \cdot \text{mol})$
$F^-$	-510	-159
$Cl^-$	-366	-96
$Br^-$	-334	-81
$I^-$	-291	-64

Hydration becomes more exothermic as the charge density of an ion increases. Thus, for ions of a given charge, the smallest is most strongly hydrated.

Stomach acid is 0.1 M HCl.



This Steuben glass design was etched using hydrofluoric acid.

As it turns out, *the deciding factor is entropy*. Note from Table 20.9 that the entropy of hydration for  $F^-$  is much more negative than for the other halides because of the high degree of ordering that occurs as the water molecules associate with the small  $F^-$  ion. Remember that a negative change in entropy is unfavorable. Thus, although the enthalpy of hydration favors dissociation of HF, the *entropy* of hydration strongly opposes it.

When all these factors are taken into account,  $\Delta G^\circ$  for the dissociation of HF in water is positive; that is,  $K_a$  is small. In contrast,  $\Delta G^\circ$  for dissociation of the other HX molecules in water is negative ( $K_a$  is large). This example illustrates the complexity of the processes that occur in aqueous solutions and the importance of entropy effects in that medium.

In practical terms, **hydrochloric acid** is the most important of the **hydrohalic acids**, the aqueous solutions of the hydrogen halides. About 3 million tons of hydrochloric acid is produced annually for use in cleaning steel before galvanizing and in the manufacture of many other chemicals.

Hydrofluoric acid is used to etch glass by reacting with the silica in glass to form the volatile gas  $\text{SiF}_4$ :



### Oxyacids and Oxyanions

All the halogens except fluorine combine with various numbers of oxygen atoms to form a series of oxyacids, as shown in Table 20.10. The strengths of these acids vary in direct proportion to the number of oxygen atoms attached to the halogen, as we discussed in Section 14.9.

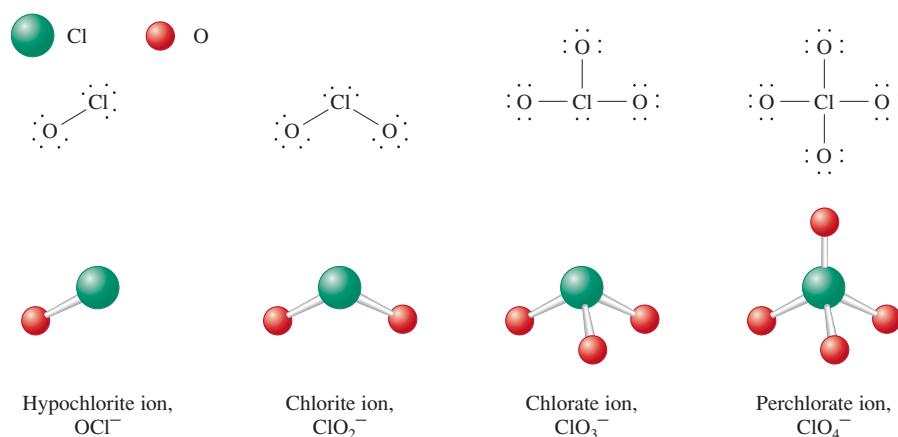
The only member of the chlorine series that has been obtained in the pure state is **perchloric acid** ( $\text{HOClO}_3$ ), a strong acid and powerful oxidizing agent. Because perchloric acid reacts explosively with many organic materials, it must be handled with great caution. The other oxyacids of chlorine are known only in solution, although salts containing their anions are well known (Fig. 20.24).

**TABLE 20.10 The Known Oxyacids of the Halogens\***

Oxidation State of Halogen	Fluorine	Chlorine	Bromine	Iodine*	General Name of Acids	General Name of Salts
+1	HOF	HOCl	HOBr	HOI	Hypohalous acid	Hypohalites, $\text{MOX}$
+3	**	HOClO	**	**	Halous acid	Halites, $\text{MXO}_2$
+5	**	HOClO <sub>2</sub>	HOBrO <sub>2</sub>	HOIO <sub>2</sub>	Halic acid	Halates, $\text{MXO}_3$
+7	**	HOClO <sub>3</sub>	HOBrO <sub>3</sub>	HOIO <sub>3</sub>	Perhalic acid	Perhalates, $\text{MXO}_4$

\*Iodine also forms  $\text{H}_4\text{I}_2\text{O}_9$  (mesodiperiodic acid) and  $\text{H}_5\text{IO}_6$  (paraperiodic acid).

\*\*Compound is unknown.



**FIGURE 20.24**  
The structures of the oxychloro anions.

*Hypochlorous acid* ( $\text{HOCl}$ ) is formed when chlorine gas is dissolved in cold water:



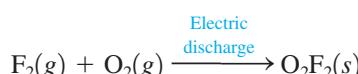
Note that in this reaction chlorine is both oxidized (from 0 in  $\text{Cl}_2$  to +1 in  $\text{HOCl}$ ) and reduced (from 0 in  $\text{Cl}_2$  to -1 in  $\text{Cl}^-$ ). Such a reaction, where a given element is both oxidized and reduced, is called a **disproportionation reaction**. Hypochlorous acid and its salts are strong oxidizing agents, and solutions of them are widely used as household bleaches and disinfectants.

*Chlorate salts*, such as  $\text{KClO}_3$ , are also strong oxidizing agents and are used as weed killers and as oxidizers in fireworks (see Chapter 7) and explosives.

Fluorine forms only one oxyacid, hypofluorous acid ( $\text{HOF}$ ), but at least two oxides. When fluorine gas is bubbled into a dilute solution of sodium hydroxide, the compound *oxygen difluoride* ( $\text{OF}_2$ ) is formed:



Oxygen difluoride is a pale yellow gas ( $\text{bp} = -145^\circ\text{C}$ ), which is a strong oxidizing agent. The oxide *dioxygen difluoride* ( $\text{O}_2\text{F}_2$ ) is an orange solid that can be prepared by passing an electric discharge through an equimolar mixture of fluorine and oxygen gases:



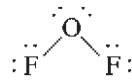
### Sample Exercise 20.5

### Bonding Description of $\text{OF}_2$

Give the Lewis structure, molecular structure, and hybridization of the oxygen atom for  $\text{OF}_2$ .

#### Solution

The  $\text{OF}_2$  molecule has 20 valence electrons and the Lewis structure is



The four effective pairs around the oxygen are arranged tetrahedrally. Therefore, the oxygen atom is  $sp^3$  hybridized. The molecule is bent (V-shaped), and the bond angle is predicted to be smaller than 109.5 degrees because of the lone-pair repulsions.

*See Exercise 20.37.*

The name for  $\text{OF}_2$  is *oxygen difluoride* rather than difluorine oxide because fluorine has a higher electronegativity than oxygen and thus is named as if it were an anion.

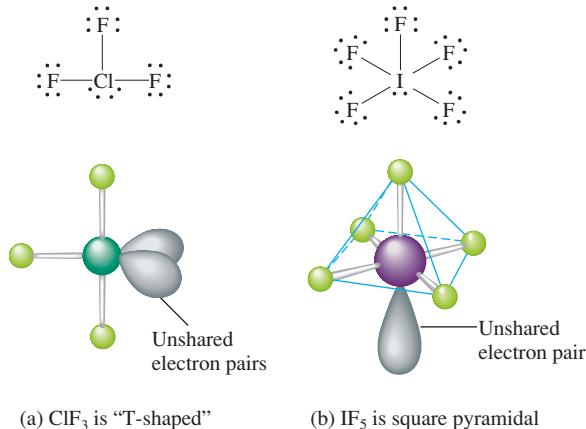
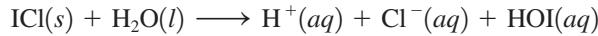
**TABLE 20.11 Some Compounds of the Halogens with Nonmetals**

Compounds with Group 3A Nonmetals	Compounds with Group 4A Nonmetals	Compounds with Group 5A Nonmetals	Compounds with Group 6A Nonmetals	Compounds with Group 7A Nonmetals
$\text{BX}_3$ ( $\text{X} = \text{F, Cl, Br, I}$ ) $\text{BF}_4^-$	$\text{CX}_4$ ( $\text{X} = \text{F, Cl, Br, I}$ ) $\text{SiF}_4$ $\text{SiF}_6^{2-}$ $\text{SiCl}_4$ $\text{GeF}_4$ $\text{GeF}_6^{2-}$ $\text{GeCl}_4$	$\text{NX}_3$ ( $\text{X} = \text{F, Cl, Br, I}$ ) $\text{N}_2\text{F}_4$ $\text{PX}_3$ ( $\text{X} = \text{F, Cl, Br, I}$ ) $\text{PF}_5$ $\text{PCl}_5$ $\text{PBr}_5$ $\text{AsF}_3$ $\text{AsF}_5$ $\text{SbF}_3$ $\text{SbF}_5$	$\text{OF}_2$ $\text{O}_2\text{F}_2$ $\text{OCl}_2$ $\text{OBr}_2$ $\text{SF}_2$ $\text{SCl}_2$ $\text{S}_2\text{F}_2$ $\text{S}_2\text{Cl}_2$ $\text{SF}_4$ $\text{SCl}_4$ $\text{SF}_6$ $\text{SeF}_4$ $\text{SeF}_6$ $\text{SeCl}_2$ $\text{SeCl}_4$ $\text{SeBr}_4$ $\text{TeF}_4$ $\text{TeF}_6$ $\text{TeCl}_4$ $\text{TeBr}_4$ $\text{TeI}_4$	$\text{ICl}$ $\text{IBr}$ $\text{BrF}$ $\text{BrCl}$ $\text{ClF}$ $\text{ClF}_3$ $\text{BrF}_3$ $\text{ICl}_3$ $\text{IF}_3$ $\text{ClF}_5$ $\text{BrF}_5$ $\text{IF}_5$ $\text{IF}_7$

## Other Halogen Compounds

The halogens react readily with most nonmetals to form a variety of compounds, some of which are shown in Table 20.11.

Halogens react with each other to form **interhalogen compounds** with the general formula  $\text{AB}_n$ , where  $n$  is typically 1, 3, 5, or 7 and A is the larger of the two halogens. The structures of these compounds (see Fig. 20.25) are predicted accurately by the VSEPR model. The interhalogens are volatile, highly reactive compounds that act as strong oxidizing agents. They react readily with water, forming the halide ion of the more electronegative halogen and the hypohalous acid of the less electronegative halogen. For example,

**FIGURE 20.25**

The idealized structures of the interhalogens  $\text{ClF}_3$  and  $\text{IF}_5$ . In reality, the lone pairs cause the bond angles to be slightly less than 90 degrees.



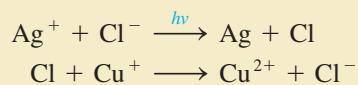
## CHEMICAL IMPACT

### Automatic Sunglasses

Sunglasses can be troublesome. It seems they are always getting lost or sat on. One solution to this problem for people who wear glasses is photochromic glass—glass that darkens in response to intense light. Recall that glass is a complex, noncrystalline material that is composed of polymeric silicates (see Chapter 10). Of course, glass transmits visible light—its transparency is its most useful property.

Glass can be made photochromic by adding tiny silver chloride crystals that get trapped in the glass matrix as the glass solidifies. Silver chloride has the unusual property of darkening when struck by light—the property that makes the silver halide salts so useful for photographic films. This darkening occurs because light causes an electron transfer from  $\text{Cl}^-$  to  $\text{Ag}^+$  in the silver chloride crystal, forming a silver atom and a chlorine atom. The silver atoms formed in this way tend to migrate to the surface of the silver chloride crystal, where they aggregate to form a tiny crystal of silver metal, which is opaque to light.

In photography the image defined by the grains of silver is fixed by chemical treatment so that it remains permanent. However, in photochromic glass this process must be reversible—the glass must become fully transparent again when the person goes back indoors. The secret to the reversibility of photochromic glass is the presence of  $\text{Cu}^+$  ions. The added  $\text{Cu}^+$  ions serve two important functions. First, they reduce the  $\text{Cl}$  atoms formed in the light-induced reaction. This prevents them from escaping from the crystal:



Glasses with photosensitive lenses. The right lens has been exposed to light and the left one has not.

Second, when the exposure to intense light ends (the person goes indoors), the  $\text{Cu}^{2+}$  ions migrate to the surface of the silver chloride crystal, where they accept electrons from silver atoms as the tiny crystal of silver atoms disintegrates:



The  $\text{Ag}^+$  ions are re-formed in this way, then return to their places in the silver chloride crystal, making the glass transparent once again.

Typical photochromic glass decreases to about 20% transmittance (transmits 20% of the light that strikes it) in strong sunlight, and then over a period of a few minutes returns to about 80% transmittance indoors (normal glass has 92% transmittance).

## 20.8 The Group 8A Elements

8A

He

Ne

Ar

Kr

Xe

Rn

The Group 8A elements, the **noble gases**, are characterized by filled *s* and *p* valence orbitals (electron configuration of  $2s^2$  for helium and  $ns^2np^6$  for the others). Because of this, these elements are very unreactive. In fact, no noble gas compounds were known 50 years ago. Selected properties of the Group 8A elements are summarized in Table 20.12.

*Helium* was identified by its characteristic emission spectrum as a component of the sun before it was found on earth. The major sources of helium on earth are natural gas deposits, where helium was formed from  $\alpha$ -particle decay of radioactive elements. The  $\alpha$  particle is a helium nucleus that can easily pick up electrons from the environment to form a helium atom. Although helium forms no compounds, it is an important substance that is used as a coolant, as a pressurizing gas for rocket fuels, as a diluent in the gases used for deep-sea diving and spaceship atmospheres, and as the gas in lighter-than-air airships (blimps).



Neon, a noble gas, is used in luminescent lighting (neon signs).

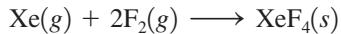
**TABLE 20.12 Selected Properties of Group 8A Elements**

Element	Melting Point (°C)	Boiling Point (°C)	Atmospheric Abundance (% by Volume)	Examples of Compounds
Helium	-270	-269	$5 \times 10^{-4}$	None
Neon	-249	-246	$1 \times 10^{-3}$	None
Argon	-189	-186	$9 \times 10^{-1}$	None
Krypton	-157	-153	$1 \times 10^{-4}$	$\text{KrF}_2$
Xenon	-112	-107	$9 \times 10^{-6}$	$\text{XeF}_4, \text{XeO}_3, \text{XeF}_6$

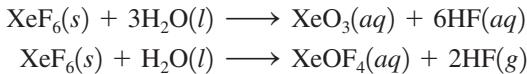
Like helium, *neon* and *argon* form no compounds but are used extensively. For example, neon is employed in luminescent lighting (neon signs), and argon is used to provide the noncorrosive atmosphere in incandescent light bulbs, which prolongs the life of the tungsten filament.

Of the Group 8A elements, only *krypton* and *xenon* have been observed to form chemical compounds. The first of these was prepared in 1962 by Neil Bartlett, an English chemist who used  $\text{Xe}(g)$  and  $\text{PtF}_6(g)$  to make the ionic compound with the empirical formula  $\text{XePtF}_6$ .

Less than a year after Bartlett's report of  $\text{XePtF}_6$ , a group at Argonne National Laboratory near Chicago prepared xenon tetrafluoride by reaction of xenon and fluorine gases in a nickel reaction vessel at  $400^\circ\text{C}$  and 6 atm:



Xenon tetrafluoride forms stable colorless crystals. Two other xenon fluorides,  $\text{XeF}_2$  and  $\text{XeF}_6$ , were synthesized by the group at Argonne, and a highly explosive xenon oxide ( $\text{XeO}_3$ ) also was found. The xenon fluorides react with water to form hydrogen fluoride and oxycompounds. For example,



In the past 40 years, other xenon compounds have been prepared—for example,  $\text{XeO}_4$  (explosive),  $\text{XeO}_2\text{F}_4$ ,  $\text{XeO}_2\text{F}_2$ , and  $\text{XeO}_3\text{F}_2$ . These compounds contain discrete molecules with covalent bonds between the xenon and the other atoms. The structures of some of these xenon compounds are summarized in Fig. 20.26. A few compounds of krypton, such as  $\text{KrF}_2$  and  $\text{KrF}_4$ , also have been observed. There is evidence that radon also reacts with fluorine, but the radioactivity of radon makes its chemistry very difficult to study.

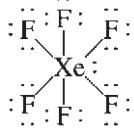
### Sample Exercise 20.6

### The Structure of $\text{XeF}_6$

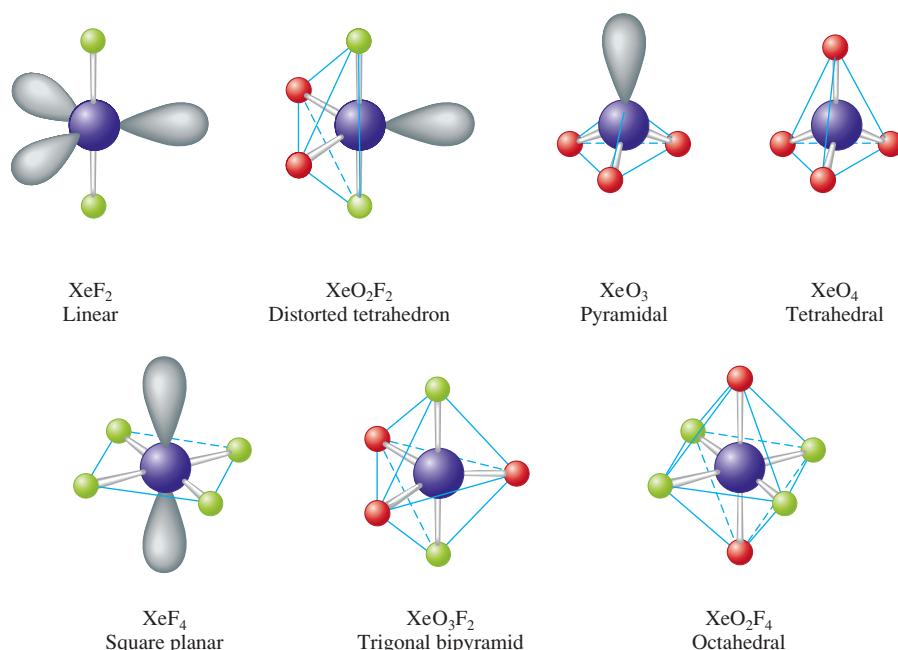
Use the VSEPR model to predict whether  $\text{XeF}_6$  has an octahedral structure.

#### Solution

The  $\text{XeF}_6$  molecule contains 50  $[8 + 6(7)]$  valence electrons and the Lewis structure is



The xenon atom has seven pairs of electrons around it (one lone pair and six bonding pairs), one more pair than can be accommodated in an octahedral arrangement. Thus  $\text{XeF}_6$

**FIGURE 20.26**

The structures of several known xenon compounds.

will not have an octahedral structure, but should be distorted from this geometry by the extra electron pair. There is experimental evidence that the structure of  $\text{XeF}_6$  is not octahedral.

*See Exercises 20.43 and 20.44.*

## Key Terms

### Section 20.2

Haber process  
nitrogen fixation  
nitrogen-fixing bacteria  
denitrification  
nitrogen cycle  
ammonia  
hydrazine  
nitric acid  
Ostwald process

### Section 20.3

phosphoric (orthophosphoric) acid  
condensation reactions  
phosphorous acid  
superphosphate of lime

### Section 20.5

ozone  
ozonolysis

### Section 20.6

Frasch process  
sulfuric acid  
thiosulfate ion

## For Review

### Group 5A

- Elements show a wide variety of chemical properties
  - Nitrogen and phosphorus are nonmetals
  - Antimony and bismuth tend to be metallic, although no ionic compounds containing  $\text{Sb}^{5+}$  and  $\text{Bi}^{5+}$  are known; the compounds containing Sb(V) and Bi(V) are molecular rather than ionic
  - All group members except N form molecules with five covalent bonds
  - The ability to form  $\pi$  bonds decreases dramatically after N
- Chemistry of nitrogen
  - Most nitrogen-containing compounds decompose exothermically, forming the very stable  $\text{N}_2$  molecule, which explains the power of nitrogen-based explosives
  - The nitrogen cycle, which consists of a series of steps, shows how nitrogen is cycled in the natural environment
  - Nitrogen fixation changes the  $\text{N}_2$  in air into compounds useful to plants
    - The Haber process is a synthetic method of nitrogen fixation
    - In the natural world, nitrogen fixation occurs through nitrogen-fixing bacteria in the root nodules of certain plants and through lightning in the atmosphere
  - Ammonia is the most important hydride of nitrogen
    - Contains pyramidal  $\text{NH}_3$  molecules
    - Widely used as a fertilizer
  - Hydrazine ( $\text{N}_2\text{H}_4$ ) is a powerful reducing agent

**Section 20.7**

halogens  
hydrochloric acid  
hydrohalic acids  
disproportionation reaction  
interhalogen compounds

**Section 20.8**

noble gases

- Nitrogen forms a series of oxides including  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{N}_2\text{O}_5$
- Nitric acid ( $\text{HNO}_3$ ) is a very important strong acid manufactured by the Ostwald process
- Chemistry of phosphorus
  - Exists in three elemental forms: white (contains  $\text{P}_4$  molecules), red, and black
  - Phosphine ( $\text{PH}_3$ ) has bond angles close to 90 degrees
  - Phosphorus forms oxides including  $\text{P}_4\text{O}_6$  and  $\text{P}_4\text{O}_{10}$  (which dissolves in water to form phosphoric acid,  $\text{H}_3\text{PO}_4$ )

**Group 6A**

- Metallic character increases going down the group but no element behaves as a typical metal
- The lighter members tend to gain two electrons to form  $\text{X}^{2-}$  ions in compounds with metals
- Chemistry of oxygen
  - Elemental forms are  $\text{O}_2$  and  $\text{O}_3$
  - Oxygen forms a wide variety of oxides
  - $\text{O}_2$  and especially  $\text{O}_3$  are powerful oxidizing agents
- Chemistry of sulfur
  - The elemental forms are called rhombic and monoclinic sulfur, both of which contain  $\text{S}_8$  molecules
  - The most important oxides are  $\text{SO}_2$  (which forms  $\text{H}_2\text{SO}_3$  in water) and  $\text{SO}_3$  (which forms  $\text{H}_2\text{SO}_4$  in water)
  - Sulfur forms a wide variety of compounds in which it shows the oxidation states +6, +4, +2, 0, and -2

**Group 7A (halogens)**

- All nonmetals
- Form hydrides of the type  $\text{HX}$  that behave as strong acids in water except for  $\text{HF}$ , which is a weak acid
- The oxyacids of the halogens become stronger as more oxygen atoms are present
- The interhalogens contain two or more different halogens

**Group 8A (noble gases)**

- All elements are monatomic gases and are generally very unreactive
- The heavier elements form compounds with electronegative elements such as fluorine and oxygen

**REVIEW QUESTIONS**

1. What is the valence electron configuration for Group 5A elements? Metallic character increases when going down a group. Give some examples illustrating how Bi and Sb have metallic characteristics not associated with N, P, and As. The Group 5A elements can form molecules or ions that involve three, five, or six covalent bonds;  $\text{NH}_3$ ,  $\text{AsCl}_5$ , and  $\text{PF}_6^-$  are examples. Draw the Lewis structure for each of these substances and predict the molecular structure and hybridization for each. Why doesn't  $\text{NF}_5$  or  $\text{NCl}_6^-$  form?
2. Table 20.2 lists some common nitrogen compounds having oxidation states ranging from -3 to +5. Rationalize this spread in oxidation states. For each substance listed in Table 20.2, list some of its special properties.
3. Ammonia forms hydrogen-bonding intermolecular forces resulting in an unusually high boiling point for a substance with the small size of  $\text{NH}_3$ . Can hydrazine,  $\text{N}_2\text{H}_4$ , also form hydrogen-bonding interactions?

The synthesis of ammonia gas from nitrogen gas and hydrogen gas is a classic case in which a knowledge of kinetics and equilibrium was exploited to

make a desired chemical reaction economically feasible. Explain how each of the following conditions helps to maximize the yield of ammonia:

- running the reaction at an elevated temperature
- removing the ammonia from the reaction mixture as it forms
- using a catalyst
- running the reaction at high pressure

In many natural waters, nitrogen and phosphorus are the least abundant nutrients available for plant life. Some waters that become polluted from agricultural runoff or municipal sewage become infested with algae. The algae consume most of the dissolved oxygen in the water, and fish life dies off as a result. Describe how these events are chemically related.

- White phosphorus is much more reactive than black or red phosphorus. Explain. How is phosphine's ( $\text{PH}_3$ ) structure different from that of ammonia? Phosphoric acid ( $\text{H}_3\text{PO}_4$ ) is a triprotic acid, phosphorous acid ( $\text{H}_3\text{PO}_3$ ) is a diprotic acid, and hypophosphorous acid ( $\text{H}_3\text{PO}_2$ ) is a monoprotic acid. Explain this phenomenon.
- What is the valence electron configuration of Group 6A elements? What are some property differences between oxygen and polonium? What are the Lewis structures for the two allotropic forms of oxygen? How can the paramagnetism of  $\text{O}_2$  be explained using the molecular orbital model? What is the molecular structure and the bond angle in ozone? Ozone is desirable in the upper atmosphere and undesirable in the lower atmosphere. A dictionary states that ozone has the scent of a fresh spring day. How can these seemingly conflicting statements be reconciled in terms of the chemical properties of ozone?
- The most stable form of solid sulfur is the rhombic form; however, a solid form called monoclinic sulfur can also form. What is the difference between rhombic and monoclinic sulfur? Explain why  $\text{O}_2$  is much more stable than  $\text{S}_2$  or  $\text{SO}$ . When  $\text{SO}_2(s)$  or  $\text{SO}_3(g)$  reacts with water, an acidic solution forms. Explain. What are the molecular structures and bond angles in  $\text{SO}_2$  and  $\text{SO}_3$ ? Explain the bonding in  $\text{SO}_2$  and  $\text{SO}_3$ .  $\text{H}_2\text{SO}_4$  is a powerful dehydrating agent: What does this mean?
- What is the valence electron configuration of the halogens? Why do the boiling points and melting points of the halogens increase steadily from  $\text{F}_2$  to  $\text{I}_2$ ? Give two reasons why  $\text{F}_2$  is the most reactive of the halogens. Explain why HF is a weak acid, whereas HCl, HBr, and HI are all strong acids.

Explain why the boiling point of HF is much higher than the boiling points of HCl, HBr, and HI. In nature, the halogens are generally found as halide ions in various minerals and seawater. What is a halide ion, and why are halide salts so stable? The oxidation states of the halogens vary from  $-1$  to  $+7$ . Identify compounds of chlorine that have  $-1$ ,  $+1$ ,  $+3$ ,  $+5$ , and  $+7$  oxidation states. How does the oxyacid strength of the halogens vary as the number of oxygens in the formula increases?

- Table 20.11 lists many compounds or ions that halogens form with other non-metals. For each compound or ion, give the molecular structure, including bond angles, and give the hybridization of the central atom in each species (ignore  $\text{IF}_7$ ). Why does  $\text{ICl}_3$  form but not  $\text{FCl}_3$ ?
- What special property of the noble gases makes them unreactive? The boiling points and melting points of the noble gases increase steadily from He to Xe. Explain. Although He is the second most abundant element in the universe, it is very rare on earth. Why? The noble gases were among the last elements discovered; their existence was not predicted by Mendeleev when he published his first periodic table. Explain. In chemistry textbooks written before 1962, the noble gases were referred to as the inert gases. Why do we no longer use this term?
- For the structures of the xenon compounds in Figure 20.26, give the bond angles exhibited and the hybridization of the central atom in each compound.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

## Questions

- Elemental nitrogen exists as N<sub>2</sub>, whereas in the gas phase the elements phosphorus, arsenic, and antimony consist of P<sub>4</sub>, As<sub>4</sub>, and Sb<sub>4</sub> molecules, respectively. Give a possible reason for this difference between N<sub>2</sub> and the other group 5A elements.
- What is nitrogen fixation? Give some examples of nitrogen fixation.
- In large doses, selenium is toxic. However, in moderate intake, selenium is a physiologically important element. How is selenium physiologically important?
- Ozone is a possible replacement for chlorine in municipal water purification. Unlike chlorine, virtually no ozone remains after treatment. This has good and bad consequences. Explain.
- Sulfur forms a wide variety of compounds in which it has +6, +4, +2, 0, and -2 oxidation states. Give examples of sulfur compounds having each of these oxidation states.
- When a halogen is a central atom in a compound, the compound typically is sp<sup>3</sup>, dsp<sup>3</sup>, or d<sup>2</sup>sp<sup>3</sup> hybridized. Using bromine as your central atom, give example compounds for each type of hybridization. What is the molecular structure for each of your examples?
- Explain the following observations regarding reactions of halogens.
  - In the hydrogen-chlorine cannon lecture demonstration, a lit magnesium strip is held to a mixture of H<sub>2</sub> and Cl<sub>2</sub>, resulting in a reaction that sends the stopper to the cannon flying across the lecture room.
  - When a brown bromine solution is added dropwise to an organic compound called an alkene, the brown color disappears, resulting in a colorless reaction mixture.
  - When aluminum is reacted with iodine, the reaction container emits sparks and a deep purple colored smoke.
- There is evidence that radon reacts with fluorine to form compounds similar to those formed by xenon and fluorine. Predict the formulas of these RaF<sub>x</sub> compounds. Why is the chemistry of radon difficult to study?

## Exercises

In this section similar exercises are paired.

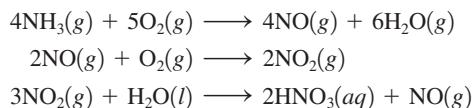
### Group 5A Elements

- The oxyanion of nitrogen in which it has the highest oxidation state is the nitrate ion (NO<sub>3</sub><sup>-</sup>). The corresponding oxyanion of phosphorus is PO<sub>4</sub><sup>3-</sup>. The NO<sub>4</sub><sup>3-</sup> ion is known but not very stable. The PO<sub>3</sub><sup>-</sup> ion is not known. Account for these differences in terms of the bonding in the four anions.
- In each of the following pairs of substances, one is stable and known, and the other is unstable. For each pair, choose the stable substance, and explain why the other is unstable.
  - NF<sub>5</sub> or PF<sub>5</sub>
  - AsF<sub>5</sub> or AsI<sub>5</sub>
  - NF<sub>3</sub> or NBr<sub>3</sub>

11. Several important compounds contain only nitrogen and oxygen. Place the following compounds in order of increasing mass percent of nitrogen.

- NO, a gas formed by the reaction of N<sub>2</sub> with O<sub>2</sub> in internal combustion engines
- NO<sub>2</sub>, a brown gas mainly responsible for the brownish color of photochemical smog
- N<sub>2</sub>O<sub>4</sub>, a colorless liquid used as fuel in space shuttles
- N<sub>2</sub>O, a colorless gas sometimes used as anesthetic by dentists (known as laughing gas)

12. Nitric acid is produced commercially by the Ostwald process, represented by the following equations:



What mass of NH<sub>3</sub> must be used to produce 1.0 × 10<sup>6</sup> kg HNO<sub>3</sub> by the Ostwald process? Assume 100% yield in each reaction and assume that the NO produced in the third step is not recycled.

13. Complete and balance each of the following reactions.

- the decomposition of solid ammonium nitrate
- the decomposition of gaseous dinitrogen pentoxide
- the reaction between solid potassium phosphide and water
- the reaction between liquid phosphorus tribromide and water
- the reaction between aqueous ammonia and aqueous sodium hypochlorite

14. Arsenic reacts with oxygen to form oxides that react with water in a manner analogous to that of the phosphorus oxides. Write balanced chemical equations describing the reaction of arsenic with oxygen and the reaction of the resulting oxide with water.

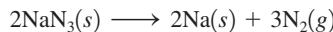
15. Phosphorus occurs naturally in the form of fluorapatite, CaF<sub>2</sub> · 3Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, where the dot indicates 1 part CaF<sub>2</sub> to 3 parts Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. This mineral is reacted with an aqueous solution of sulfuric acid in the preparation of a fertilizer. The products are phosphoric acid, hydrogen fluoride, and gypsum, CaSO<sub>4</sub> · 2H<sub>2</sub>O. Write and balance the chemical equation describing this process.

16. Lewis structures can be used to understand why some molecules react in certain ways. Write the Lewis structure for the reactants and products in the reactions described below.

- Nitrogen dioxide dimerizes to produce dinitrogen tetroxide.
- Boron trihydride accepts a pair of electrons from ammonia, forming BH<sub>3</sub>NH<sub>3</sub>.

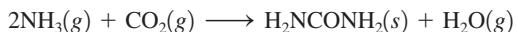
Give a possible explanation for why these two reactions occur.

17. Air bags are activated when a severe impact causes a steel ball to compress a spring and electrically ignite a detonator cap. This causes sodium azide (NaN<sub>3</sub>) to decompose explosively according to the following reaction:



How many moles of NaN<sub>3</sub>(s) must be reacted to inflate an air bag to 70.0 L at STP?

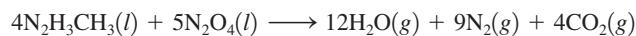
- 18.** Urea ( $\text{H}_2\text{NCONH}_2$ ) is used extensively as a nitrogen source in fertilizers. It is produced commercially from the reaction of ammonia and carbon dioxide:



Ammonia gas at  $223^\circ\text{C}$  and 90. atm flows into a reactor at a rate of 500. L/min. Carbon dioxide at  $223^\circ\text{C}$  and 45 atm flows into the reactor at a rate of 600. L/min. What mass of urea is produced per minute by this reaction assuming a 100% yield?

- 19.** Hydrazine ( $\text{N}_2\text{H}_4$ ) is used as a fuel in liquid-fueled rockets. When hydrazine reacts with oxygen gas, nitrogen gas and water vapor are produced. Write a balanced equation and use bond energies from Table 8.4 to estimate  $\Delta H$  for this reaction.

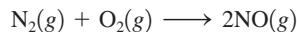
- 20.** The space shuttle orbiter utilizes the oxidation of methylhydrazine by dinitrogen tetroxide for propulsion:



Calculate  $\Delta H^\circ$  for this reaction using data in Appendix 4. Compare your answer to the  $\Delta H$  value determined in Sample Exercise 20.2. Explain any discrepancies.

- 21.** Many oxides of nitrogen have positive values for the standard free energy of formation. Using NO as an example, explain why this is the case.

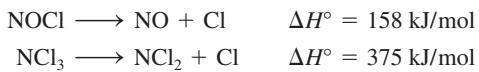
- 22.** Using data from Appendix 4 calculate  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  for the reaction



Why does NO form in an automobile engine but then does not readily decompose back to  $\text{N}_2$  and  $\text{O}_2$  in the atmosphere?

- 23.** Compare the Lewis structures with the molecular orbital view of the bonding in NO,  $\text{NO}^+$ , and  $\text{NO}^-$ . Account for any discrepancies between the two models.

- 24.** The energy to break a particular bond is not always constant. It takes about 200 kJ/mol less energy to break the N—Cl bond in  $\text{NOCl}$  as compared with  $\text{NCl}_3$ :



Why is there such a great discrepancy in the apparent N—Cl bond energies? Hint: Consider what happens to the nitrogen–oxygen bond in the first reaction.

- 25.** Predict the relative acid strengths of the following compounds.

a.  $\text{H}_3\text{PO}_4$  and  $\text{H}_3\text{PO}_3$       b.  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{HPO}_4^{2-}$

- 26.** Trisodium phosphate (TSP) is an effective grease remover. Like many cleaners, TSP acts as a base in water. Write a balanced equation to account for this behavior.

- 27.** Isohypophosphonic acid ( $\text{H}_4\text{P}_2\text{O}_6$ ) and diprophosphonic acid ( $\text{H}_4\text{P}_2\text{O}_5$ ) are tri- and diprotic acids, respectively. Draw Lewis structures for these acids that are consistent with these facts.

- 28.** One of the most strongly acidic solutions known is a mixture of antimony pentafluoride ( $\text{SbF}_5$ ) and fluorosulfonic acid ( $\text{HSO}_3\text{F}$ ). The dominant equilibria are

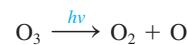


- a.** Draw Lewis structures for all the species shown in the preceding reactions. Predict the hybridization of the central Sb and S atoms in each structure.

- b.** This *superacid* solution is capable of protonating (adding  $\text{H}^+$  to) virtually every known organic compound. What is the active protonating agent in the superacid solution?

### Group 6A Elements

- 29.** Use bond energies to estimate the maximum wavelength of light that will cause the reaction



- 30.** The xerographic (dry writing) process was invented in 1938 by C. Carlson. In xerography, an image is produced on a photoconductor by exposing it to light. Selenium is commonly used, since its conductivity increases three orders of magnitude upon exposure to light in the range from 400 to 500 nm. What color light should be used to cause selenium to become conductive? (See Figure 7.2.)

- 31.** Complete and balance each of the following reactions.

- a. the reaction between sulfur dioxide gas and oxygen gas
- b. the reaction between sulfur trioxide gas and water
- c. the reaction between aqueous sodium thiosulfate and aqueous iodine
- d. the reaction between copper metal and aqueous hot sulfuric acid

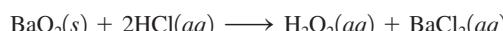
- 32.** Write a balanced equation describing the reduction of  $\text{H}_2\text{SeO}_4$  by  $\text{SO}_2$  to produce selenium.

- 33.** For each of the following, write the Lewis structure(s), predict the molecular structure (including bond angles), and give the expected hybridization of the central atom.

- a.  $\text{SO}_3^{2-}$
- c.  $\text{SCl}_2$
- e.  $\text{TeF}_6$
- b.  $\text{O}_3$
- d.  $\text{SeBr}_4$

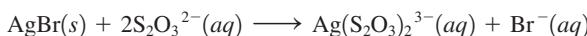
- 34.** Disulfur dinitride ( $\text{S}_2\text{N}_2$ ) exists as a ring of alternating sulfur and nitrogen atoms.  $\text{S}_2\text{N}_2$  will polymerize to polythiazyl, which acts as a metallic conductor of electricity along the polymer chain. Write a Lewis structure for  $\text{S}_2\text{N}_2$ .

- 35.** Hydrogen peroxide is used as a cleaning agent in the treatment of cuts and abrasions for several reasons. It is an oxidizing agent that can directly kill many microorganisms; it decomposes upon contact with blood, releasing elemental oxygen gas (which inhibits the growth of anaerobic microorganisms); and it foams upon contact with blood, which provides a cleansing action. In the laboratory, small quantities of hydrogen peroxide can be prepared by the action of an acid on an alkaline earth metal peroxide, such as barium peroxide:



What mass of hydrogen peroxide should result when 1.50 g of barium peroxide is treated with 25.0 mL of hydrochloric acid solution containing 0.0272 g of HCl per mL? What mass of which reagent is left unreacted?

- 36.** During the developing process of black-and-white film, silver bromide is removed from photographic film by the fixer. The major component of the fixer is sodium thiosulfate. The net ionic equation for the reaction is



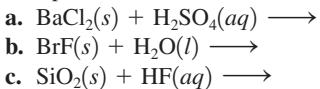
## 938 Chapter Twenty The Representative Elements: Groups 5A Through 8A

What mass of AgBr can be dissolved by 1.00 L of 0.200 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>? (Assume the reaction goes to completion.)

### Group 7A Elements

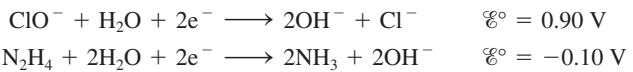
- 37.** Write the Lewis structure for O<sub>2</sub>F<sub>2</sub>. Predict the bond angles and hybridization of the two central oxygen atoms. Assign oxidation states and formal charges to the atoms in O<sub>2</sub>F<sub>2</sub>. The compound O<sub>2</sub>F<sub>2</sub> is a vigorous and potent oxidizing and fluorinating agent. Are oxidation states or formal charges more useful in accounting for these properties of O<sub>2</sub>F<sub>2</sub>?
- 38.** For each of the following, write the Lewis structure(s), predict the molecular structure (including bond angles), and give the expected hybridization of the central atom.
- a. Freon-12 (CCl<sub>2</sub>F<sub>2</sub>)
  - b. perchloric acid
  - c. iodine trichloride
  - d. bromine pentafluoride

- 39.** Complete and balance each of the following reactions.

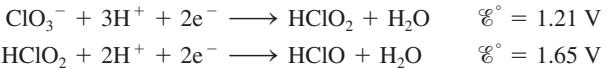


- 40.** Hypofluorous acid is the most recently prepared of the halogen oxyacids. Weighable amounts were first obtained in 1971 by M. H. Studies and E. N. Appelman using the fluorination of ice. Hypofluorous acid is exceedingly unstable, decomposing spontaneously (with a half-life of 30 min) to HF and O<sub>2</sub> in a Teflon container at room temperature. It reacts rapidly with water to produce HF, H<sub>2</sub>O<sub>2</sub>, and O<sub>2</sub>. In dilute acid, H<sub>2</sub>O<sub>2</sub> is the major product; in dilute base, O<sub>2</sub> is the major product.
- a. Write balanced equations for the reactions described above.
  - b. Assign oxidation states to the elements in hypofluorous acid. Does this suggest why hypofluorous acid is so unstable?

- 41.** Hydrazine is somewhat toxic. Use the following half-reactions to explain why household bleach (highly alkaline solution of sodium hypochlorite) should not be mixed with household ammonia or glass cleaners that contain ammonia.



- 42.** What is a disproportionation reaction? Use the following reduction potentials



to predict whether HClO<sub>2</sub> will disproportionate.

### Group 8A Elements

- 43.** The xenon halides and oxides are isoelectronic with many other compounds and ions containing halogens. Give a molecule or ion in which iodine is the central atom that is isoelectronic with each of the following.
- a. xenon tetroxide
  - b. xenon trioxide
  - c. xenon difluoride
  - d. xenon tetrafluoride
  - e. xenon hexafluoride
- 44.** For each of the following, write the Lewis structure(s), predict the molecular structure (including bond angles), and give the expected hybridization of the central atom.
- a. KrF<sub>2</sub>
  - b. KrF<sub>4</sub>
  - c. XeO<sub>2</sub>F<sub>2</sub>
  - d. XeO<sub>2</sub>F<sub>4</sub>

- 45.** Xenon difluoride has proven to be a versatile fluorinating agent. For example, in the reaction



the by-products Xe and HF are easily removed, leaving pure C<sub>6</sub>H<sub>5</sub>F. Xenon difluoride is stored in an inert atmosphere free from oxygen and water. Why is this necessary?

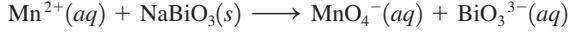
- 46.** Using the data in Table 20.12, calculate the mass of argon at 25°C and 1.0 atm in a room 10.0 m × 10.0 m × 10.0 m. How many Ar atoms are in this room? How many Ar atoms do you inhale in one breath (approximately 2 L) of air at 25°C and 1.0 atm? Argon gas is inert, so it poses no serious health risks. However, if significant amounts of radon were inhaled into the lungs, lung cancer is a possible result. Explain the health-risk differences between argon gas and radon gas.

- 47.** Which do you think would be the greater health hazard, the release of a radioactive nuclide of Sr or a radioactive nuclide of Xe into the environment? Assume the amount of radioactivity is the same in each case. Explain your answer on the basis of the chemical properties of Sr and Xe. Why are the chemical properties of a radioactive substance important in assessing its potential health hazards?

- 48.** The most significant source of natural radiation is radon-222. <sup>222</sup>Rn, a decay product of <sup>238</sup>U, is continuously generated in the earth's crust, allowing gaseous Rn to seep into the basements of buildings. Because <sup>222</sup>Rn is an α-particle producer with a relatively short half-life of 3.82 days, it can cause biological damage when inhaled.
- a. How many α particles and β particles are produced when <sup>238</sup>U decays to <sup>222</sup>Rn? What nucleus is produced when <sup>222</sup>Rn decays?
  - b. Radon is a noble gas so one would expect it to pass through the body quickly. Why is there a concern over inhaling <sup>222</sup>Rn?

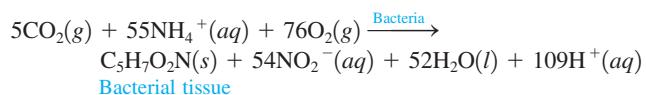
### Additional Exercises

- 49.** The compound NF<sub>3</sub> is quite stable, but NCl<sub>3</sub> was first synthesized in 1811 by P. L. Dulong, who lost three fingers and an eye studying its properties. The compounds NBr<sub>3</sub> and NI<sub>3</sub> are rare, although the explosive compound NI<sub>3</sub> · NH<sub>3</sub> is known. Account for the instability of these halides of nitrogen.
- 50.** The N<sub>2</sub>O molecule is linear and polar.
- a. On the basis of this experimental evidence, which arrangement, NNO or NON, is correct? Explain your answer.
  - b. On the basis of your answer in part a, write the Lewis structure of N<sub>2</sub>O (including resonance forms). Give the formal charge on each atom and the hybridization of the central atom.
  - c. How would the multiple bonding in :N≡N—O: be described in terms of orbitals?
- 51.** Oxidation of the cyanide ion produces the stable cyanate ion, OCN<sup>-</sup>. The fulminate ion, CNO<sup>-</sup>, on the other hand, is very unstable. Fulminate salts explode when struck; Hg(CNO)<sub>2</sub> is used in blasting caps. Write the Lewis structures and assign formal charges for the cyanate and fulminate ions. Why is the fulminate ion so unstable?
- 52.** Sodium bismuthate (NaBiO<sub>3</sub>) is used to test for the presence of Mn<sup>2+</sup> in solution by the following reaction:



- a. Balance this equation.  
 b. Given that bismuth does not form double bonds with oxygen in  $\text{BiO}_3^-$  and that  $\text{NaBiO}_3$  is relatively insoluble in water, what type of structure must  $\text{NaBiO}_3$  have to account for this behavior?

53. Bacterial digestion is an economical method of sewage treatment. The reaction

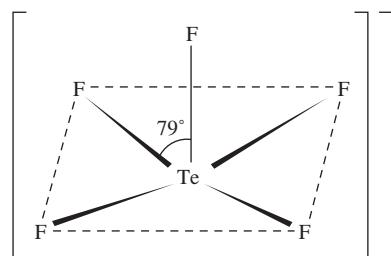


is an intermediate step in the conversion of the nitrogen in organic compounds into nitrate ions. How much bacterial tissue is produced in a treatment plant for every  $1.0 \times 10^4$  kg of wastewater containing 3.0%  $\text{NH}_4^+$  ions by mass? Assume that 95% of the ammonium ions are consumed by the bacteria.

54. An unknown element is a nonmetal and has a valence electron configuration of  $ns^2np^4$ .

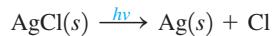
- a. How many valence electrons does this element have?
- b. What are some possible identities for this element?
- c. What is the formula of the compound this element would form with lithium?
- d. Would this element have a larger or smaller radius than barium?
- e. Would this element have a greater or smaller ionization energy than fluorine?

55. The structure of  $\text{TeF}_5^-$  is



Draw a complete Lewis structure for  $\text{TeF}_5^-$ , and explain the distortion from the ideal square pyramidal structure.

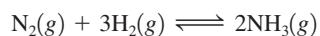
56. Photogray lenses contain small embedded crystals of solid silver chloride. Silver chloride is light-sensitive because of the reaction



Small particles of metallic silver cause the lenses to darken. In the lenses this process is reversible. When the light is removed, the reverse reaction occurs. However, when pure white silver chloride is exposed to sunlight it darkens; the reverse reaction does not occur in the dark.

- a. How do you explain this difference?
- b. Photogray lenses do become permanently dark in time. How do you account for this?

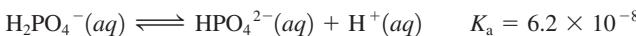
57. Ammonia is produced by the Haber process, in which nitrogen and hydrogen are reacted directly using an iron mesh impregnated with oxides as a catalyst. For the reaction



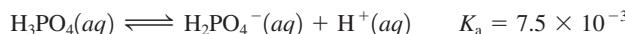
equilibrium constants ( $K_p$  values) as a function of temperature are  
 $300^\circ\text{C}, \quad 4.34 \times 10^{-3}$   
 $500^\circ\text{C}, \quad 1.45 \times 10^{-5}$   
 $600^\circ\text{C}, \quad 2.25 \times 10^{-6}$

Is the reaction exothermic or endothermic?

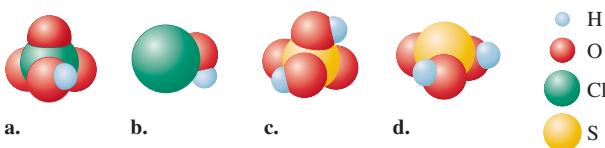
58. Phosphate buffers are important in regulating the pH of intracellular fluids at pH values generally between 7.1 and 7.2. What is the concentration ratio of  $\text{H}_2\text{PO}_4^{2-}$  to  $\text{HPO}_4^{2-}$  in intracellular fluid at pH = 7.15?



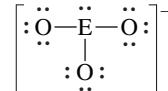
Why is a buffer composed of  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{PO}_4^{2-}$  ineffective in buffering the pH of intracellular fluid?



59. Commercial cold packs and hot packs are available for treating athletic injuries. Both types contain a pouch of water and a dry chemical. When the pack is struck, the pouch of water breaks, dissolving the chemical, and the solution becomes either hot or cold. Many hot packs use magnesium sulfate, and many cold packs use ammonium nitrate. Write reactions to show how these strong electrolytes break apart when they dissolve in water.
60. Classify each of the following as a strong acid or a weak acid.

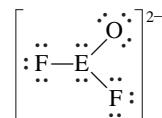


61. Consider the following Lewis structure where E is an unknown element:



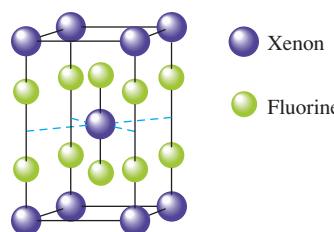
What are some possible identities for element E? Predict the molecular structure (including bond angles) for this ion.

62. Consider the following Lewis structure where E is an unknown element:



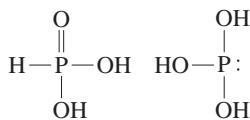
What are some possible identities for element E? Predict the molecular structure (including bond angles) for this ion.

63. The unit cell for a pure xenon fluoride compound is shown below. What is the formula of the compound?



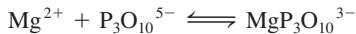
## Challenge Problems

- 64.** Many structures of phosphorus-containing compounds are drawn with some  $P=O$  bonds. These bonds are not the typical  $\pi$  bonds we've considered, which involve the overlap of two  $p$  orbitals. Instead, they result from the overlap of a  $d$  orbital on the phosphorus atom with a  $p$  orbital on oxygen. This type of  $\pi$  bonding is sometimes used as an explanation for why  $H_3PO_3$  has the first structure below rather than the second:



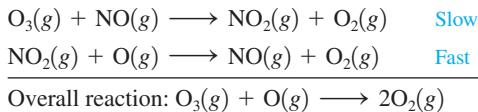
Draw a picture showing how a  $d$  orbital and a  $p$  orbital overlap to form a  $\pi$  bond.

- 65.** Use bond energies (Table 8.4) to show that the preferred products for the decomposition of  $N_2O_3$  are  $NO_2$  and  $NO$  rather than  $O_2$  and  $N_2O$ . (The N—O single bond energy is 201 kJ/mol.) Hint: Consider the reaction kinetics.
- 66.** Sodium tripolyphosphate ( $Na_5P_3O_{10}$ ) is used in many synthetic detergents to soften the water by complexing  $Mg^{2+}$  and  $Ca^{2+}$  ions. It also increases the efficiency of surfactants (wetting agents) that lower a liquid's surface tension. The  $K$  value for the formation of  $MgP_3O_{10}^{3-}$  is  $4.0 \times 10^8$ . The reaction is

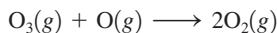


Calculate the concentration of  $Mg^{2+}$  in a solution that was originally 50. ppm of  $Mg^{2+}$  (50. mg/L of solution) after 40. g  $Na_5P_3O_{10}$  is added to 1.0 L of the solution.

- 67.** One pathway for the destruction of ozone in the upper atmosphere is

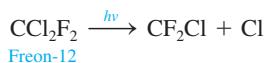


- a. Which species is a catalyst?  
 b. Which species is an intermediate?  
 c. The activation energy  $E_a$  for the uncatalyzed reaction



is 14.0 kJ.  $E_a$  for the same reaction when catalyzed by the presence of  $NO$  is 11.9 kJ. What is the ratio of the rate constant for the catalyzed reaction to that for the uncatalyzed reaction at 25°C? Assume that the frequency factor  $A$  is the same for each reaction.

- d. One of the concerns about the use of Freons is that they will migrate to the upper atmosphere, where chlorine atoms can be generated by the reaction



Chlorine atoms also can act as a catalyst for the destruction of ozone. The first step of a proposed mechanism for chlorine-catalyzed ozone destruction is



Assuming a two-step mechanism, propose the second step in the mechanism and give the overall balanced equation.

- e. The activation energy for Cl-catalyzed destruction of ozone is 2.1 kJ/mol. Estimate the efficiency with which Cl atoms destroy ozone as compared with NO molecules at 25°C. Assume that the frequency factor  $A$  is the same for each catalyzed reaction and assume similar rate laws for each catalyzed reaction.
- 68.** Using data from Appendix 4, calculate  $\Delta H^\circ$ ,  $\Delta G^\circ$ , and  $K_p$  (at 298 K) for the production of ozone from oxygen:



At 30 km above the surface of the earth, the temperature is about 230. K, and the partial pressure of oxygen is about  $1.0 \times 10^{-3}$  atm. Estimate the partial pressure of ozone in equilibrium with oxygen at 30 km above the earth's surface. Is it reasonable to assume that the equilibrium between oxygen and ozone is maintained under these conditions? Explain.

- 69.** You travel to a distant, cold planet where the ammonia flows like water. In fact, the inhabitants of this planet use ammonia (an abundant liquid on their planet) much as earthlings use water. Ammonia is also similar to water in that it is amphoteric and undergoes autoionization. The  $K$  value for the autoionization of ammonia is  $1.8 \times 10^{-12}$  at the standard temperature of the planet. What is the pH of ammonia at this temperature?
- 70.** Nitrogen gas reacts with hydrogen gas to form ammonia gas. You have an equimolar mixture of nitrogen and hydrogen gases in a 15.0-L container fitted with a piston in a room with a pressure of 1.00 atm. The piston apparatus allows the container volume to change in order to keep the pressure constant at 1.00 atm. Assume ideal behavior, constant temperature, and complete reaction.
- What is the partial pressure of ammonia in the container when the reaction is complete?
  - What is the mole fraction of ammonia in the container when the reaction is complete?
  - What is the volume of the container when the reaction is complete?

- 71.** A cylinder fitted with a movable piston initially contains 2.00 mol  $O_2(g)$  and an unknown amount of  $SO_2(g)$ . The oxygen is known to be in excess. The density of the mixture is 0.8000 g/L at some  $T$  and  $P$ . After the reaction has gone to completion, forming  $SO_3(g)$ , the density of the resulting gaseous mixture is 0.8471 g/L at the same  $T$  and  $P$ . Calculate the mass of  $SO_3$  formed in the reaction.
- 72.** One way to determine  $K_{sp}$  for the salt  $Ca(IO_3)_2$  is to titrate it with sodium thiosulfate ( $Na_2S_2O_3$ ). First, make a saturated solution of calcium iodate. Then, add KI and a strong acid (hydrochloric acid and sulfuric acid are generally used). The iodate ion will react according to the equation



Note that molecular iodine is a product of this reaction. Adding a starch indicator will turn the solution of  $I_2$  a dark blue-black color. A solution of sodium thiosulfate is added through a buret, which reacts with iodine as follows:



The dark blue-black color disappears, when all of the  $I_2$  has reacted. This is the endpoint of the titration.

Consider starting with a 10.0-mL sample of a saturated calcium iodate solution. Upon titrating, you find that 14.9 mL of 0.100 M  $\text{Na}_2\text{S}_2\text{O}_3$  is required to reach the end point of the titration. Calculate  $K_{\text{sp}}$  for  $\text{Ca}(\text{IO}_3)_2$ .

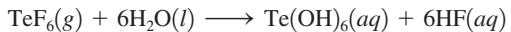
## Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

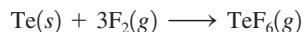
- 73.** Although nitrogen trifluoride ( $\text{NF}_3$ ) is a thermally stable compound, nitrogen triiodide ( $\text{NI}_3$ ) is known to be a highly explosive material.  $\text{NI}_3$  can be synthesized according to the equation



- a. What is the enthalpy of formation for  $\text{NI}_3(s)$  given the enthalpy of reaction (-307 kJ) and the enthalpies of formation for  $\text{BN}(s)$  (-254 kJ/mol),  $\text{IF}(g)$  (-96 kJ/mol), and  $\text{BF}_3(g)$  (-1136 kJ/mol)?
  - b. It is reported that when the synthesis of  $\text{NI}_3$  is conducted using 4 mol IF for every 1 mol BN, one of the by-products isolated is  $[\text{IF}_2]^{+}[\text{BF}_4]^{-}$ . What are the molecular geometries of the species in this by-product? What are the hybridizations of the central atoms in each species in the by-product?
- 74.** While selenic acid has the formula  $\text{H}_2\text{SeO}_4$  and thus is directly related to sulfuric acid, telluric acid is best visualized as  $\text{H}_6\text{TeO}_6$  or  $\text{Te(OH)}_6$ .
- a. What is the oxidation state of tellurium in  $\text{Te(OH)}_6$ ?
  - b. Despite its structural differences with sulfuric and selenic acid, telluric acid is a diprotic acid with  $\text{p}K_{\text{a}1} = 7.68$  and  $\text{p}K_{\text{a}2} = 11.29$ . Telluric acid can be prepared by hydrolysis of tellurium hexafluoride according to the equation



Tellurium hexafluoride can be prepared by the reaction of elemental tellurium with fluorine gas:



If a cubic block of tellurium (density = 6.240 g/cm<sup>3</sup>) measuring 0.545 cm on edge is allowed to react with 2.34 L of fluorine gas at 1.06 atm and 25°C, what is the pH of a solution of  $\text{Te(OH)}_6$  formed by dissolving the isolated  $\text{TeF}_6(g)$  in 115 mL of water?

## Marathon Problem

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

- 75.** Captain Kirk has set a trap for the Klingons who are threatening an innocent planet. He has sent small groups of fighter rockets to sites that are invisible to Klingon radar and put a decoy in the

open. He calls this the “fishhook” strategy. Mr. Spock has sent a coded message to the chemists on the fighters to tell the ships what to do next. The outline of the message is

(1)	(2)	(3)	(4)	(5)	(6)
(7)	(8)	(9)	(10)	(11)	(12)

Fill in the blanks of the message using the following clues.

- (1) Symbol of the halogen whose hydride has the second highest boiling point in the series of HX compounds that are hydrogen halides.
- (2) Symbol of the halogen that is the only hydrogen halide, HX, that is a weak acid in aqueous solution.
- (3) Symbol of the element whose existence on the sun was known before its existence on earth was discovered.
- (4) Symbol of the element whose presence can interfere with the qualitative analysis for  $\text{Pb}^{2+}$ ,  $\text{Hg}_2^{2+}$ , and  $\text{Ag}^+$ . When chloride ions are added to an aqueous solution of this metal ion, a white precipitate forms with formula MOCl.
- (5) Symbol of the Group 6A element that, like selenium, is a semiconductor.
- (6) Symbol for the element known in rhombic and monoclinic forms.
- (7) Symbol for the element that exists as diatomic molecules in a yellow-green gas when not combined with another element; its silver, lead, and mercury(I) salts are white and insoluble in water.
- (8) Symbol for the most abundant element in and near the earth's crust.
- (9) Symbol for the element that seems to give some protection against cancer when a diet rich in this element is consumed.
- (10) Symbol for the only noble gas besides xenon that has been shown to form compounds under some circumstances (write the symbol backward and split the letters as shown).
- (11) Symbol for the toxic element that, like phosphorus and antimony, forms tetrameric molecules when uncombined with other elements (split the letters of the symbol as shown).
- (12) Symbol for the element that occurs as an inert component of air but is a very prominent part of fertilizers and explosives.



Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at [college.hmco.com/](http://college.hmco.com/) PIC/zumdahl7e.

# 21 Transition Metals and Coordination Chemistry

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Copper ore deposit in Namibia.

# T

Transition metals have many uses in our society. Iron is used for steel; copper for electrical wiring and water pipes; titanium for paint; silver for photographic paper; manganese, chromium, vanadium, and cobalt as additives to steel; platinum for industrial and automotive catalysts; and so on.

One indication of the importance of transition metals is the great concern shown by the U.S. government for continuing the supply of these elements. In recent years the United States has been a net importer of about 60 “strategic and critical” minerals, including cobalt, manganese, platinum, palladium, and chromium. All these metals play a vital role in the U.S. economy and defense, and approximately 90% of the required amounts must be imported (see Table 21.1).

In addition to being important in industry, transition metal ions play a vital role in living organisms. For example, complexes of iron provide for the transport and storage of oxygen, molybdenum and iron compounds are catalysts in nitrogen fixation, zinc is found in more than 150 biomolecules in humans, copper and iron play a crucial role in the respiratory cycle, and cobalt is found in essential biomolecules such as vitamin B<sub>12</sub>.

In this chapter we explore the general properties of transition metals, paying particular attention to the bonding, structure, and properties of the complex ions of these metals.

## 21.1 The Transition Metals: A Survey

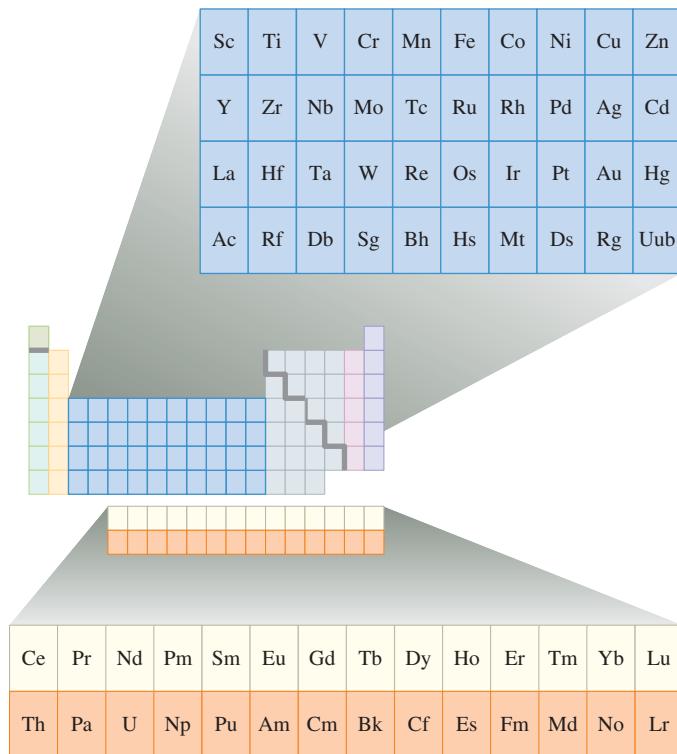
### General Properties

One striking characteristic of the representative elements is that their chemistry changes markedly across a given period as the number of valence electrons changes. The chemical similarities occur mainly within the vertical groups. In contrast, *the transition metals show great similarities within a given period as well as within a given vertical group*. This difference occurs because the last electrons added for transition metals are inner electrons: *d* electrons for the *d*-block transition metals and *f* electrons for the lanthanides and actinides. These inner *d* and *f* electrons cannot participate as easily in bonding as can the valence *s* and *p* electrons. Thus the chemistry of the transition elements is not affected as greatly by the gradual change in the number of electrons as is the chemistry of the representative elements.

Group designations are traditionally given on the periodic table for the *d*-block transition metals (see Fig. 21.1). However, these designations do not relate as directly to the

**TABLE 21.1 Some Transition Metals Important to the U.S. Economy and Defense**

Metal	Uses	Percentage Imported
Chromium	Stainless steel (especially for parts exposed to corrosive gases and high temperatures)	~91%
Cobalt	High-temperature alloys in jet engines, magnets, catalysts, drill bits	~93%
Manganese	Steelmaking	~97%
Platinum and palladium	Catalysts	~87%



chemical behavior of these elements as they do for the representative elements (the A groups), so we will not use them.

As a class, the transition metals behave as typical metals, possessing metallic luster and relatively high electrical and thermal conductivities. Silver is the best conductor of heat and electric current. However, copper is a close second, which explains copper's wide use in the electrical systems of homes and factories.

d-block transition elements										
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
	Ac†	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub

**FIGURE 21.1**

The position of the transition elements on the periodic table. The d-block elements correspond to filling the 3d, 4d, 5d, or 6d orbitals. The inner transition metals correspond to filling the 4f (lanthanides) or 5f (actinides) orbitals.

*Lanthanides	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
†Actinides	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr



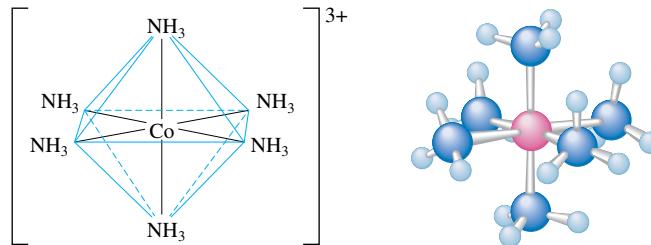
Sterling silver candlesticks and bowl from Japan.

Despite their many similarities, the transition metals do vary considerably in certain properties. For example, tungsten has a melting point of 3400°C and is used for filaments in light bulbs; mercury is a liquid at 25°C. Some transition metals such as iron and titanium are hard and strong and make very useful structural materials; others such as copper, gold, and silver are relatively soft. The chemical reactivity of the transition metals also varies significantly. Some react readily with oxygen to form oxides. Of these metals, some, such as chromium, nickel, and cobalt, form oxides that adhere tightly to the metallic surface, protecting the metal from further oxidation. Others, such as iron, form oxides that scale off, constantly exposing new metal to the corrosion process. On the other hand, the noble metals—primarily gold, silver, platinum, and palladium—do not readily form oxides.

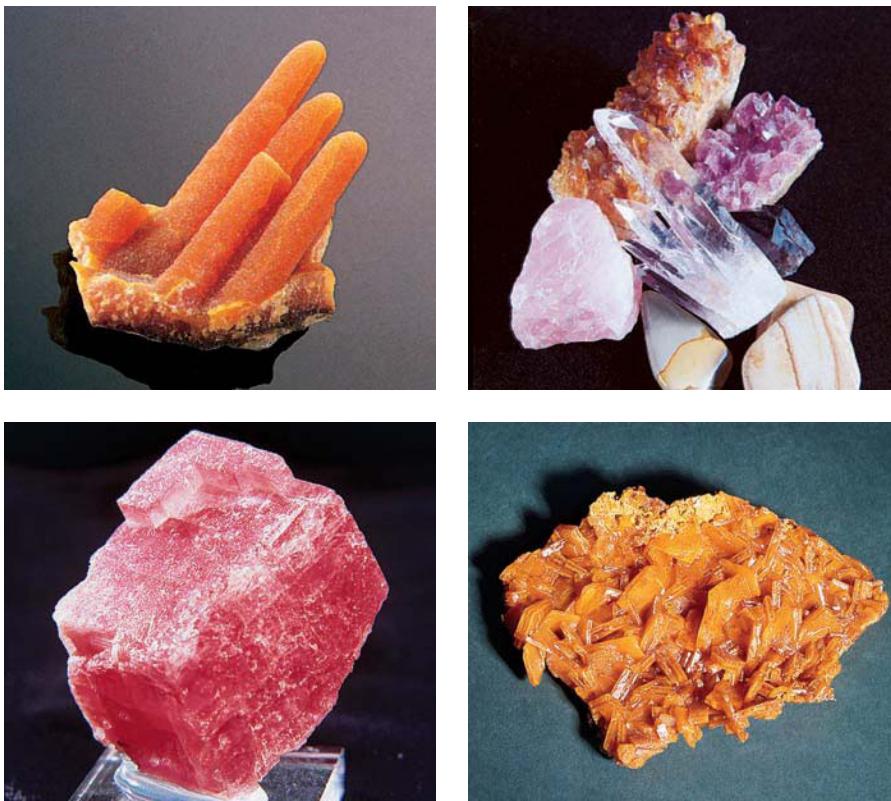
In forming ionic compounds with nonmetals, the transition metals exhibit several typical characteristics:

More than one oxidation state is often found. For example, iron combines with chlorine to form  $\text{FeCl}_2$  and  $\text{FeCl}_3$ .

The cations are often **complex ions**, species where *the transition metal ion is surrounded by a certain number of ligands* (molecules or ions that behave as Lewis bases). For example, the compound  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  contains the  $\text{Co}(\text{NH}_3)_6^{3+}$  cation and  $\text{Cl}^-$  anions.



The  $\text{Co}(\text{NH}_3)_6^{3+}$  ion



(clockwise from upper left) Calcite stalactites colored by traces of iron. Quartz is often colored by the presence of transition metals such as Mn, Fe, and Ni. Wulfenite contains  $\text{PbMoO}_4$ . Rhodochrosite is a mineral containing  $\text{MnCO}_3$ .

Most compounds are colored, because the transition metal ion in the complex ion can absorb visible light of specific wavelengths.

Many compounds are paramagnetic (they contain unpaired electrons).

In this chapter we will concentrate on the **first-row transition metals** (scandium through zinc) because they are representative of the other transition series and because they have great practical significance. Some important properties of these elements are summarized in Table 21.2 and are discussed in the next section.

## Electron Configurations

The electron configurations of the first-row transition metals were discussed in Section 7.11. The  $3d$  orbitals begin to fill after the  $4s$  orbital is complete, that is, after calcium ( $[\text{Ar}]4s^2$ ). The first transition metal, *scandium*, has one electron in the  $3d$  orbitals; the second, *titanium*, has two; and the third, *vanadium*, has three. We would expect *chromium*, the fourth transition metal, to have the electron configuration  $[\text{Ar}]4s^23d^4$ . However, the actual configuration is  $[\text{Ar}]4s^13d^5$ , which shows a half-filled  $4s$  orbital and a half-filled set of  $3d$  orbitals (one electron in each of the five  $3d$  orbitals). It is tempting to say that the configuration results because half-filled “shells” are especially stable. Although there are some reasons to think that this explanation might be valid, it is an oversimplification. For instance, *tungsten*, which is in the same vertical group as chromium, has the configuration  $[\text{Xe}]6s^24f^{14}5d^4$ , where half-filled  $s$  and  $d$  shells are not found. There are several similar cases.

Basically, the chromium configuration occurs because the energies of the  $3d$  and  $4s$  orbitals are very similar for the first-row transition elements. We saw in Section 7.11 that when electrons are placed in a set of degenerate orbitals, they first occupy each orbital



(from left to right) Aqueous solutions containing the metal ions  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Ni}^{2+}$ .

**TABLE 21.2 Selected Properties of the First-Row Transition Metals**

	Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc
Atomic number	21	22	23	24	25	26	27	28	29	30
Electron configuration*	$4s^23d^1$	$4s^23d^2$	$4s^23d^3$	$4s^13d^5$	$4s^23d^5$	$4s^23d^6$	$4s^23d^7$	$4s^23d^8$	$4s^13d^{10}$	$4s^23d^{10}$
Atomic radius (pm)	162	147	134	130	135	126	125	124	128	138
Ionization energies (eV/atom)										
First	6.54	6.82	6.74	6.77	7.44	7.87	7.86	7.64	7.73	9.39
Second	12.80	13.58	14.65	16.50	15.64	16.18	17.06	18.17	20.29	17.96
Third	24.76	27.49	29.31	30.96	33.67	30.65	33.50	35.17	36.83	39.72
Reduction potential† (V)	-2.08	-1.63	-1.2	-0.91	-1.18	-0.44	-0.28	-0.23	+0.34	-0.76
Common oxidation states	+3	+2,+3, +4	+2,+3, +4,+5	+2,+3, +6	+2,+3, +4,+7	+2,+3	+2,+3	+2	+1,+2	+2
Melting point (°C)	1397	1672	1710	1900	1244	1530	1495	1455	1083	419
Density (g/cm³)	2.99	4.49	5.96	7.20	7.43	7.86	8.9	8.90	8.92	7.14
Electrical conductivity‡	—	2	3	10	2	17	24	24	97	27

\*Each atom has an argon inner-core configuration.

†For the reduction process  $M^{2+} + 2e^- \rightarrow M$  (except for scandium, where the ion is  $Sc^{3+}$ ).

‡Compared with an arbitrarily assigned value of 100 for silver.

Chromium has the electron configuration  $[Ar]4s^13d^5$ .

A set of orbitals with the same energy is said to be *degenerate*.

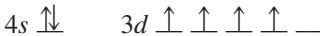
Copper has the electron configuration  $[Ar]4s^13d^{10}$ .

In transition metal ions, the  $3d$  orbitals are lower in energy than the  $4s$  orbitals.

singly to minimize electron repulsions. Since the  $4s$  and  $3d$  orbitals are virtually degenerate in the chromium atom, we would expect the configuration



rather than



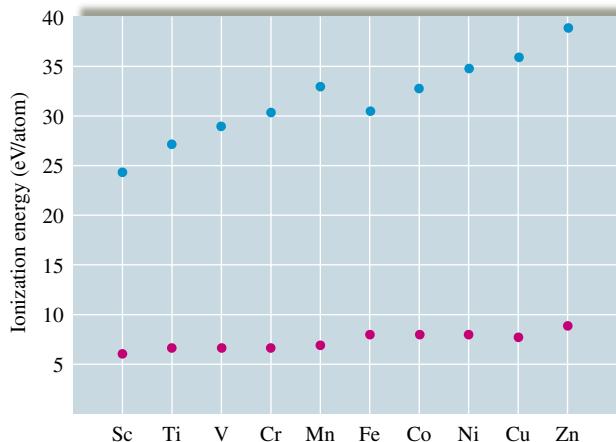
since the second arrangement has greater electron–electron repulsions and thus a higher energy.

The only other unexpected configuration among the first-row transition metals is that of copper, which is  $[Ar]4s^13d^{10}$  rather than the expected  $[Ar]4s^23d^9$ .

In contrast to the neutral transition metals, where the  $3d$  and  $4s$  orbitals have very similar energies, the *energy of the  $3d$  orbitals in transition metal ions is significantly less than that of the  $4s$  orbital*. This means that the electrons remaining after the ion is formed occupy the  $3d$  orbitals, since they are lower in energy. *First-row transition metal ions do not have  $4s$  electrons*. For example, manganese has the configuration  $[Ar]4s^23d^5$ , while that of  $Mn^{2+}$  is  $[Ar]3d^5$ . The neutral titanium atom has the configuration  $[Ar]4s^23d^2$ , while that of  $Ti^{3+}$  is  $[Ar]3d^1$ .

## Oxidation States and Ionization Energies

The transition metals can form a variety of ions by losing one or more electrons. The common oxidation states of these elements are shown in Table 21.2. Note that for the

**FIGURE 21.2**

Plots of the first (red dots) and third (blue dots) ionization energies for the first-row transition metals.

first five metals the maximum possible oxidation state corresponds to the loss of all the 4s and 3d electrons. For example, the maximum oxidation state of chromium ( $[Ar]4s^13d^5$ ) is +6. Toward the right end of the period, the maximum oxidation states are not observed; in fact, the  $2+$  ions are the most common. The higher oxidation states are not seen for these metals because the 3d orbitals become lower in energy as the nuclear charge increases, and the electrons become increasingly difficult to remove. From Table 21.2 we see that ionization energy increases gradually going from left to right across the period. However, the third ionization energy (when an electron is removed from a 3d orbital) increases faster than the first ionization energy, clear evidence of the significant decrease in the energy of the 3d orbitals going across the period (see Fig. 21.2).

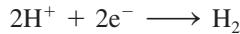
### Standard Reduction Potentials

When a metal acts as a *reducing agent*, the half-reaction is

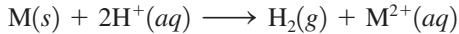


This is the reverse of the conventional listing for half-reactions in tables. Thus, to rank the transition metals in order of reducing ability, it is most convenient to reverse the reactions and the signs given in Table 21.2. The metal with the most positive potential is then the best reducing agent. The transition metals are listed in order of reducing ability in Table 21.3.

Since  $\mathcal{E}^\circ$  is zero for the process



all the metals except copper can reduce  $H^+$  ions to hydrogen gas in 1 M aqueous solutions of strong acid:



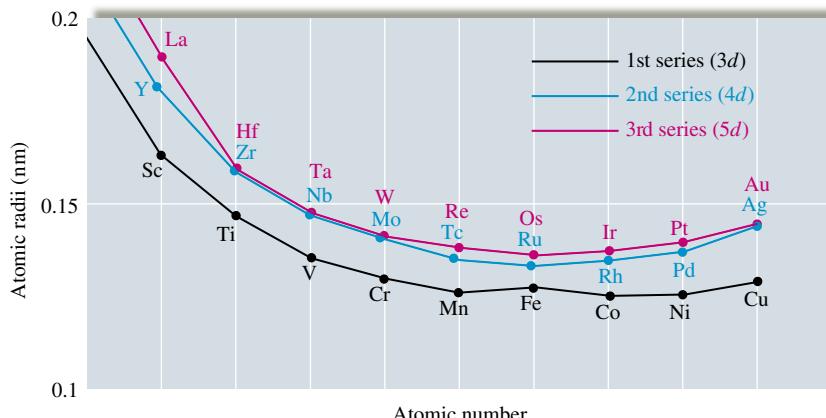
As Table 21.3 shows, the reducing abilities of the first-row transition metals generally decrease going from left to right across the period. Only chromium and zinc do not follow this trend.

### The 4d and 5d Transition Series

In comparing the 3d, 4d, and 5d transition series, it is instructive to consider the atomic radii of these elements (Fig. 21.3). Note that there is a general, although not regular,

**TABLE 21.3 Relative Reducing Abilities of the First-Row Transition Metals in Aqueous Solution**

Reaction	Potential (V)	Reducing ability ↑
$Sc \rightarrow Sc^{3+} + 3e^-$	2.08	
$Ti \rightarrow Ti^{2+} + 2e^-$	1.63	
$V \rightarrow V^{2+} + 2e^-$	1.2	
$Mn \rightarrow Mn^{2+} + 2e^-$	1.18	
$Cr \rightarrow Cr^{2+} + 2e^-$	0.91	
$Zn \rightarrow Zn^{2+} + 2e^-$	0.76	
$Fe \rightarrow Fe^{2+} + 2e^-$	0.44	
$Co \rightarrow Co^{2+} + 2e^-$	0.28	
$Ni \rightarrow Ni^{2+} + 2e^-$	0.23	
$Cu \rightarrow Cu^{2+} + 2e^-$	-0.34	

**FIGURE 21.3**

Atomic radii of the 3d, 4d, and 5d transition series.

decrease in size going from left to right for each of the series. Also note that although there is a significant increase in radius in going from the 3d to the 4d metals, the 4d and 5d metals are remarkably similar in size. This latter phenomenon is the result of the **lanthanide contraction**. In the **lanthanide series**, consisting of the elements between lanthanum and hafnium (see Fig. 21.1), electrons are filling the 4f orbitals. Since the 4f orbitals are buried in the interior of these atoms, the additional electrons do not add to the atomic size. In fact, the increasing nuclear charge (remember that a proton is added to the nucleus for each electron) causes the radii of the lanthanide elements to decrease significantly going from left to right. This lanthanide contraction just offsets the normal increase in size due to going from one principal quantum level to another. Thus the 5d elements, instead of being significantly larger than the 4d elements, are almost identical to them in size. This leads to a great similarity in the chemistry of the 4d and 5d elements in a given vertical group. For example, the chemical properties of hafnium and zirconium are remarkably similar, and they always occur together in nature. Their separation, which is probably more difficult than the separation of any other pair of elements, often requires fractional distillation of their compounds.

In general, the differences between the 4d and 5d elements in a group increase gradually going from left to right. For example, niobium and tantalum are also quite similar, but less so than zirconium and hafnium.

Although generally less well known than the 3d elements, the 4d and 5d transition metals have certain very useful properties. For example, zirconium and zirconium oxide ( $\text{ZrO}_2$ ) have great resistance to high temperatures and are used, along with niobium and molybdenum alloys, for space vehicle parts that are exposed to high temperatures during reentry into the earth's atmosphere. Niobium and molybdenum are also important alloying materials for certain types of steel. Tantalum, which has a high resistance to attack by body fluids, is often used for replacement of bones. The *platinum group metals*—ruthenium, osmium, rhodium, iridium, palladium, and platinum—are all quite similar and are widely used as catalysts for many types of industrial processes.

Niobium was originally called *columbium* and is still occasionally referred to by that name.

## 21.2 The First-Row Transition Metals

We have seen that the transition metals are similar in many ways but also show important differences. We will now explore some of the specific properties of each of the 3d transition metals.

*Scandium* is a rare element that exists in compounds mainly in the +3 oxidation state—for example, in  $\text{ScCl}_3$ ,  $\text{Sc}_2\text{O}_3$ , and  $\text{Sc}_2(\text{SO}_4)_3$ . The chemistry of scandium strongly resembles that of the lanthanides, with most of its compounds being colorless and



An X ray of a patient who has had a hip replacement. The normal hip joint is on the left; the hip joint constructed from tantalum metal is on the right.



$\text{Ti}(\text{H}_2\text{O})_6^{3+}$  is purple in solution.

The manufacture of sulfuric acid was discussed at the end of Chapter 3.

The most common oxidation state for vanadium is +5.

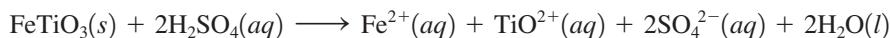
diamagnetic. This is not surprising; as we will see in Section 21.6, the color and magnetism of transition metal compounds usually arise from the *d* electrons on the metal ion, and  $\text{Sc}^{3+}$  has no *d* electrons. Scandium metal, which can be prepared by electrolysis of molten  $\text{ScCl}_3$ , is not widely used because of its rarity, but it is found in some electronic devices, such as high-intensity lamps.

Titanium is widely distributed in the earth's crust (0.6% by mass). Because of its relatively low density and high strength, titanium is an excellent structural material, especially in jet engines, where light weight and stability at high temperatures are required. Nearly 5000 kg of titanium alloys is used in each engine of a Boeing 747 jetliner. In addition, the resistance of titanium to chemical attack makes it a useful material for pipes, pumps, and reaction vessels in the chemical industry.

The most familiar compound of titanium is no doubt responsible for the white color of this paper. Titanium dioxide, or more correctly, *titanium(IV) oxide* ( $\text{TiO}_2$ ), is a highly opaque substance used as the white pigment in paper, paint, linoleum, plastics, synthetic fibers, whitewall tires, and cosmetics (sunscreens, for example). Approximately 700,000 tons is used annually in these and other products. Titanium(IV) oxide is widely dispersed in nature, but the main ores are rutile (impure  $\text{TiO}_2$ ) and ilmenite ( $\text{FeTiO}_3$ ). Rutile is processed by treatment with chlorine to form volatile  $\text{TiCl}_4$ , which is separated from the impurities and burned to form  $\text{TiO}_2$ :



Ilmenite is treated with sulfuric acid to form a soluble sulfate:



When this aqueous mixture is allowed to stand, under vacuum, solid  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  forms first and is removed. The mixture is then heated, and the insoluble titanium(IV) oxide hydrate ( $\text{TiO}_2 \cdot \text{H}_2\text{O}$ ) forms. The water of hydration is driven off by heating to form pure  $\text{TiO}_2$ :



In its compounds, titanium is most often found in the +4 oxidation state. Examples are  $\text{TiO}_2$  and  $\text{TiCl}_4$ , the latter a colorless liquid ( $\text{bp} = 137^\circ\text{C}$ ) that fumes in moist air to produce  $\text{TiO}_2$ :



Titanium(III) compounds can be produced by reduction of the +4 state. In aqueous solution,  $\text{Ti}^{3+}$  exists as the purple  $\text{Ti}(\text{H}_2\text{O})_6^{3+}$  ion, which is slowly oxidized to titanium(IV) by air. Titanium(II) is not stable in aqueous solution but does exist in the solid state in compounds such as  $\text{TiO}$  and the dihalides of general formula  $\text{TiX}_2$ .

Vanadium is widely spread throughout the earth's crust (0.02% by mass). It is used mostly in alloys with other metals such as iron (80% of vanadium is used in steel) and titanium. Vanadium(V) oxide ( $\text{V}_2\text{O}_5$ ) is used as an industrial catalyst in the production of materials such as sulfuric acid.

Pure vanadium can be obtained from the electrolytic reduction of fused salts, such as  $\text{VCl}_2$ , to produce a metal similar to titanium that is steel gray, hard, and corrosion resistant. Often the pure element is not required for alloying. For example, *ferrovanadium*, produced by the reduction of a mixture of  $\text{V}_2\text{O}_5$  and  $\text{Fe}_2\text{O}_3$  with aluminum, is added to iron to form *vanadium steel*, a hard steel used for engine parts and axles.

The principal oxidation state of vanadium is +5, found in compounds such as the orange  $\text{V}_2\text{O}_5$  ( $\text{mp} = 650^\circ\text{C}$ ) and the colorless  $\text{VF}_5$  ( $\text{mp} = 19.5^\circ\text{C}$ ). The oxidation states from +5 to +2 all exist in aqueous solution (see Table 21.4). The higher oxidation states,



## CHEMICAL IMPACT

### Titanium Dioxide—Miracle Coating

**T**itanium dioxide, more properly called titanium(IV) oxide, is a very important material. Approximately 1.5 million tons of the substance is produced each year in the United States for use as a pigment in paper and paints and as a component of sunscreens.

In recent years, however, scientists have found a new use for  $\text{TiO}_2$ . When surfaces are coated with titanium dioxide, they become resistant to dirt and bacteria. For example, the Pilkington Glass Company is now making glass coated with  $\text{TiO}_2$  that cleans itself. All the glass needs is sun and rain to keep itself clean. The self-cleaning action arises from two effects. First, the coating of  $\text{TiO}_2$  acts as a catalyst in the presence of ultraviolet (UV) light to break down carbon-based pollutants to carbon dioxide and water. Second, because  $\text{TiO}_2$  reduces surface tension, rainwater “sheets” instead of forming droplets on the glass, thereby washing away the grime on the surface of the glass. Although this self-cleaning glass is bad news for window washers, it could save millions of dollars in maintenance costs for owners of commercial buildings.

Because the  $\text{TiO}_2$ -treated glass requires UV light for its action, it does not work well for interior surfaces where UV light is present only in small amounts. However, a team of Japanese researchers has found that if the  $\text{TiO}_2$  coating is doped with nitrogen atoms, it will catalyze the breakdown of dirt in the presence of visible light as well as UV light. Studies also show that this N-doped  $\text{TiO}_2$  surface coating kills many types of bacteria in the presence of visible or ultraviolet light. This discovery could lead to products such as self-sterilizing bathroom tiles, counters, and toilets. In addition, because the  $\text{TiO}_2$  on the surface of glass has such a strong attraction for water molecules (greatly lowering the surface tension), water does not bead up to form droplets. Just as this effect produces sheeting action on exterior glass, so it prevents interior windows and mirrors from “fogging up.”

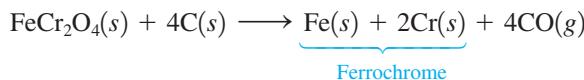
Titanium dioxide, a cheap and plentiful material, may prove to be worth its weight in gold as a surface coating.

**TABLE 21.4 Oxidation States and Species for Vanadium in Aqueous Solution**

Oxidation State of Vanadium	Species in Aqueous Solution
+5	$\text{VO}_2^+$ (yellow)
+4	$\text{VO}^{2+}$ (blue)
+3	$\text{V}^{3+}(aq)$ (blue-green)
+2	$\text{V}^{2+}(aq)$ (violet)

+5 and +4, do not exist as hydrated ions of the type  $\text{V}^{n+}(aq)$  because the highly charged ion causes the attached water molecules to be very acidic. The  $\text{H}^+$  ions are lost to give the oxycations  $\text{VO}_2^+$  and  $\text{VO}^{2+}$ . The hydrated  $\text{V}^{3+}$  and  $\text{V}^{2+}$  ions are easily oxidized and thus can function as reducing agents in aqueous solution.

Although *chromium* is relatively rare, it is a very important industrial material. The chief ore of chromium is chromite ( $\text{FeCr}_2\text{O}_4$ ), which can be reduced by carbon to give *ferrochrome*,

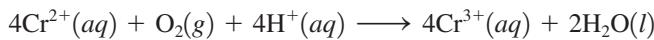


**TABLE 21.5 Typical Chromium Compounds**

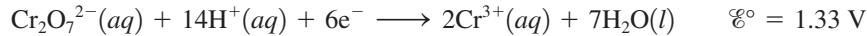
Oxidation State of Chromium	Examples of Compounds (X = halogen)
+2	$\text{CrX}_2$
+3	$\text{CrX}_3$
	$\text{Cr}_2\text{O}_3$ (green)
	$\text{Cr(OH)}_3$ (blue-green)
+6	$\text{K}_2\text{Cr}_2\text{O}_7$ (orange)
	$\text{Na}_2\text{CrO}_4$ (yellow)
	$\text{CrO}_3$ (red)

which can be added directly to iron in the steelmaking process. Chromium metal, which is often used to plate steel, is hard and brittle and maintains a bright surface by developing a tough invisible oxide coating.

Chromium commonly forms compounds in which it has the oxidation state +2, +3, or +6, as shown in Table 21.5. The  $\text{Cr}^{2+}$  (chromous) ion is a powerful reducing agent in aqueous solution. In fact, traces of  $\text{O}_2$  in other gases can be removed by bubbling through a  $\text{Cr}^{2+}$  solution:



The chromium(VI) species are excellent oxidizing agents, especially in acidic solution, where chromium(VI) as the dichromate ion ( $\text{Cr}_2\text{O}_7^{2-}$ ) is reduced to the  $\text{Cr}^{3+}$  ion:





## CHEMICAL IMPACT

### Titanium Makes Great Bicycles

One of the most interesting characteristics of the world of bicycling is the competition among various frame materials. Bicycle frames are now built from steel, aluminum, carbon fiber composites, and titanium, with each material having advantages and disadvantages. Steel is strong, economical, adaptable, and (unfortunately) "rustable." Aluminum is light and stiff but has relatively low fatigue limits (resistance to repeated stresses). Carbon fiber composites have amazing strength-to-mass ratios and have shock- and vibration-dampening properties superior to any metal; however, they are very expensive. Titanium has a density approximately 43% less than that of steel, a yield strength (when alloyed with metals such as aluminum and tin) that is 30% greater than that of steel, an extraordinary resistance to fatigue, and a high resistance to corrosion, but it is expensive and difficult to work.

Of all these materials, titanium gives the bicycle that fanatics seem to love the most. After their first ride on a bicycle with a titanium frame, most experienced cyclists find themselves shaking their heads and searching hard for the

right words to describe the experience. Typically, the word "magic" is used a great deal in the ensuing description.

The magic of titanium results from its combination of toughness, stretchability, and resilience. A bicycle that is built stiff to resist pedaling loads usually responds by giving a harsh, uncomfortable ride. A titanium bike is very stiff against high pedaling torques, but it seems to transmit much less road shock than bikes made of competitive materials. Why titanium excels in dampening vibrations is not entirely clear. Despite titanium's significantly lower density than steel, shock waves travel more slowly in titanium than in steel. Whatever the explanation for its shock-absorbing abilities, titanium provides three things that cyclists find crucial: light weight, stiffness, and a smooth ride—magic.

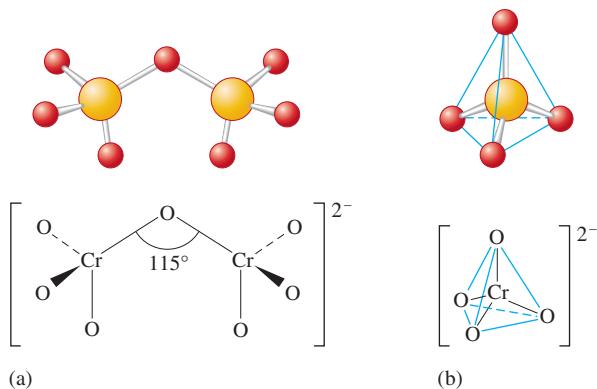
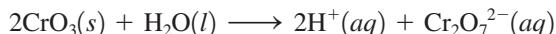
Titanium is quite abundant in the earth's crust, ranking ninth of all the elements and second among the transition elements. The metallurgy of titanium presents special challenges. Carbon, the reducing agent most commonly used to obtain metals from their oxide ores, cannot be used because it forms intractable interstitial carbides with titanium. These

The oxidizing ability of the dichromate ion is strongly pH-dependent, increasing as  $[H^+]$  increases, as predicted by Le Châtelier's principle. In basic solution, chromium(VI) exists as the chromate ion, a much less powerful oxidizing agent:



The structures of the  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{CrO}_4^{2-}$  ions are shown in Fig. 21.4.

Red chromium(VI) oxide ( $\text{CrO}_3$ ) dissolves in water to give a strongly acidic, red-orange solution:



**FIGURE 21.4**

The structures of the chromium(VI) anions: (a)  $\text{Cr}_2\text{O}_7^{2-}$ , which exists in acidic solution, and (b)  $\text{CrO}_4^{2-}$ , which exists in basic solution.

carbides are extraordinarily hard and have melting points close to 3000°C. However, if chlorine gas is used in conjunction with carbon to treat the ore, volatile TiCl<sub>4</sub> is formed, which can be distilled off and then reduced with magnesium or sodium at approximately 1000°C to form a titanium “sponge.” This sponge is then ground up, cleaned with aqua regia (a 1:3 mixture of concentrated HNO<sub>3</sub> and concentrated HCl), melted under a blanket of inert gas (to prevent reaction with oxygen), and cast into ingots. Titanium, a lustrous, silvery metal with a high melting point (1667°C), crystallizes in a hexagonal closest packed structure. Because titanium tends to become quite brittle when trace impurities such as C, N, and O are present, it must be fabricated with great care.

Titanium’s unusual ability to stretch makes it hard to machine. It tends to push away even from a very sharp cutting blade, giving a rather unpredictable final dimension. Also, because titanium is embrittled by reaction with oxygen, all welding operations must be carried out under a shielding gas such as argon.

However, the bicycle that results is worth all these difficulties. One woman described a titanium bicycle as “the one God rides on Sunday.”



A titanium bicycle.

It is possible to precipitate bright orange dichromate salts, such as K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, from these solutions. When made basic, the solution turns yellow, and chromate salts such as Na<sub>2</sub>CrO<sub>4</sub> can be obtained. A mixture of chromium(VI) oxide and concentrated sulfuric acid, commonly called *cleaning solution*, is a powerful oxidizing medium that can remove organic materials from analytical glassware, yielding a very clean surface.

Manganese is relatively abundant (0.1% of the earth’s crust), although no significant sources are found in the United States. The most common use of manganese is in the production of an especially hard steel used for rock crushers, bank vaults, and armor plate. One interesting source of manganese is from *manganese nodules* found on the ocean floor. These roughly spherical “rocks” contain mixtures of manganese and iron oxides as well as smaller amounts of other metals such as cobalt, nickel, and copper. Apparently, the nodules were formed at least partly by the action of marine organisms. Because of the abundance of these nodules, there is much interest in developing economical methods for their recovery and processing.

Manganese can exist in all oxidation states from +2 to +7, although +2 and +7 are the most common. Manganese(II) forms an extensive series of salts with all the common anions. In aqueous solution Mn<sup>2+</sup> forms Mn(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>, which has a light pink color. Manganese(VII) is found in the intensely purple permanganate ion (MnO<sub>4</sub><sup>-</sup>). Widely used as an analytical reagent in acidic solution, the MnO<sub>4</sub><sup>-</sup> ion behaves as a strong oxidizing agent, with the manganese becoming Mn<sup>2+</sup>:



Several typical compounds of manganese are shown in Table 21.6.

**TABLE 21.6 Some Compounds of Manganese in Its Most Common Oxidation States**

Oxidation State of Manganese	Examples of Compounds
+2	Mn(OH) <sub>2</sub> (pink) MnS (salmon) MnSO <sub>4</sub> (reddish) MnCl <sub>2</sub> (pink)
+4	MnO <sub>2</sub> (dark brown)
+7	KMnO <sub>4</sub> (purple)

**TABLE 21.7 Typical Compounds of Iron**

Oxidation State of Iron	Examples of Compounds
+2	FeO (black) FeS (brownish black) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (green) $\text{K}_4\text{Fe}(\text{CN})_6$ (yellow)
+3	$\text{FeCl}_3$ (brownish black) $\text{Fe}_2\text{O}_3$ (reddish brown) $\text{K}_3\text{Fe}(\text{CN})_6$ (red) $\text{Fe}(\text{SCN})_3$ (red) $\text{Fe}_3\text{O}_4$ (black) $\text{KFe}[\text{Fe}(\text{CN})_6]$ (deep blue, “Prussian blue”)
+2, +3 (mixture)	

*Iron* is the most abundant heavy metal (4.7% of the earth’s crust) and the most important to our civilization. It is a white, lustrous, not particularly hard metal that is very reactive toward oxidizing agents. For example, in moist air it is rapidly oxidized by oxygen to form rust, a mixture of iron oxides.

The chemistry of iron mainly involves its +2 and +3 oxidation states. Typical compounds are shown in Table 21.7. In aqueous solutions iron(II) salts are generally light green because of the presence of  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ . Although the  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  ion is colorless, aqueous solutions of iron(III) salts are usually yellow to brown in color due to the presence of  $\text{Fe}(\text{OH})(\text{H}_2\text{O})_5^{2+}$ , which results from the acidity of  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  ( $K_a = 6 \times 10^{-3}$ ):



Although *cobalt* is relatively rare, it is found in ores such as smaltite ( $\text{CoAs}_2$ ) and cobaltite ( $\text{CoAsS}$ ) in large enough concentrations to make its production economically feasible. Cobalt is a hard, bluish white metal mainly used in alloys such as stainless steel and stellite, an alloy of iron, copper, and tungsten that is used in surgical instruments.

The chemistry of cobalt involves mainly its +2 and +3 oxidation states, although compounds containing cobalt in the 0, +1, or +4 oxidation state are known. Aqueous solutions of cobalt(II) salts contain the  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  ion, which has a characteristic rose color. Cobalt forms a wide variety of coordination compounds, many of which will be discussed in later sections of this chapter. Some typical cobalt compounds are shown in Table 21.8.

*Nickel*, which ranks twenty-fourth in elemental abundance in the earth’s crust, is found in ores, where it is combined mainly with arsenic, antimony, and sulfur. Nickel metal, a silvery white substance with high electrical and thermal conductivities, is quite resistant to corrosion and is often used for plating more active metals. Nickel is also widely used in the production of alloys such as steel.

Nickel in compounds is almost exclusively in the +2 oxidation state. Aqueous solutions of nickel(II) salts contain the  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  ion, which has a characteristic emerald green color. Coordination compounds of nickel(II) will be discussed later in this chapter. Some typical nickel compounds are shown in Table 21.9.



An aqueous solution containing the  $\text{Ni}^{2+}$  ion.

**TABLE 21.8 Typical Compounds of Cobalt**

Oxidation State	Examples of Compounds
+2	$\text{CoSO}_4$ (dark blue) $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$ (pink) $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ (red) $\text{CoS}$ (black) $\text{CoO}$ (greenish brown)
+3	$\text{CoF}_3$ (brown) $\text{Co}_2\text{O}_3$ (charcoal) $\text{K}_3[\text{Co}(\text{CN})_6]$ (yellow) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (yellow)

**TABLE 21.9 Typical Compounds of Nickel**

Oxidation State of Nickel	Examples of Compounds
+2	$\text{NiCl}_2$ (yellow) $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ (green) $\text{NiO}$ (greenish black) $\text{NiS}$ (black) $[\text{Ni}(\text{H}_2\text{O})_6]\text{SO}_4$ (green) $[\text{Ni}(\text{NH}_3)_6](\text{NO}_3)_2$ (blue)

**TABLE 21.10 Alloys Containing Copper**

Alloy	Composition (% by mass in parentheses)
Brass	Cu (20–97), Zn (2–80), Sn (0–14), Pb (0–12), Mn (0–25)
Bronze	Cu (50–98), Sn (0–35), Zn (0–29), Pb (0–50), P (0–3)
Sterling silver	Cu (7.5), Ag (92.5)
Gold (18-karat)	Cu (5–15), Au (75), Ag (10–20)
Gold (14-karat)	Cu (12–28), Au (58), Ag (4–30)

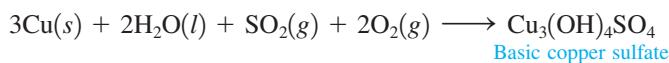
Copper roofs and bronze statues, such as the Statue of Liberty, turn green in air because  $\text{Cu}_3(\text{OH})_4\text{SO}_4$  and  $\text{Cu}_4(\text{OH})_6\text{SO}_4$  form.

**TABLE 21.11 Typical Compounds of Copper**

Oxidation State of Copper	Examples of Compounds
+1	$\text{Cu}_2\text{O}$ (red) $\text{Cu}_2\text{S}$ (black) $\text{CuCl}$ (white)
+2	$\text{CuO}$ (black) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (blue) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (green) $[\text{Cu}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ (blue)

*Copper*, widely distributed in nature in ores containing sulfides, arsenides, chlorides, and carbonates, is valued for its high electrical conductivity and its resistance to corrosion. It is widely used for plumbing, and 50% of all copper produced annually is used for electrical applications. Copper is a major constituent in several well-known alloys (see Table 21.10).

Although copper is not highly reactive (it will not reduce  $\text{H}^+$  to  $\text{H}_2$ , for example), the reddish metal does slowly corrode in air, producing the characteristic green *patina* consisting of basic copper sulfate



and other similar compounds.

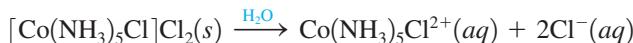
The chemistry of copper principally involves the +2 oxidation state, but many compounds containing copper(I) are also known. Aqueous solutions of copper(II) salts are a characteristic bright blue color due to the presence of the  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  ion. Table 21.11 lists some typical copper compounds.

Although trace amounts of copper are essential for life, copper in large amounts is quite toxic; copper salts are used to kill bacteria, fungi, and algae. For example, paints containing copper are used on ship hulls to prevent fouling by marine organisms.

Widely dispersed in the earth's crust, *zinc* is mainly refined from sphalerite ( $\text{ZnS}$ ), which often occurs with galena ( $\text{PbS}$ ). Zinc is a white, lustrous, very active metal that behaves as an excellent reducing agent and tarnishes rapidly. About 90% of the zinc produced is used for galvanizing steel. Zinc forms colorless salts in the +2 oxidation state.

## 21.3 Coordination Compounds

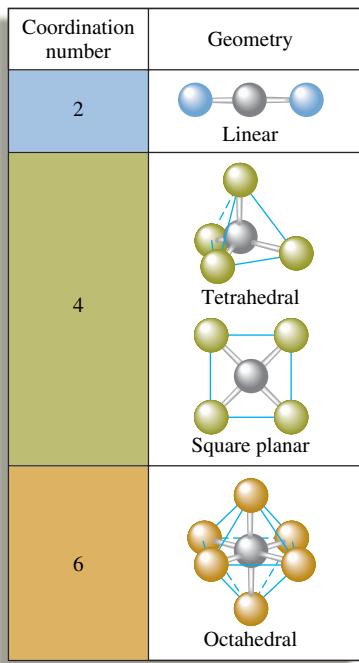
Transition metal ions characteristically form coordination compounds, which are usually colored and often paramagnetic. A **coordination compound** typically consists of a *complex ion*, a transition metal ion with its attached ligands (see Section 15.8), and **counterions**, anions or cations as needed to produce a compound with no net charge. The substance  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  is a typical coordination compound. The brackets indicate the composition of the complex ion, in this case  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ , and the two  $\text{Cl}^-$  counterions are shown outside the brackets. Note that in this compound one  $\text{Cl}^-$  acts as a ligand along with the five  $\text{NH}_3$  molecules. In the solid state this compound consists of the large  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$  cations and twice as many  $\text{Cl}^-$  anions, all packed together as efficiently as possible. When dissolved in water, the solid behaves like any ionic solid; the cations and anions are assumed to separate and move about independently:



**TABLE 21.12** Typical Coordination Numbers for Some Common Metal Ions

$M^+$	Coordination Numbers	$M^{2+}$	Coordination Numbers	$M^{3+}$	Coordination Numbers
$Cu^+$	2, 4	$Mn^{2+}$	4, 6	$Sc^{3+}$	6
$Ag^+$	2	$Fe^{2+}$	6	$Cr^{3+}$	6
$Au^+$	2, 4	$Co^{2+}$	4, 6	$Co^{3+}$	6
		$Ni^{2+}$	4, 6		
		$Cu^{2+}$	4, 6	$Au^{3+}$	4
		$Zn^{2+}$	4, 6		

Coordination compounds have been known since about 1700, but their true nature was not understood until the 1890s when a young Swiss chemist named Alfred Werner (1866–1919) proposed that transition metal ions have two types of valence (combining ability). One type of valence, which Werner called the *secondary valence*, refers to the ability of a metal ion to bind to Lewis bases (ligands) to form complex ions. The other type, the *primary valence*, refers to the ability of the metal ion to form ionic bonds with oppositely charged ions. Thus Werner explained that the compound, originally written as  $CoCl_3 \cdot 5NH_3$ , was really  $[Co(NH_3)_5Cl]Cl_2$ , where the  $Co^{3+}$  ion has a primary valence of 3, satisfied by the three  $Cl^-$  ions, and a secondary valence of 6, satisfied by the six ligands (five  $NH_3$  and one  $Cl^-$ ). We now call the primary valence the **oxidation state** and the secondary valence the **coordination number**, which reflects the number of bonds formed between the metal ion and the ligands in the complex ion.



## Coordination Number

The number of bonds formed by metal ions to ligands in complex ions varies from two to eight depending on the size, charge, and electron configuration of the transition metal ion. As shown in Table 21.12, 6 is the most common coordination number, followed closely by 4, with a few metal ions showing a coordination number of 2. Many metal ions show more than one coordination number, and there is really no simple way to predict what the coordination number will be in a particular case. The typical geometries for the various common coordination numbers are shown in Fig. 21.5. Note that six ligands produce an octahedral arrangement around the metal ion. Four ligands can form either a tetrahedral or a square planar arrangement, and two ligands give a linear structure.

## Ligands

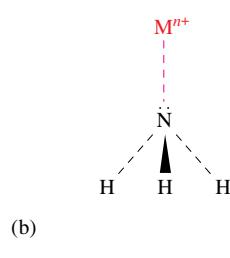
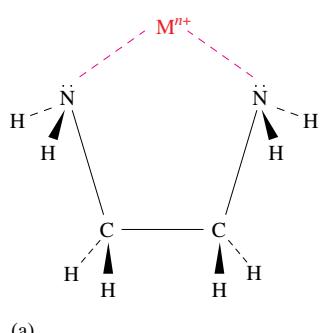
A **ligand** is a neutral molecule or ion having a lone electron pair that can be used to form a bond to a metal ion. The formation of a metal–ligand bond therefore can be described as the interaction between a Lewis base (the ligand) and a Lewis acid (the metal ion). The resulting bond is often called a **coordinate covalent bond**.

A ligand that can form one bond to a metal ion is called a **monodentate ligand**, or a **unidentate ligand** (from root words meaning “one tooth”). Examples of unidentate ligands are shown in Table 21.13.

Some ligands have more than one atom with a lone electron pair that can be used to bond to a metal ion. Such ligands are said to be **chelating ligands**, or **chelates** (from the

**FIGURE 21.5**

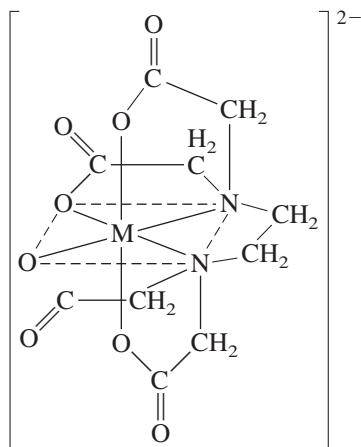
The ligand arrangements for coordination numbers 2, 4, and 6.

**FIGURE 21.6**

(a) The bidentate ligand ethylenediamine can bond to the metal ion through the lone pair on each nitrogen atom, thus forming two coordinate covalent bonds.  
 (b) Ammonia is a monodentate ligand.

**TABLE 21.13 Some Common Ligands**

Type	Examples			
Unidentate/monodentate	$\text{H}_2\text{O}$ $\text{NH}_3$	$\text{CN}^-$ $\text{NO}_2^-$ (nitrite)	$\text{SCN}^-$ (thiocyanate) $\text{OH}^-$	$\text{X}^-$ (halides)
Bidentate		Oxalate 	Ethylenediamine 	
Polydentate		Diethylenetriamine  Three coordinating atoms	Ethylenediaminetetraacetate  Six coordinating atoms	

**FIGURE 21.7**

The coordination of EDTA with a 2+ metal ion.

**TABLE 21.14 Names of Some Common Unidentate Ligands**

Neutral Molecules	
Aqua	H <sub>2</sub> O
Ammine	NH <sub>3</sub>
Methylamine	CH <sub>3</sub> NH <sub>2</sub>
Carbonyl	CO
Nitrosyl	NO
Anions	
Fluoro	F <sup>-</sup>
Chloro	Cl <sup>-</sup>
Bromo	Br <sup>-</sup>
Iodo	I <sup>-</sup>
Hydroxo	OH <sup>-</sup>
Cyano	CN <sup>-</sup>

**TABLE 21.15 Latin Names Used for Some Metal Ions in Anionic Complex Ions**

Metal	Name in an Anionic Complex
Iron	Ferrate
Copper	Cuprate
Lead	Plumbate
Silver	Argentate
Gold	Aurate
Tin	Stannate

**Sample Exercise 21.1**

\*In an older system the negatively charged ligands were named first, then neutral ligands, with positively charged ligands named last. We will follow the newer convention in this text.



(top) An aqueous solution of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ . (bottom) Solid  $\text{K}_3\text{Fe}(\text{CN})_6$ .

disregarding the prefix. Since the counterions are chloride ions, the compound is named as a chloride salt:



- b. First, we determine the oxidation state of the iron by considering the other charged species. The compound contains three  $\text{K}^+$  ions and six  $\text{CN}^-$  ions. Therefore, the iron must carry a charge of  $3+$ , giving a total of six positive charges to balance the six negative charges. The complex ion present is thus  $\text{Fe}(\text{CN})_6^{3-}$ . The cyanide ligands are each designated *cyan*, and the prefix *hexa-* indicates that six are present. Since the complex ion is an anion, we use the Latin name *ferrate*. The oxidation state is indicated by (III) at the end of the name. The anion name is therefore hexacyanoferrate(III). The cations are  $\text{K}^+$  ions, which are simply named potassium. Putting this together gives the name



(The common name of this compound is potassium ferricyanide.)

- c. We first determine the oxidation state of the iron by looking at the other charged species: four  $\text{NO}_2^-$  ions and one  $\text{SO}_4^{2-}$  ion. The ethylenediamine is neutral. Thus the two iron ions must carry a total positive charge of 6 to balance the six negative charges. This means that each iron has a  $+3$  oxidation state and is designated as iron(III).

Since the name ethylenediamine already contains *di*, we use *bis*- instead of *di*- to indicate the two en ligands. The name for  $\text{NO}_2^-$  as a ligand is *nitro*, and the prefix *di*- indicates the presence of two  $\text{NO}_2^-$  ligands. Since the anion is sulfate, the compound's name is



Because the complex ion is a cation, the Latin name for iron is not used.

*See Exercises 21.29 through 21.32.*

### Sample Exercise 21.2

### Naming Coordination Compounds II

Given the following systematic names, give the formula of each coordination compound.

- a. Triamminebromoplatinum(II) chloride  
b. Potassium hexafluorocobaltate(III)

#### Solution

- a. *Triammine* signifies three ammonia ligands, and *bromo* indicates one bromide ion as a ligand. The oxidation state of platinum is  $+2$ , as indicated by the Roman numeral II. Thus the complex ion is  $[\text{Pt}(\text{NH}_3)_3\text{Br}]^+$ . One chloride ion is needed to balance the  $1+$  charge of this cation. The formula of the compound is  $[\text{Pt}(\text{NH}_3)_3\text{Br}]\text{Cl}$ . Note that brackets enclose the complex ion.
- b. The complex ion contains six fluoride ligands attached to a  $\text{Co}^{3+}$  ion to give  $\text{CoF}_6^{3-}$ . Note that the *-ate* ending indicates that the complex ion is an anion. The cations are  $\text{K}^+$  ions, and three are required to balance the  $3-$  charge on the complex ion. Thus the formula is  $\text{K}_3[\text{CoF}_6]$ .

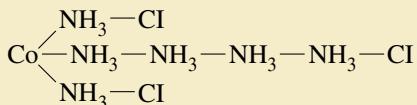
*See Exercises 21.33 and 21.34.*



## CHEMICAL IMPACT

### Alfred Werner: Coordination Chemist

**D**uring the early and middle parts of the nineteenth century, chemists prepared a large number of colored compounds containing transition metals and other substances such as ammonia, chloride ion, cyanide ion, and water. These compounds were very interesting to chemists who were trying to understand the nature of bonding (Dalton's atomic theory of 1808 was very new at this time), and many theories were suggested to explain these substances. The most widely accepted early theory was the *chain theory*, championed by Sophus Mads Jorgensen (1837–1914), professor of chemistry at the University of Copenhagen. The chain theory got its name from the postulate that metal ammine\* complexes contain chains of  $\text{NH}_3$  molecules. For example, Jorgensen proposed the structure



for the compound  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ . In the late nineteenth century this theory was used in classrooms around the world to explain the nature of metal–ammine compounds.

However, in 1890, a young Swiss chemist named Alfred Werner, who had just obtained a Ph.D. in the field of organic chemistry, became so interested in these compounds that he apparently even dreamed about them. In the middle of one night Werner awoke realizing that he had the correct

\*Ammine is the name for  $\text{NH}_3$  as a ligand.

explanation for the constitution of these compounds. Writing furiously the rest of that night and into the late afternoon of the following day, he constructed a scientific paper containing his now famous *coordination theory*. This model postulates an octahedral arrangement of ligands around the  $\text{Co}^{3+}$  ion, producing the  $\text{Co}(\text{NH}_3)_6^{3+}$  complex ion with three  $\text{Cl}^-$  ions as counterions. Thus Werner's picture of  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$  varied greatly from the chain theory.

In his paper on the coordination theory, Werner explained not only the metal–ammine compounds but also most of the other known transition metal compounds, and the importance of his contribution was recognized immediately. He was appointed professor at the University of Zurich, where he spent the rest of his life studying coordination compounds and refining his theory. Alfred Werner was a confident, impulsive man of seemingly boundless energy, who was known for his inspiring lectures, his intolerance of incompetence (he once threw a chair at a student who performed poorly on an oral exam), and his intuitive scientific brilliance. For example, he was the first to show that stereochemistry is a general phenomenon, not one exhibited only by carbon, as was previously thought. He also recognized and named many types of isomerism.

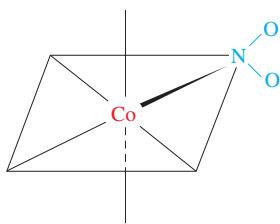
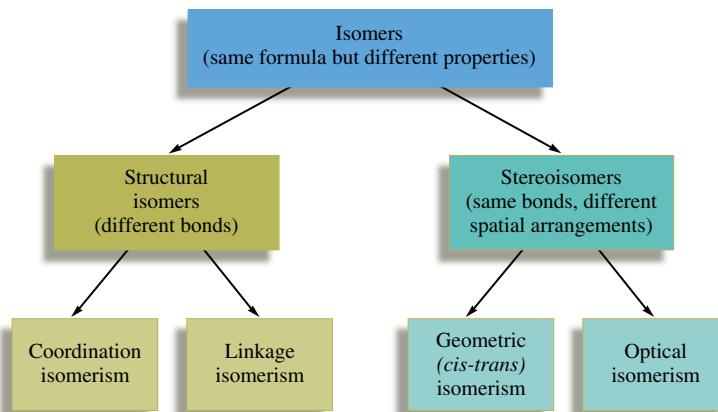
In 1913, for his work on coordination chemistry and stereochemistry, Werner became the fourteenth Nobel Prize winner in chemistry and the first Swiss chemist to be so honored. Werner's work is even more remarkable when one realizes that his ideas preceded by many years any real understanding of the nature of covalent bonds.

## 21.4 Isomerism

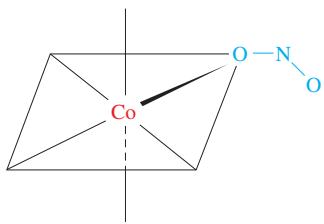
When two or more species have the same formula but different properties, they are said to be **isomers**. Although isomers contain exactly the same types and numbers of atoms, the arrangements of the atoms differ, and this leads to different properties. We will consider two main types of isomerism: **structural isomerism**, where the isomers contain the same atoms but one or more bonds differ, and **stereoisomerism**, where all the bonds in the isomers are the same but the spatial arrangements of the atoms are different. Each of these classes also has subclasses (see Fig. 21.8), which we will now consider.

### Structural Isomerism

The first type of structural isomerism we will consider is **coordination isomerism**, in which the composition of the complex ion varies. For example,  $[\text{Cr}(\text{NH}_3)_5\text{SO}_4]\text{Br}$  and  $[\text{Cr}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  are coordination isomers. In the first case,  $\text{SO}_4^{2-}$  is coordinated to  $\text{Cr}^{3+}$ , and  $\text{Br}^-$  is the counterion; in the second case, the roles of these ions are reversed.



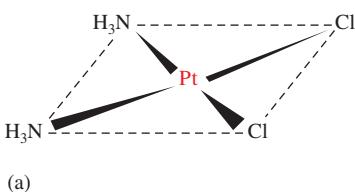
(a)



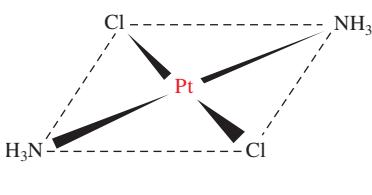
(b)

**FIGURE 21.9**

As a ligand,  $\text{NO}_2^-$  can bond to a metal ion (a) through a lone pair on the nitrogen atom or (b) through a lone pair on one of the oxygen atoms.



(a)



(b)

**FIGURE 21.10**

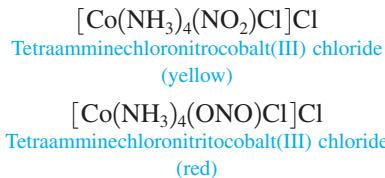
- (a) The *cis* isomer of  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$  (yellow).  
 (b) The *trans* isomer of  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$  (pale yellow).

**FIGURE 21.8**

Some classes of isomers.

Another example of coordination isomerism is the  $[\text{Co}(\text{en})_3][\text{Cr}(\text{ox})_3]$  and  $[\text{Cr}(\text{en})_3][\text{Co}(\text{ox})_3]$  pair, where ox represents the oxalate ion, a bidentate ligand shown in Table 21.13.

In a second type of structural isomerism, **linkage isomerism**, the composition of the complex ion is the same, but the point of attachment of at least one of the ligands differs. Two ligands that can attach to metal ions in different ways are thiocyanate ( $\text{SCN}^-$ ), which can bond through lone electron pairs on the nitrogen or the sulfur atom, and the nitrite ion ( $\text{NO}_2^-$ ), which can bond through lone electron pairs on the nitrogen or the oxygen atom. For example, the following two compounds are linkage isomers:



In the first case, the  $\text{NO}_2^-$  ligand is called *nitro* and is attached to  $\text{Co}^{3+}$  through the nitrogen atom; in the second case, the  $\text{NO}_2^-$  ligand is called *nitrito* and is attached to  $\text{Co}^{3+}$  through an oxygen atom (see Fig. 21.9).

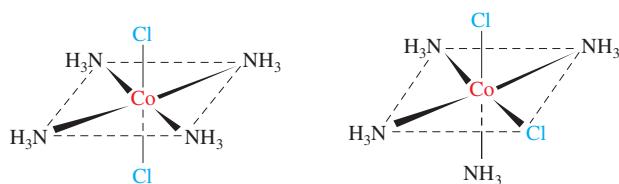
### Stereoisomerism

Stereoisomers have the same bonds but different spatial arrangements of the atoms. One type, **geometrical isomerism**, or ***cis-trans* isomerism**, occurs when atoms or groups of atoms can assume different positions around a rigid ring or bond. An important example is the compound  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ , which has a square planar structure. The two possible arrangements of the ligands are shown in Fig. 21.10. In the ***trans* isomer**, the ammonia molecules are across (*trans*) from each other. In the ***cis* isomer**, the ammonia molecules are next (*cis*) to each other.

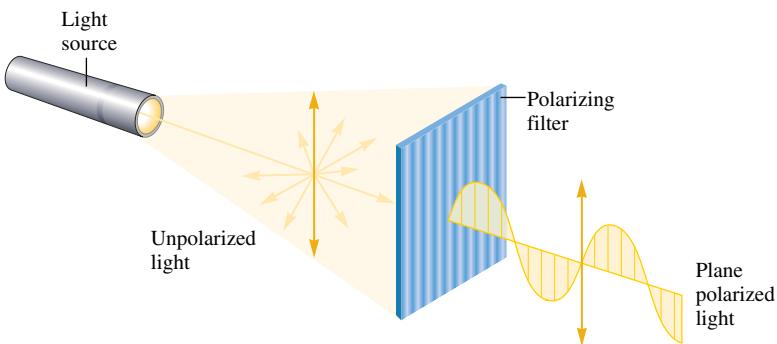
Geometrical isomerism also occurs in octahedral complex ions. For example, the compound  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  has *cis* and *trans* isomers (Fig. 21.11).

A second type of stereoisomerism is called **optical isomerism** because the isomers have opposite effects on plane-polarized light. When light is emitted from a source such as a glowing filament, the oscillating electric fields of the photons in the beam are oriented randomly, as shown in Fig. 21.12. If this light is passed through a polarizer, only the photons with electric fields oscillating in a single plane remain, constituting *plane-polarized light*.

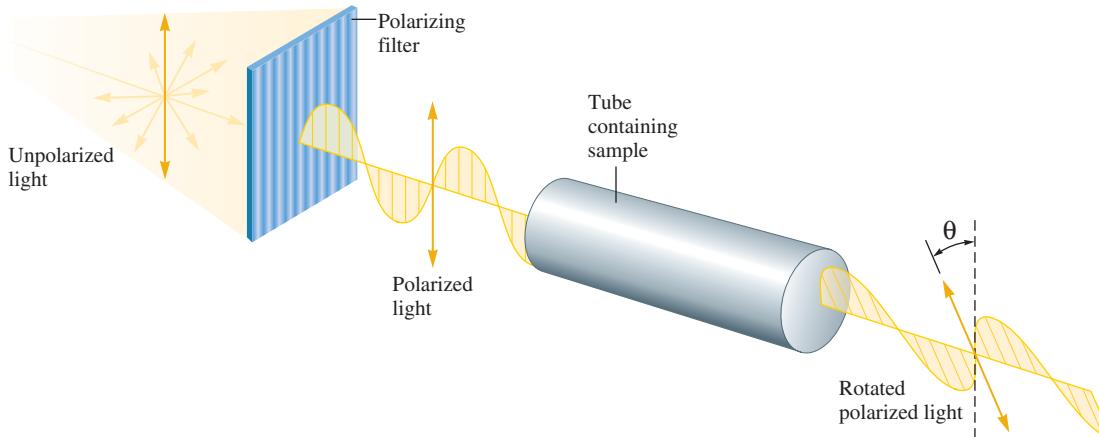
In 1815, a French physicist, Jean Biot (1774–1862), showed that certain crystals could rotate the plane of polarization of light. Later it was found that solutions of certain

**FIGURE 21.11**(a) The *trans* isomer of  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ .

The chloride ligands are directly across from each other. (b) The *cis* isomer of  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ . The chloride ligands in this case share an edge of the octahedron. Because of their different structures, the *trans* isomer of  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  is green and the *cis* isomer is violet.

**FIGURE 21.12**

Unpolarized light consists of waves vibrating in many different planes (indicated by the arrows). The polarizing filter blocks all waves except those vibrating in a given plane.

**FIGURE 21.13**

The rotation of the plane of polarized light by an optically active substance. The angle of rotation is called theta ( $\theta$ ).

compounds could do the same thing (see Fig. 21.13). Louis Pasteur (1822–1895) was the first to understand this behavior. In 1848 he noted that solid sodium ammonium tartrate ( $\text{NaNH}_4\text{C}_4\text{H}_4\text{O}_4$ ) existed as a mixture of two types of crystals, which he painstakingly separated with tweezers. Separate solutions of these two types of crystals rotated plane-polarized light in exactly opposite directions. This led to a connection between optical activity and molecular structure.



## CHEMICAL IMPACT

### The Importance of Being *cis*

Some of the most important advancements of science are the results of accidental discoveries—for example, penicillin, Teflon, and the sugar substitutes cyclamate and aspartame. Another important chance discovery occurred in 1964, when a group of scientists using platinum electrodes to apply an electric field to a colony of *E. coli* bacteria noticed that the bacteria failed to divide but continued to grow, forming long fibrous cells. Further study revealed that cell division was inhibited by small concentrations of *cis*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and *cis*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub> formed electrolytically in the solution.

Cancerous cells multiply very rapidly because cell division is uncontrolled. Thus these and similar platinum complexes were evaluated as *antitumor agents*, which inhibit the division of cancer cells. The results showed that

*cis*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> was active against a wide variety of tumors, including testicular and ovarian tumors, which are very resistant to treatment by more traditional methods. However, although the *cis* complex showed significant antitumor activity, the corresponding *trans* complex had no effect on tumors. This shows the importance of isomerism in biologic systems. When drugs are synthesized, great care must be taken to obtain the correct isomer.

Although *cis*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> has proven to be a valuable drug, unfortunately it has some troublesome side effects, the most serious being kidney damage. As a result, the search continues for even more effective antitumor agents. Promising candidates are shown in Fig. 21.14. Note that they are all *cis* complexes.

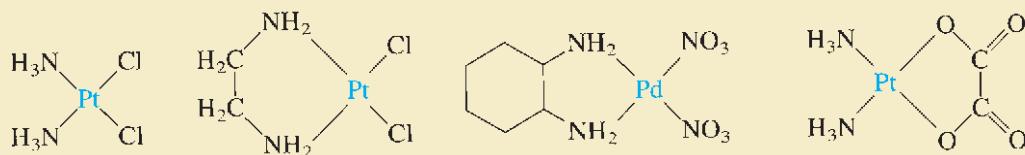


FIGURE 21.14

Some *cis* complexes of platinum and palladium that show significant antitumor activity. It is thought that the *cis* complexes work by losing two adjacent ligands and forming coordinate covalent bonds to adjacent bases on a DNA molecule.

We now realize that optical activity is exhibited by molecules that have *nonsuperimposable mirror images*. Your hands are nonsuperimposable mirror images (Fig. 21.15). The two hands are related like an object and its mirror image; one hand cannot be turned to make it identical to the other. Many molecules show this same feature, such as the

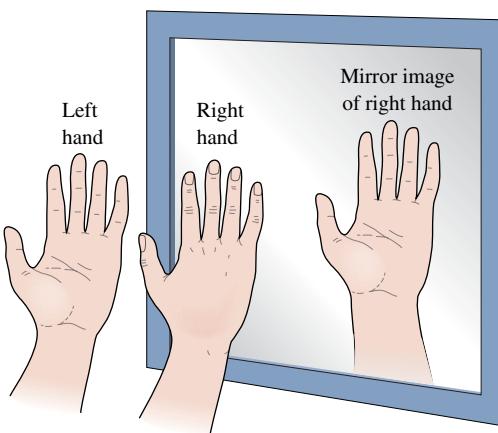
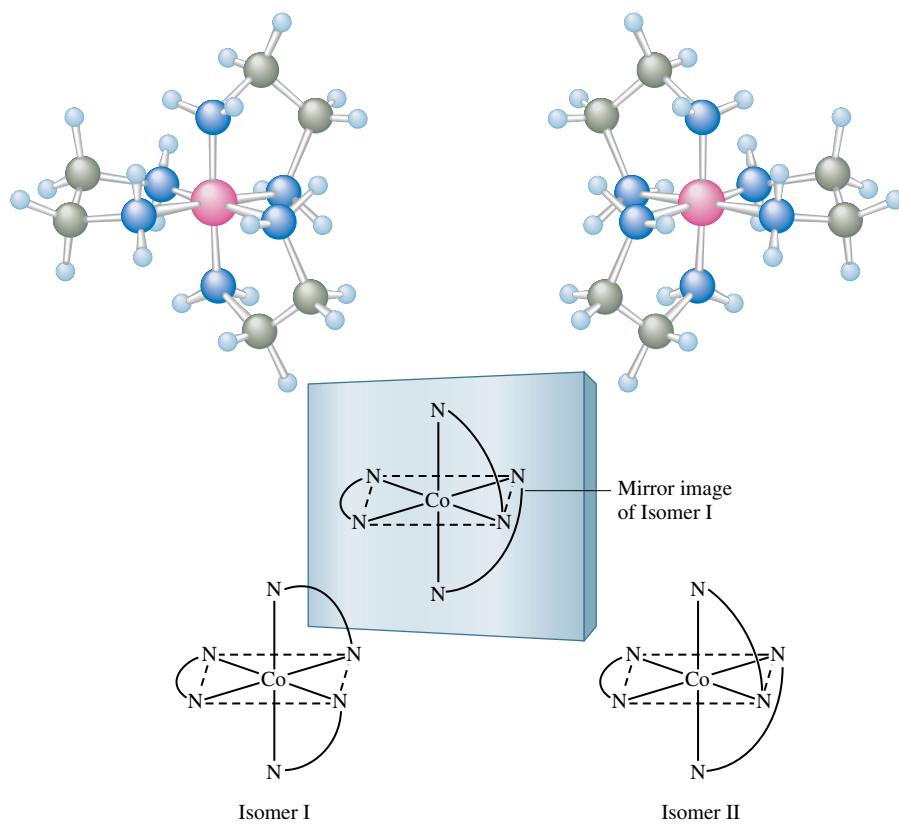


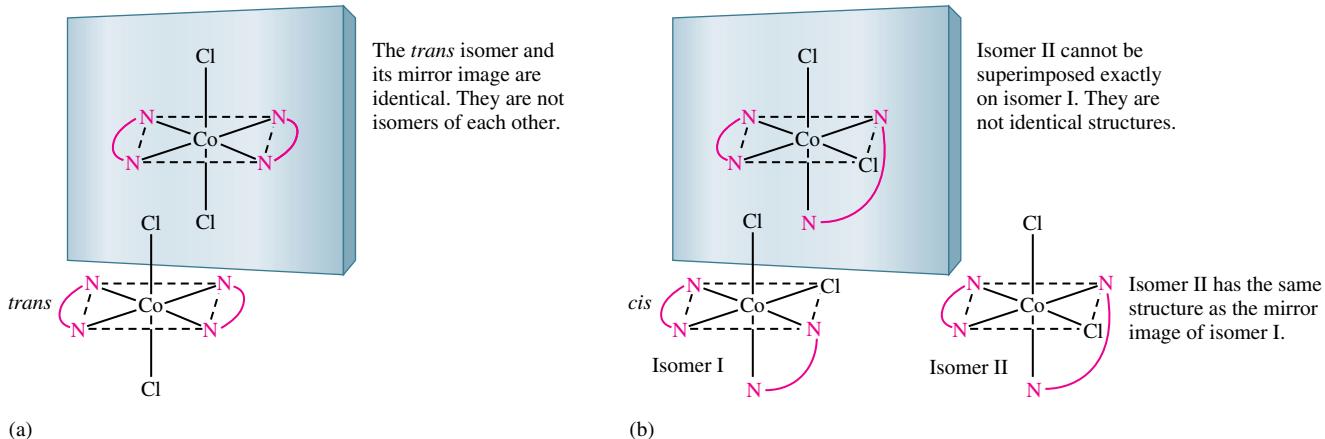
FIGURE 21.15

A human hand exhibits a nonsuperimposable mirror image. Note that the mirror image of the right hand (while identical to the left hand) cannot be turned in any way to make it identical to (superimposable on) the actual right hand.



complex ion  $[\text{Co}(\text{en})_3]^{3+}$  shown in Fig. 21.16. Objects that have nonsuperimposable mirror images are said to be **chiral** (from the Greek word *cheir*; meaning “hand”).

The isomers of  $[\text{Co}(\text{en})_3]^{3+}$  (Fig. 21.17) are nonsuperimposable mirror images called **enantiomers**, which rotate plane-polarized light in opposite directions and are thus optical isomers. The isomer that rotates the plane of light to the right (when viewed down the beam of oncoming light) is said to be *dextrorotatory*, designated by *d*. The isomer that rotates the plane of light to the left is *levorotatory* (*l*). An equal mixture of the *d* and



**FIGURE 21.17**

(a) The *trans* isomer of  $\text{Co}(\text{en})_2\text{Cl}_2^+$  and its mirror image are identical (superimposable). (b) The *cis* isomer of  $\text{Co}(\text{en})_2\text{Cl}_2^+$  and its mirror image are not superimposable and are thus a pair of optical isomers.

*l* forms in solution, called a *racemic mixture*, does not rotate the plane of the polarized light at all because the two opposite effects cancel each other.

Geometrical isomers are not necessarily optical isomers. For instance, the *trans* isomer of  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  shown in Fig. 21.17 is identical to its mirror image. Since this isomer is superimposable on its mirror image, it does not exhibit optical isomerism and is not chiral. On the other hand, *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  is *not* superimposable on its mirror image; a pair of enantiomers exists for this complex ion (the *cis* isomer is chiral).

Most important biomolecules are chiral, and their reactions are highly structure dependent. For example, a drug can have a particular effect because its molecules can bind to chiral molecules in the body. To bind correctly, however, the correct optical isomer of the drug must be administered. Just as the right hand of one person requires the right hand of another to perform a handshake, a given isomer in the body requires a specific isomer of the drug to bind together. Because of this, the syntheses of drugs, which are usually very complicated molecules, must be carried out in a way that produces the correct “handedness,” a requirement that greatly adds to the synthetic difficulties.

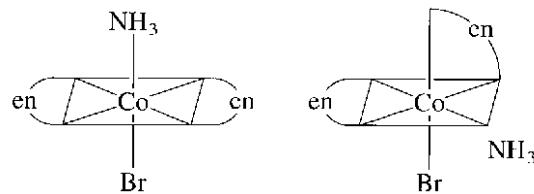
### Sample Exercise 21.3

### Geometrical and Optical Isomerism

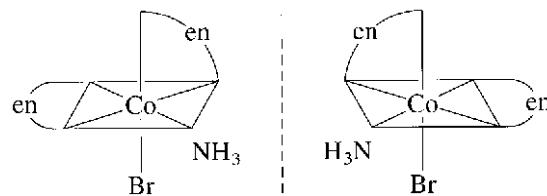
Does the complex ion  $[\text{Co}(\text{NH}_3)\text{Br}(\text{en})_2]^{2+}$  exhibit geometrical isomerism? Does it exhibit optical isomerism?

#### Solution

The complex ion exhibits geometrical isomerism because the ethylenediamine ligands can be across from or next to each other:



The *cis* isomer of the complex ion also exhibits optical isomerism because its mirror images

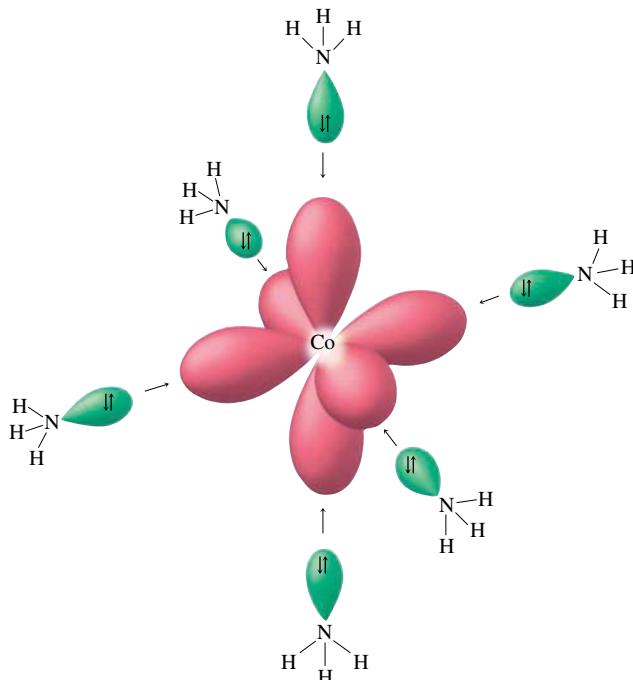


cannot be turned in any way to make them superimposable. Thus these mirror-image isomers of the *cis* complex are shown to be enantiomers that will rotate plane-polarized light in opposite directions.

*See Exercises 21.41 and 21.42.*

## 21.5 Bonding in Complex Ions: The Localized Electron Model

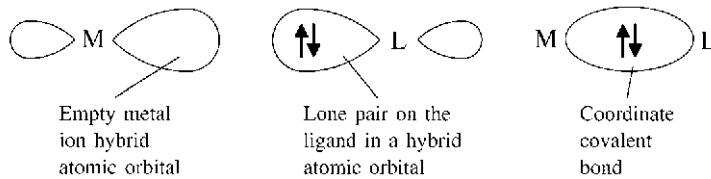
In Chapters 8 and 9 we considered the localized electron model, a very useful model for describing the bonding in molecules. Recall that a central feature of this model is the formation of hybrid atomic orbitals that are used to share electron pairs to form  $\sigma$  bonds

**FIGURE 21.18**

A set of six  $d^2sp^3$  hybrid orbitals on  $\text{Co}^{3+}$  can accept an electron pair from each of six  $\text{NH}_3$  ligands to form the  $\text{Co}(\text{NH}_3)_6^{3+}$  ion.

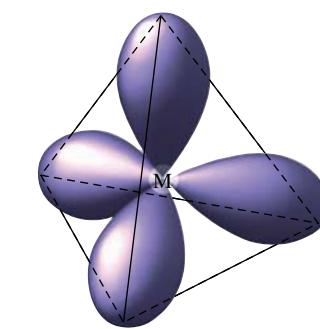
between atoms. This same model can be used to account for the bonding in complex ions, but there are two important points to keep in mind:

1. The VSEPR model for predicting structure generally *does not work for complex ions*. However, we can safely assume that a complex ion with a coordination number of 6 will have an octahedral arrangement of ligands, and complexes with two ligands will be linear. On the other hand, complex ions with a coordination number of 4 can be either tetrahedral or square planar, and there is no completely reliable way to predict which will occur in a particular case.
2. The interaction between a metal ion and a ligand can be viewed as a Lewis acid–base reaction with the ligand donating a lone pair of electrons to an *empty* orbital of the metal ion to form a coordinate covalent bond:

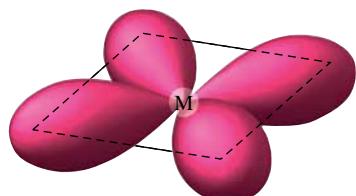


The hybrid orbitals used by the metal ion depend on the number and arrangement of the ligands. For example, accommodating the lone pairs from the six ammonia molecules in the octahedral  $\text{Co}(\text{NH}_3)_6^{3+}$  ion requires a set of six empty hybrid atomic orbitals in an octahedral arrangement. As we discussed in Section 9.1, an octahedral set of orbitals is formed by the hybridization of two  $d$ , one  $s$ , and three  $p$  orbitals to give a set of six  $d^2sp^3$  orbitals (see Fig. 21.18).

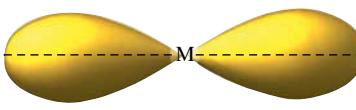
The hybrid orbitals required on a metal ion in a four-coordinate complex depend on whether the structure is tetrahedral or square planar. For a tetrahedral arrangement of ligands, an  $sp^3$  hybrid set is required (see Fig. 21.19). For example, in the tetrahedral  $\text{CoCl}_4^{2-}$  ion, the  $\text{Co}^{2+}$  can be described as  $sp^3$  hybridized. A square planar arrangement of ligands requires a  $dsp^2$  hybrid orbital set on the metal ion (see Fig. 21.19). For example, in the square planar  $\text{Ni}(\text{CN})_4^{2-}$  ion, the  $\text{Ni}^{2+}$  is described as  $dsp^2$  hybridized.



Tetrahedral ligand arrangement;  $sp^3$  hybridization



Square planar ligand arrangement;  $dsp^2$  hybridization



Linear ligand arrangement;  $sp$  hybridization

**FIGURE 21.19**

The hybrid orbitals required for tetrahedral, square planar, and linear complex ions. The metal ion hybrid orbitals are empty, and the metal bonds to the ligands by accepting lone pairs.

A linear complex requires two hybrid orbitals 180 degrees from each other. This arrangement is given by an  $sp$  hybrid set (see Fig. 21.19). Thus, in the linear  $\text{Ag}(\text{NH}_3)_2^+$  ion, the  $\text{Ag}^+$  can be described as  $sp$  hybridized.

Although the localized electron model can account in a general way for metal-ligand bonds, it is rarely used today because it cannot readily account for important properties of complex ions, such as magnetism and color. Thus we will not pursue the model any further.

## 21.6 The Crystal Field Model

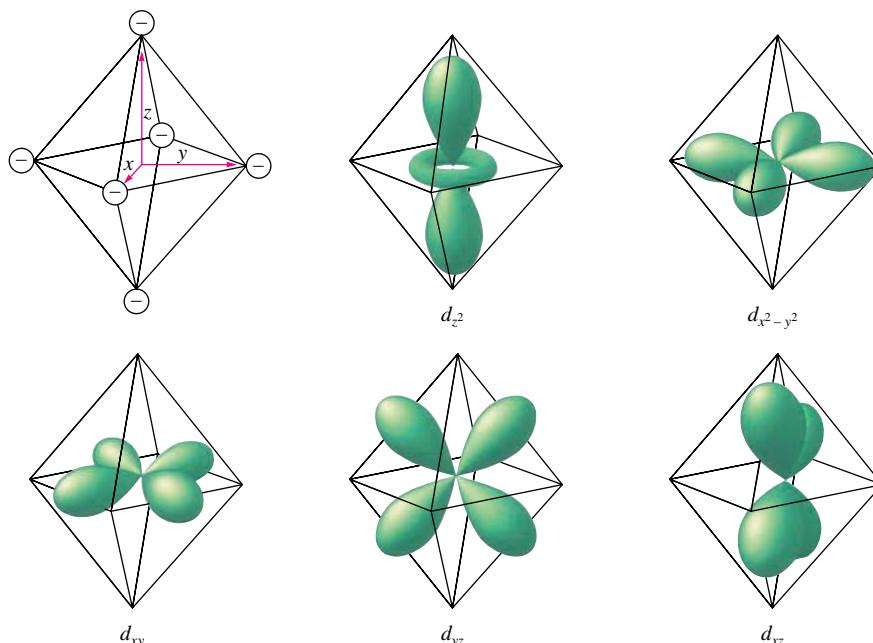
The main reason the localized electron model cannot fully account for the properties of complex ions is that it gives no information about how the energies of the  $d$  orbitals are affected by complex ion formation. This is critical because, as we will see, the color and magnetism of complex ions result from changes in the energies of the metal ion  $d$  orbitals caused by the metal-ligand interactions.

The **crystal field model** focuses on the energies of the  $d$  orbitals. In fact, this model is not so much a bonding model as it is an attempt to account for the colors and magnetic properties of complex ions. In its simplest form, the crystal field model assumes that the ligands can be approximated by *negative point charges* and that metal-ligand bonding is *entirely ionic*.

### Octahedral Complexes

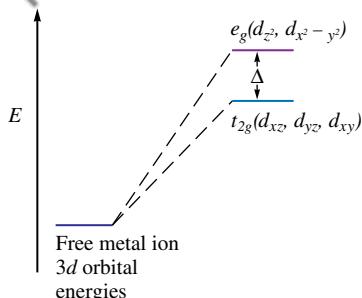
We will illustrate the fundamental principles of the crystal field model by applying it to an octahedral complex. Figure 21.20 shows the orientation of the  $3d$  orbitals relative to an octahedral arrangement of point-charge ligands. The important thing to note is that two of the orbitals,  $d_{z^2}$  and  $d_{x^2 - y^2}$ , point their lobes *directly at* the point-charge ligands and three of the orbitals,  $d_{xz}$ ,  $d_{yz}$ , and  $d_{xy}$ , point their lobes *between* the point charges.

To understand the effect of this difference, we need to consider which type of orbital is lower in energy. Because the negative point-charge ligands repel negatively charged electrons, the electrons will first fill the  $d$  orbitals farthest from the ligands to minimize repulsions. In other words, the  $d_{xz}$ ,  $d_{yz}$ , and  $d_{xy}$  orbitals (known as the  $t_{2g}$  set) are at a *lower*



**FIGURE 21.20**

An octahedral arrangement of point-charge ligands and the orientation of the  $3d$  orbitals.

**FIGURE 21.21**

The energies of the 3d orbitals for a metal ion in an octahedral complex. The 3d orbitals are degenerate (all have the same energy) in the free metal ion. In the octahedral complex the orbitals are split into two sets as shown. The difference in energy between the two sets is designated as  $\Delta$  (delta).

energy in the octahedral complex than are the  $d_{z^2}$  and  $d_{x^2 - y^2}$  orbitals (the  $e_g$  set). This is shown in Fig. 21.21. The negative point-charge ligands increase the energies of all the  $d$  orbitals. However, the orbitals that point at the ligands are raised in energy more than those that point between the ligands.

It is this **splitting of the 3d orbital energies** (symbolized by  $\Delta$ ) that explains the color and magnetism of complex ions of the first-row transition metal ions. For example, in an octahedral complex of  $\text{Co}^{3+}$  (a metal ion with six 3d electrons), there are two possible ways to place the electrons in the split 3d orbitals (Fig. 21.22). If the splitting produced by the ligands is very large, a situation called the **strong-field case**, the electrons will pair in the lower-energy  $t_{2g}$  orbitals. This gives a *diamagnetic* complex in which all the electrons are paired. On the other hand, if the splitting is small (the **weak-field case**), the electrons will occupy all five orbitals before pairing occurs. In this case the complex has four unpaired electrons and is *paramagnetic*.

The crystal field model allows us to account for the differences in the magnetic properties of  $\text{Co}(\text{NH}_3)_6^{3+}$  and  $\text{CoF}_6^{3-}$ . The  $\text{Co}(\text{NH}_3)_6^{3+}$  ion is known to be diamagnetic and thus corresponds to the strong-field case, also called the **low-spin case**, since it yields the *minimum* number of unpaired electrons. In contrast, the  $\text{CoF}_6^{3-}$  ion, which is known to have four unpaired electrons, corresponds to the weak-field case, also known as the **high-spin case**, since it gives the *maximum* number of unpaired electrons.

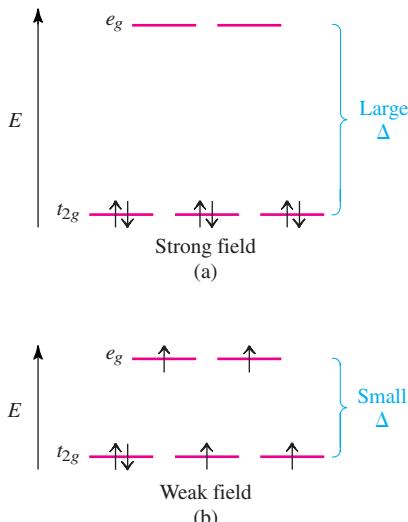
### Sample Exercise 21.4

### Crystal Field Model I

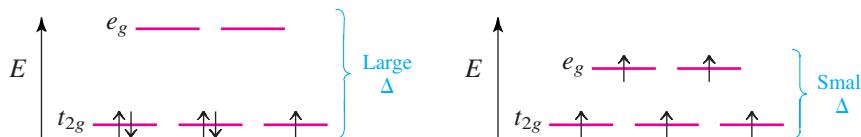
The  $\text{Fe}(\text{CN})_6^{3-}$  ion is known to have one unpaired electron. Does the  $\text{CN}^-$  ligand produce a strong or weak field?

#### Solution

Since the ligand is  $\text{CN}^-$  and the overall complex ion charge is  $3-$ , the metal ion must be  $\text{Fe}^{3+}$ , which has a  $3d^5$  electron configuration. The two possible arrangements of the five electrons in the  $d$  orbitals split by the octahedrally arranged ligands are

**FIGURE 21.22**

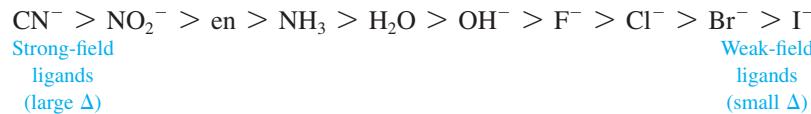
Possible electron arrangements in the split 3d orbitals in an octahedral complex of  $\text{Co}^{3+}$  (electron configuration  $3d^5$ ). (a) In a strong field (large  $\Delta$  value), the electrons fill the  $t_{2g}$  set first, giving a diamagnetic complex. (b) In a weak field (small  $\Delta$  value), the electrons occupy all five orbitals before any pairing occurs.



The strong-field case gives one unpaired electron, which agrees with the experimental observation. The  $\text{CN}^-$  ion is a strong-field ligand toward the  $\text{Fe}^{3+}$  ion.

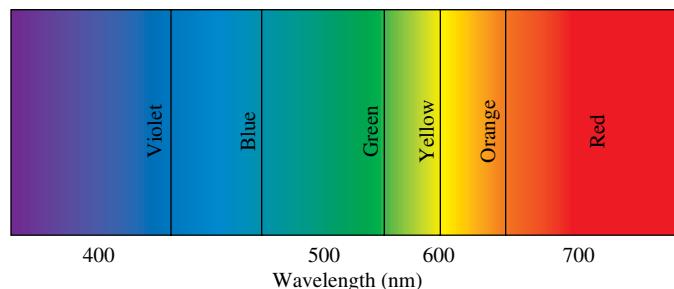
**See Exercises 21.45 and 21.46.**

From studies of many octahedral complexes, we can arrange ligands in order of their ability to produce  $d$ -orbital splitting. A partial listing of ligands in this **spectrochemical series** is



The ligands are arranged in order of decreasing  $\Delta$  values toward a given metal ion.

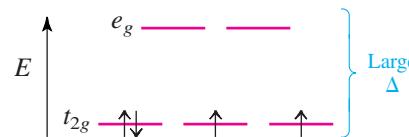
It also has been observed that *the magnitude of  $\Delta$  for a given ligand increases as the charge on the metal ion increases*. For example,  $\text{NH}_3$  is a weak-field ligand toward  $\text{Co}^{2+}$  but acts as a strong-field ligand toward  $\text{Co}^{3+}$ . This makes sense; as the metal ion charge increases, the ligands will be drawn closer to the metal ion because of the increased charge density. As the ligands move closer, they cause greater splitting of the  $d$  orbitals and produce a larger  $\Delta$  value.

**FIGURE 21.23**

The visible spectrum.

**Sample Exercise 21.5****Crystal Field Model II**Predict the number of unpaired electrons in the complex ion  $[\text{Cr}(\text{CN})_6]^{4-}$ .**Solution**

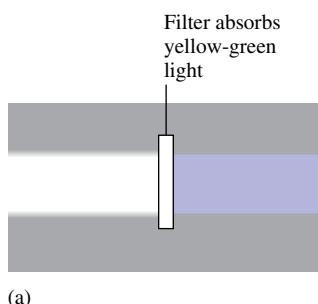
The net charge of  $4-$  means that the metal ion present must be  $\text{Cr}^{2+}$  ( $-6 + 2 = -4$ ), which has a  $3d^4$  electron configuration. Since  $\text{CN}^-$  is a strong-field ligand (see the spectrochemical series), the correct crystal field diagram for  $[\text{Cr}(\text{CN})_6]^{4-}$  is



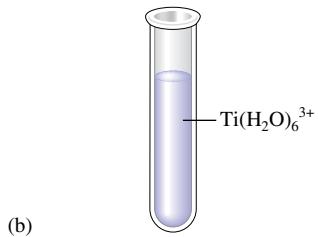
The complex ion will have two unpaired electrons. Note that the  $\text{CN}^-$  ligand produces such a large splitting that all four electrons will occupy the  $t_{2g}$  set even though two of the electrons must be paired in the same orbital.

**See Exercises 21.47 and 21.48.**

We have seen how the crystal field model can account for the magnetic properties of octahedral complexes. The same model also can explain the colors of these complex ions. For example,  $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ , an octahedral complex of  $\text{Ti}^{3+}$ , which has a  $3d^1$  electron configuration, is violet because it absorbs light in the middle of the visible region of the spectrum (see Fig. 21.23). When a substance absorbs certain wavelengths of light in the visible region, the color of the substance is determined by the wavelengths of visible light that remain. We say that the substance exhibits the color *complementary* to those absorbed. The  $\text{Ti}(\text{H}_2\text{O})_6^{3+}$  ion is violet because it absorbs light in the yellow-green region, thus letting red light and blue light pass, which gives the observed violet color. This is shown schematically in Fig. 21.24. Table 21.16 shows the general relationship between the wavelengths of visible light absorbed and the approximate color observed.



(a)

**FIGURE 21.24**

(a) When white light shines on a filter that absorbs in the yellow-green region, the emerging light is violet. (b) Because the complex ion  $\text{Ti}(\text{H}_2\text{O})_6^{3+}$  absorbs yellow-green light, a solution of it is violet.

**TABLE 21.16 Approximate Relationship of Wavelength of Visible Light Absorbed to Color Observed**

Absorbed Wavelength in nm (Color)	Observed Color
400 (violet)	Greenish yellow
450 (blue)	Yellow
490 (blue-green)	Red
570 (yellow-green)	Violet
580 (yellow)	Dark blue
600 (orange)	Blue
650 (red)	Green



## CHEMICAL IMPACT

### Transition Metal Ions Lend Color to Gems

The beautiful pure color of gems, so valued by cultures everywhere, arises from trace transition metal ion impurities in minerals that would otherwise be colorless. For example, the stunning red of a ruby, the most valuable of all gemstones, is caused by Cr<sup>3+</sup> ions, which replace about 1% of the Al<sup>3+</sup> ions in the mineral corundum, which is a form of aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) that is nearly as hard as diamond. In the corundum structure the Cr<sup>3+</sup> ions are surrounded by six oxide ions at the vertices of an octahedron. This leads to the characteristic octahedral splitting of chromium's 3d orbitals, such that the Cr<sup>3+</sup> ions absorb strongly in the blue-violet and yellow-green regions of the visible spectrum but transmit red light to give the characteristic ruby color. (On the other hand, if some of the Al<sup>3+</sup> ions in corundum are replaced by a mixture of Fe<sup>2+</sup>, Fe<sup>3+</sup>,

and Ti<sup>4+</sup> ions, the gem is a sapphire with its brilliant blue color; or if some of the Al<sup>3+</sup> ions are replaced by Fe<sup>3+</sup> ions, the stone is a yellow topaz.)

Emeralds are derived from the mineral beryl, a beryllium aluminum silicate (empirical formula 3BeO · Al<sub>2</sub>O<sub>3</sub> · 6SiO<sub>2</sub>). When some of the Al<sup>3+</sup> ions in beryl are replaced by Cr<sup>3+</sup> ions, the characteristic green color of emerald results. In this environment the splitting of the Cr<sup>3+</sup> 3d orbitals causes it to strongly absorb yellow and blue-violet light and to transmit green light.

A gem closely related to ruby and emerald is alexandrite, named after Alexander II of Russia. This gem is based on the mineral chrysoberyl, a beryllium aluminate with the empirical formula BeO · Al<sub>2</sub>O<sub>3</sub> in which approximately 1% of the Al<sup>3+</sup> ions are replaced by Cr<sup>3+</sup> ions. In the chrysoberyl environment Cr<sup>3+</sup> absorbs strongly in the yellow region of

The reason that the Ti(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> ion absorbs a specific wavelength of visible light can be traced to the transfer of the lone d electron between the split d orbitals, as shown in Fig. 21.25. A given photon of light can be absorbed by a molecule only if the wavelength of the light provides exactly the energy needed by the molecule. In other words, the wavelength absorbed is determined by the relationship

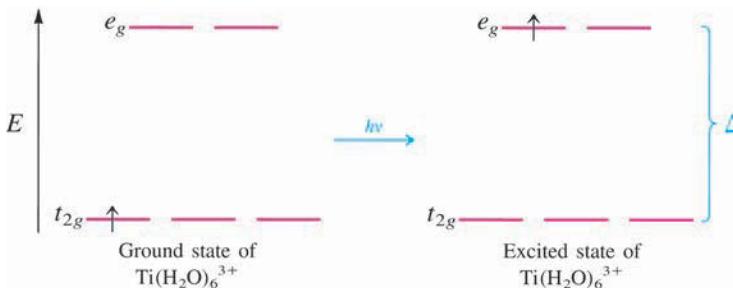
$$\Delta E = \frac{hc}{\lambda}$$

where  $\Delta E$  represents the energy spacing in the molecule (we have used simply  $\Delta$  in this chapter) and  $\lambda$  represents the wavelength of light needed. Because the d-orbital splitting in most octahedral complexes corresponds to the energies of photons in the visible region, octahedral complex ions are usually colored.

Since the ligands coordinated to a given metal ion determine the size of the d-orbital splitting, the color changes as the ligands are changed. This occurs because a change in  $\Delta$  means a change in the wavelength of light needed to transfer electrons between the  $t_{2g}$  and  $e_g$  orbitals. Several octahedral complexes of Cr<sup>3+</sup> and their colors are listed in Table 21.17.

### Other Coordination Geometries

Using the same principles developed for octahedral complexes, we will now consider complexes with other geometries. For example, Fig. 21.26 shows a tetrahedral arrangement of



**FIGURE 21.25**

The complex ion Ti(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> can absorb visible light in the yellow-green region to transfer the lone d electron from the  $t_{2g}$  to the  $e_g$  set.

the spectrum. Alexandrite has the interesting property of changing colors depending on the light source. When the first alexandrite stone was discovered deep in a mine in the Russian Ural Mountains in 1831, it appeared to be a deep red color in the firelight of the miners' lamps. However, when the stone was brought to the surface, its color was blue. This seemingly magical color change occurs because the firelight of a miner's helmet is rich in the yellow and red wavelengths of the visible spectrum but does not contain much blue. Absorption of the yellow by the stone produces a reddish color. However, daylight has much more intensity in the blue region than firelight. Thus the extra blue in the light transmitted by the stone gives it bluish color in daylight.

Once the structure of a natural gem is known, it is usually not very difficult to make the gem artificially. For example, rubies and sapphires are made on a large scale by fusing  $\text{Al}(\text{OH})_3$  with the appropriate transition metal salts at approximately  $1200^\circ\text{C}$  to make the "doped" corundum. With these techniques



Alexandrite, a gem closely related to ruby and emerald.

gems of astonishing size can be manufactured: Rubies as large as 10 lb and sapphires up to 100 lb have been synthesized. Smaller synthetic stones produced for jewelry are virtually identical to the corresponding natural stones, and it takes great skill for a gemologist to tell the difference.

point charges in relation to the  $3d$  orbitals of a metal ion. There are two important facts to note:

1. None of the  $3d$  orbitals "point at the ligands" in the tetrahedral arrangement, as the  $d_{x^2 - y^2}$  and  $d_{z^2}$  orbitals do in the octahedral case. Thus the tetrahedrally arranged ligands do not differentiate the  $d$  orbitals as much in the tetrahedral case as in the octahedral case. That is, the difference in energy between the split  $d$  orbitals will be significantly less in tetrahedral complexes. Although we will not derive it here, the tetrahedral splitting is  $\frac{4}{9}$  that of the octahedral splitting for a given ligand and metal ion:

$$\Delta_{\text{tet}} = \frac{4}{9}\Delta_{\text{oct}}$$

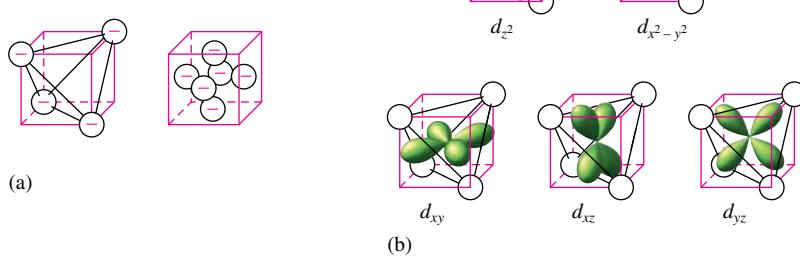
2. Although not exactly pointing at the ligands, the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals are closer to the point charges than are the  $d_z^2$  and  $d_{x^2 - y^2}$  orbitals. This means that the tetrahedral  $d$ -orbital splitting will be opposite to that for the octahedral arrangement. The two arrangements are contrasted in Fig. 21.27. Because the  $d$ -orbital splitting is relatively small for the tetrahedral case, the weak-field case (high-spin case) *always* applies. There are no known ligands powerful enough to produce the strong-field case in a tetrahedral complex.

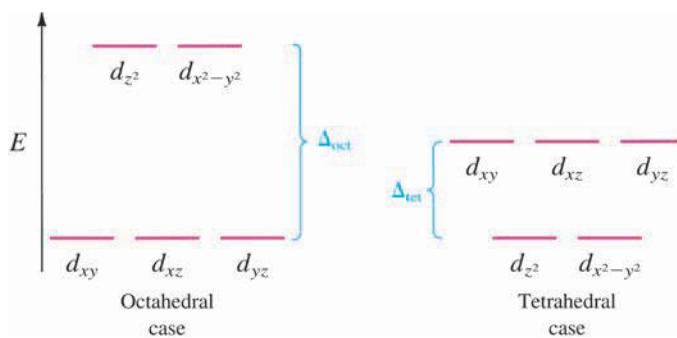


Solutions of  $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$  (yellow) and  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  (purple).

**FIGURE 21.26**

(a) Tetrahedral and octahedral arrangements of ligands shown inscribed in cubes. Note that in the two types of arrangements, the point charges occupy opposite parts of the cube; the octahedral point charges are at the centers of the cube faces, and the tetrahedral point charges occupy opposite corners of the cube. (b) The orientations of the  $3d$  orbitals relative to the tetrahedral set of point charges.



**FIGURE 21.27**

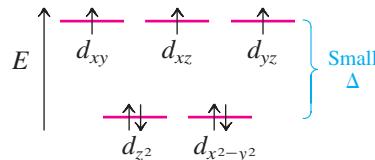
The crystal field diagrams for octahedral and tetrahedral complexes. The relative energies of the sets of  $d$  orbitals are reversed. For a given type of ligand, the splitting is much larger for the octahedral complex ( $\Delta_{\text{oct}} > \Delta_{\text{tet}}$ ) because in this arrangement the  $d_z^2$  and  $d_{x^2-y^2}$  orbitals point their lobes directly at the point charges and are thus relatively high in energy.

**Sample Exercise 21.6****Crystal Field Model III**

Give the crystal field diagram for the tetrahedral complex ion  $\text{CoCl}_4^{2-}$ .

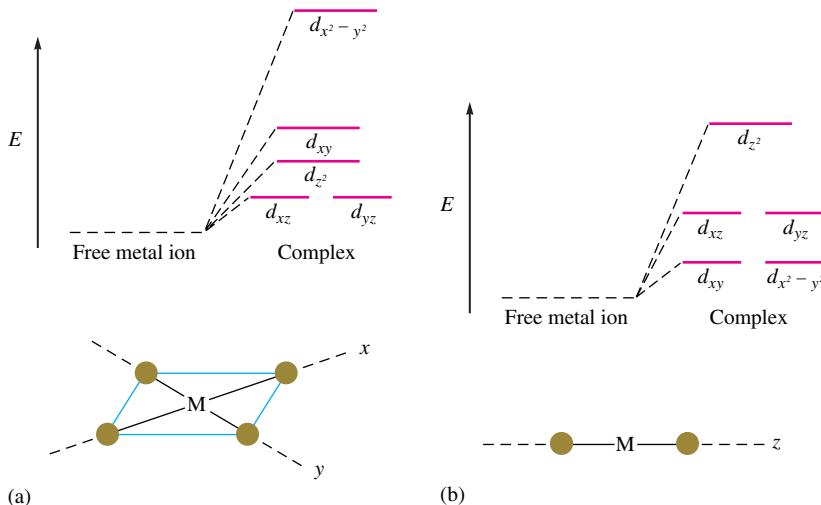
**Solution**

The complex ion contains  $\text{Co}^{2+}$ , which has a  $3d^7$  electron configuration. The splitting of the  $d$  orbitals will be small, since this is a tetrahedral complex, giving the high-spin case with three unpaired electrons.



*See Exercises 21.53 through 21.56.*

The crystal field model also applies to square planar and linear complexes. The crystal field diagrams for these cases are shown in Fig. 21.28. The ranking of orbitals in these diagrams can be explained by considering the relative orientations of the point charges and the orbitals. The diagram in Fig. 21.27 for the octahedral arrangement can be used to obtain these orientations. We can obtain the square planar complex by removing the two point charges along the  $z$  axis. This will greatly lower the energy of  $d_z^2$ , leaving only  $d_{x^2-y^2}$ ,

**FIGURE 21.28**

(a) The crystal field diagram for a square planar complex oriented in the  $xy$  plane with ligands along the  $x$  and  $y$  axes. The position of the  $d_z^2$  orbital is higher than those of the  $d_{xz}$  and  $d_{yz}$  orbitals because of the “doughnut” of electron density in the  $xy$  plane. The actual position of  $d_z^2$  is somewhat uncertain and varies in different square planar complexes. (b) The crystal field diagram for a linear complex where the ligands lie along the  $z$  axis.

which points at the four remaining ligands as the highest-energy orbital. We can obtain the linear complex from the octahedral arrangement by leaving the two ligands along the  $z$  axis and removing the four in the  $xy$  plane. This means that only the  $d_{z^2}$  points at the ligands and is highest in energy.

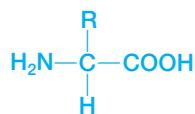
## 21.7 The Biologic Importance of Coordination Complexes

The ability of metal ions to coordinate with and release ligands and to easily undergo oxidation and reduction makes them ideal for use in biologic systems. For example, metal ion complexes are used in humans for the transport and storage of oxygen, as electron-transfer agents, as catalysts, and as drugs. Most of the first-row transition metals are essential for human health, as summarized in Table 21.18. We will concentrate on iron's role in biologic systems, since several of its coordination complexes have been studied extensively.

Iron plays a central role in almost all living cells. In mammals, the principal source of energy comes from the oxidation of carbohydrates, proteins, and fats. Although oxygen is the oxidizing agent for these processes, it does not react directly with these molecules. Instead, the electrons from the breakdown of these nutrients are passed along a complex chain of molecules, called the *respiratory chain*, eventually reaching the  $O_2$  molecule. The principal electron-transfer molecules in the respiratory chain are iron-containing species called **cytochromes**, consisting of two main parts: an iron complex called **heme** and a protein. The structure of the heme complex is shown in Fig. 21.29. Note that it contains an iron ion (it can be either  $Fe^{2+}$  or  $Fe^{3+}$ ) coordinated to a rather complicated planar ligand called a **porphyrin**. As a class, porphyrins all contain the same central ring structure but have different substituent groups at the edges of the rings. The various porphyrin molecules act as tetradentate ligands for many metal ions, including iron, cobalt, and magnesium. In fact, *chlorophyll*, a substance essential to the process of photosynthesis, is a magnesium–porphyrin complex of the type shown in Fig. 21.30.

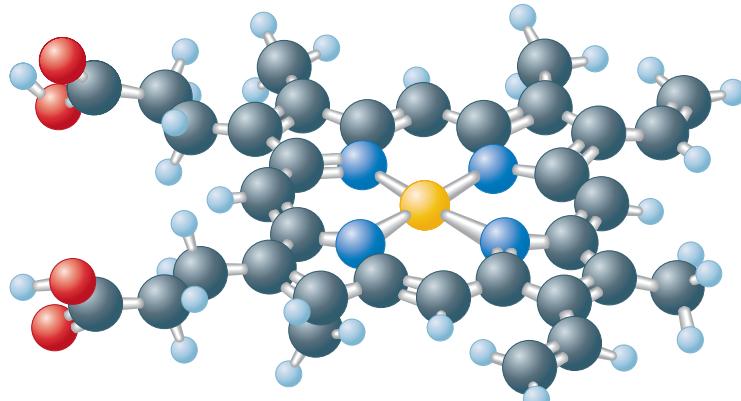
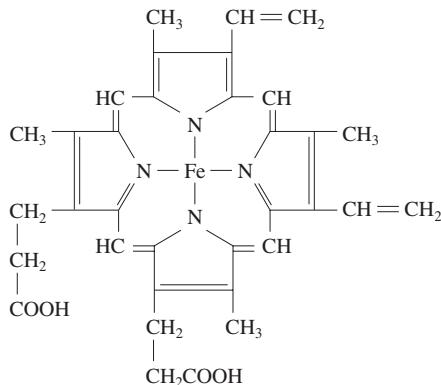
In addition to participating in the transfer of electrons from nutrients to oxygen, iron plays a principal role in the transport and storage of oxygen in mammalian blood and tissues. Oxygen is stored in a molecule called **myoglobin**, which consists of a heme

A protein is a large molecule assembled from amino acids, which have the general structure in which R represents various groups.



**TABLE 21.18** The First-Row Transition Metals and Their Biologic Significance

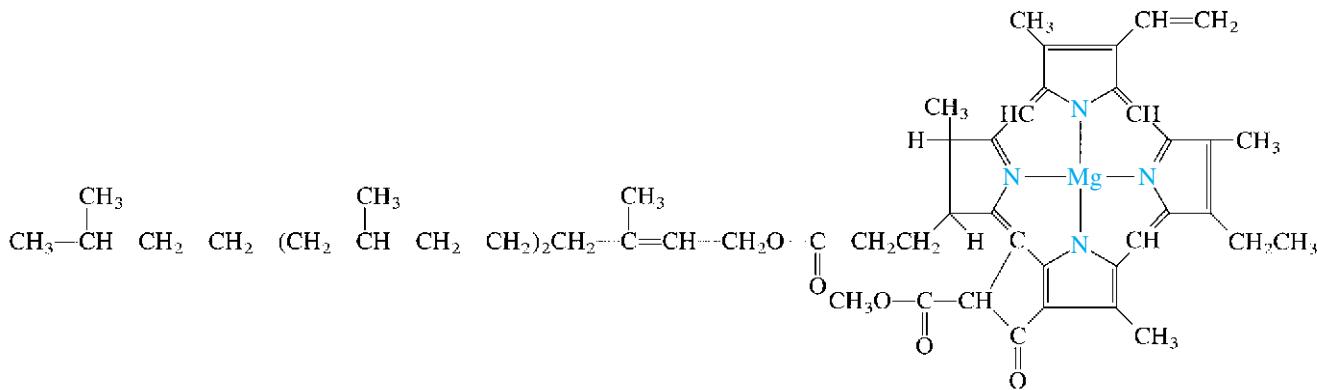
First-Row Transition Metal	Biologic Function(s)
Scandium	None known.
Titanium	None known.
Vanadium	None known in humans.
Chromium	Assists insulin in the control of blood sugar; may also be involved in the control of cholesterol.
Manganese	Necessary for a number of enzymatic reactions.
Iron	Component of hemoglobin and myoglobin; involved in the electron-transport chain.
Cobalt	Component of vitamin $B_{12}$ , which is essential for the metabolism of carbohydrates, fats, and proteins.
Nickel	Component of the enzymes urease and hydrogenase.
Copper	Component of several enzymes; assists in iron storage; involved in the production of color pigments of hair, skin, and eyes.
Zinc	Component of insulin and many enzymes.

**FIGURE 21.29**

The heme complex, in which an  $\text{Fe}^{2+}$  ion is coordinated to four nitrogen atoms of a planar porphyrin ligand.

complex and a protein in a structure very similar to that of the cytochromes. In myoglobin, the  $\text{Fe}^{2+}$  ion is coordinated to four nitrogen atoms of the porphyrin ring and to a nitrogen atom of the protein chain, as shown in Fig. 21.31. Since  $\text{Fe}^{2+}$  is normally six-coordinate, this leaves one position open for attachment of an  $\text{O}_2$  molecule.

One especially interesting feature of myoglobin is that it involves an  $\text{O}_2$  molecule attaching directly to  $\text{Fe}^{2+}$ . However, if gaseous  $\text{O}_2$  is bubbled into an aqueous solution containing heme, the  $\text{Fe}^{2+}$  is immediately oxidized to  $\text{Fe}^{3+}$ . This oxidation of the  $\text{Fe}^{2+}$  in heme does not happen in myoglobin. This fact is of crucial importance because  $\text{Fe}^{3+}$  does

**FIGURE 21.30**

Chlorophyll is a porphyrin complex of  $\text{Mg}^{2+}$ . There are two similar forms of chlorophyll, one of which is shown here.



## CHEMICAL IMPACT

### The Danger of Mercury\*

In August 1989, four family members from Lincoln Park, Michigan, died under mysterious circumstances. All four victims had severe tissue damage to the esophagus and lungs, which led doctors to suspect exposure to some type of caustic chemical. Subsequently, local police and fire investigators discovered a crude laboratory in the basement that was used to recover valuable silver from stolen dental amalgams. A dental amalgam is a metal alloy that a dentist uses to fill a tooth. The alloy typically contains silver, tin, copper, and zinc dissolved in liquid mercury. The mixture is placed in a cavity, where it hardens, resulting in a standard “filling.”

One of the victims worked at a manufacturing facility for amalgams and was stealing some of the products. At home in his crude lab he heated the amalgam to drive off the mercury (which vaporized at relatively low temperatures) so that he could recover the silver that was left behind. In the process, the colorless, odorless, tasteless mercury vapor entered the ductwork of the home, which was contaminated with mercury at levels 1500 times normal—levels certain to result in death to those exposed. In fact, postmortem analysis revealed extreme levels of mercury in the vital organs of all four victims. Mercury vapor was the silent killer.

The toxicity of mercury varies significantly depending on the route of entry into the body. Inhalation is the most dangerous route because mercury vapor entering the lungs quickly passes across the lung–blood barrier and into the bloodstream, where it can interfere with normal blood chemistry. One of the reactions that takes place in the blood is

the decomposition of hydrogen peroxide (a metabolic waste product) by the enzyme peroxidase:



When elemental mercury enters the bloodstream, it reacts with hydrogen peroxide in the presence of peroxidase to produce mercury(II) oxide and water:



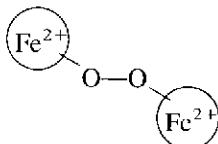
If this conversion to mercury(II) occurs within vital tissues, the mercury(II) cation can denature proteins, inhibit enzyme activity, and disrupt cell membranes. Death often results from respiratory or kidney failure.

If mercury is so toxic, how can it be used in dental fillings? Surprisingly, unlike elemental mercury in the vapor form, mercury bound as a solid in a dental amalgam presents little, if any, risk. Because the mercury is not mobile, even in the harsh environment of the human mouth, the American Dental Association has determined it to be a minimal health risk to dental patients. Even if a filling loosens and is accidentally swallowed, it is passed through the digestive system and excreted before it can pose any risk. The mercury that the four victims in this story were exposed to resulted from heating the amalgam in a smelting furnace, thus vaporizing the mercury and exposing the occupants of the house to the most hazardous route of entry—inhalation.

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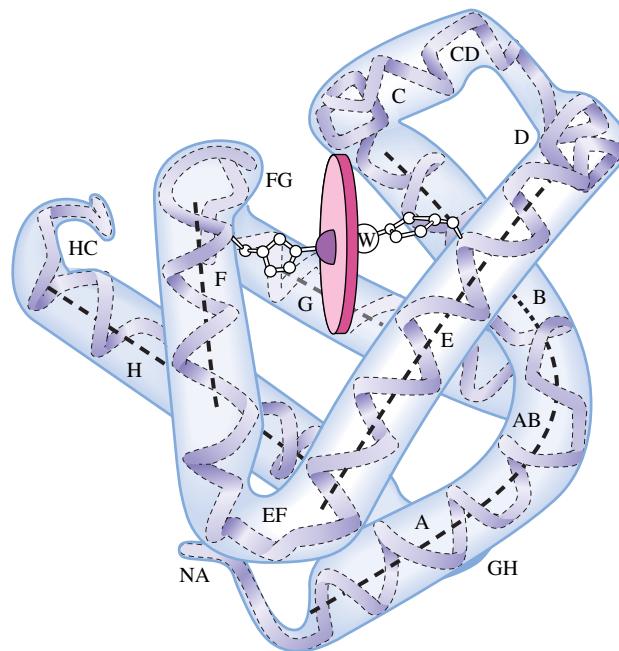
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not form a coordinate covalent bond with  $\text{O}_2$ , and myoglobin would not function if the bound  $\text{Fe}^{2+}$  could be oxidized. Since the  $\text{Fe}^{2+}$  in the “bare” heme complex can be oxidized, it must be the protein that somehow prevents the oxidation. How? Based on much research, the answer seems to be that the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  involves an oxygen bridge between two iron ions (the circles indicate the ligands):



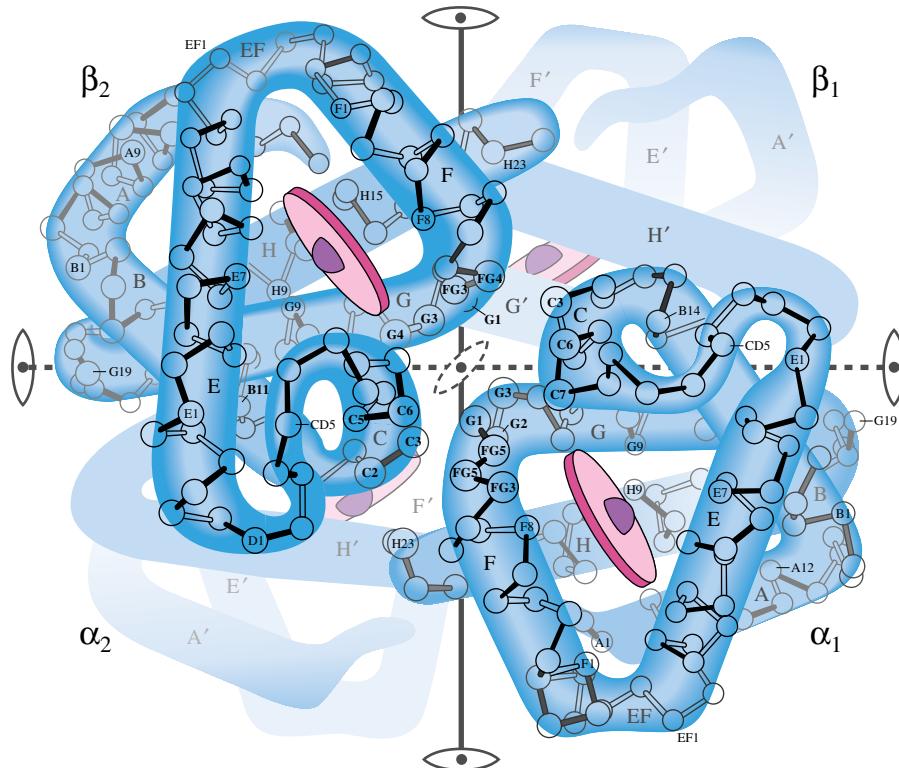
The bulky protein around the heme group in myoglobin prevents two molecules from getting close enough to form the oxygen bridge, and so oxidation of the  $\text{Fe}^{2+}$  is prevented.

The transport of  $\text{O}_2$  in the blood is carried out by **hemoglobin**, a molecule consisting of four myoglobin-like units, as shown in Fig. 21.32. Each hemoglobin can therefore

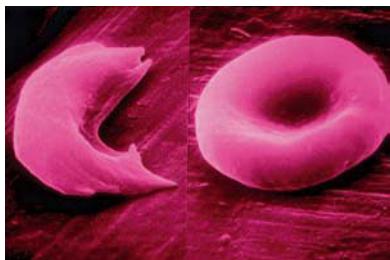
**FIGURE 21.31**

A representation of the myoglobin molecule. The  $\text{Fe}^{2+}$  ion is coordinated to four nitrogen atoms in the porphyrin of the heme (represented by the disk in the figure) and on nitrogen from the protein chain. This leaves a sixth coordination position (indicated by the W) available for an oxygen molecule.

bind four  $\text{O}_2$  molecules to form a bright red diamagnetic complex. The diamagnetism occurs because oxygen is a strong-field ligand toward  $\text{Fe}^{2+}$ , which has a  $3d^6$  electron configuration. When the oxygen molecule is released, water molecules occupy the sixth coordination position around each  $\text{Fe}^{2+}$ , giving a bluish paramagnetic complex ( $\text{H}_2\text{O}$  is a weak-field ligand toward  $\text{Fe}^{2+}$ ) that gives venous blood its characteristic bluish tint.

**FIGURE 21.32**

A representation of the hemoglobin structure. There are two slightly different types of protein chains ( $\alpha$  and  $\beta$ ). Each hemoglobin has two  $\alpha$  chains and two  $\beta$  chains, each with a heme complex near the center. Thus each hemoglobin molecule can complex with four  $\text{O}_2$  molecules.

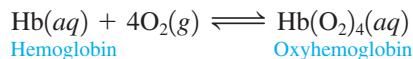


**FIGURE 21.33**

A normal red blood cell (right) and a sickle cell (left), both magnified 18,000 times.

Hemoglobin dramatically demonstrates how sensitive the function of a biomolecule is to its structure. In certain people, in the synthesis of the proteins needed for hemoglobin, an improper amino acid is inserted into the protein in two places. This may not seem very serious, since there are several hundred amino acids present. However, because the incorrect amino acid has a nonpolar substituent instead of the polar one found on the proper amino acid, the hemoglobin drastically changes its shape. The red blood cells are then sickle-shaped rather than disk-shaped, as shown in Fig. 21.33. The misshapen cells can aggregate, causing clogging of tiny capillaries. This condition, known as *sickle cell anemia*, is the subject of intense research.

Our knowledge of the workings of hemoglobin allows us to understand the effects of high altitudes on humans. The reaction between hemoglobin and oxygen can be represented by the following equilibrium:



At high altitudes, where the oxygen content of the air is lower, the position of this equilibrium will shift to the left, according to Le Châtelier's principle. Because less oxyhemoglobin is formed, fatigue, dizziness, and even a serious illness called *high-altitude sickness* can result. One way to combat this problem is to use supplemental oxygen, as most high-altitude mountain climbers do. However, this is impractical for people who live at high elevations. In fact, the human body adapts to the lower oxygen concentrations by making more hemoglobin, causing the equilibrium to shift back to the right. Someone moving from Chicago to Boulder, Colorado (5300 feet), would notice the effects of the new altitude for a couple of weeks, but as the hemoglobin level increased, the effects would disappear. This change is called *high-altitude acclimatization*, which explains why athletes who want to compete at high elevations should practice there for several weeks prior to the event.

Our understanding of the biologic role of iron also allows us to explain the toxicities of substances such as carbon monoxide and the cyanide ion. Both CO and CN<sup>-</sup> are very good ligands toward iron and so can interfere with the normal workings of the iron complexes in the body. For example, carbon monoxide has about 200 times the affinity for the Fe<sup>2+</sup> in hemoglobin as oxygen does. The resulting stable complex, **carboxyhemoglobin**, prevents the normal uptake of O<sub>2</sub>, thus depriving the body of needed oxygen. Asphyxiation can result if enough carbon monoxide is present in the air. The mechanism for the toxicity of the cyanide ion is somewhat different. Cyanide coordinates strongly to cytochrome oxidase, an iron-containing cytochrome enzyme that catalyzes the oxidation-reduction reactions of certain cytochromes. The coordinated cyanide thus prevents the electron-transfer process and rapid death results. Because of its behavior, cyanide is called a *respiratory inhibitor*.





## CHEMICAL IMPACT

### Supercharged Blood

**D**uring the 1964 Winter Olympics in Innsbruck, Austria, a Finn named Eero Maentyranta won three gold medals in cross-country skiing and immediately became a national hero. His success was due in no small part to the fact that his blood carried 25% to 50% more hemoglobin than the average man's blood. Maentyranta suffered from a rare genetic disorder that results in unusually elevated levels of red blood cells. This extra oxygen-carrying capacity lends itself to increased stamina and endurance, certainly an advantage in the rigorous sport of cross-country skiing. Several years later, geneticists at the University of Helsinki determined that the disorder was due to a mutation of a protein responsible for red blood cell production called the *erythropoietin receptor* (EPO-R). The mutation, which was common in the Maentyranta family, resulted in a protein that was missing 70 amino acids (out of 550). This mutation deleted the portion of the protein that contained the "off switch" for red blood cell production.

Since the discovery of EPO's role in red blood cell production, genetic engineers have been able to synthesize EPO

by bioengineering techniques. The protein, marketed in the United States by Amgen of Thousand Oaks, California, is used by kidney dialysis, AIDS, and cancer patients to boost red blood cell production. It has become biotechnology's biggest revenue producer, with over \$1 billion in annual sales.

While the potential benefits of this protein are obvious, the potential for abuse may be even greater. The Tour de France, thought by many to be the world's greatest endurance race, was rocked in 1998 by controversy when several riders (including three race favorites) were expelled from the race over allegations of blood doping with the red blood cell-enhancing hormone EPO. EPO has become the drug of choice for many endurance athletes trying to gain an unfair advantage because it is metabolized quickly and, being identical to the body's own EPO, is almost impossible to detect by blood or urine analysis. But the hazards are great. Endurance athletes are especially at risk from abuse of EPO due to extreme water loss during the athletic competition, which, when coupled with elevated levels of EPO, results in an



A steel mill in Brazil.

## 21.8 Metallurgy and Iron and Steel Production

In the preceding section we saw the importance of iron in biologic systems. Of course, iron is also very important in many other ways in our world. In this section we will discuss the isolation of metals from their natural sources and the formulation of metals into useful materials, with special emphasis on the role of iron.

Metals are very important for structural applications, electrical wires, cooking utensils, tools, decorative items, and many other purposes. However, because the main chemical characteristic of a metal is its ability to give up electrons, almost all metals in nature are found in ores, combined with nonmetals such as oxygen, sulfur, and the halogens. To recover and use these metals, we must separate them from their ores and reduce the metal ions. Then, because most metals are unsuitable for use in the pure state, we must form alloys that have the desired properties. The process of separating a metal from its ore and preparing it for use is known as **metallurgy**. The steps in this process are typically

1. Mining
2. Pretreatment of the ore
3. Reduction to the free metal
4. Purification of the metal (refining)
5. Alloying

An ore can be viewed as a mixture containing **minerals** (relatively pure metal compounds) and **gangue** (sand, clay, and rock). Some typical minerals are listed in Table 21.19. Although silicate minerals are the most common in the earth's crust, they are typically

extreme thickening of the blood. This puts an obvious strain on the heart. Since EPO became available in 1986, several world-class athletes (mostly bicyclists and distance runners) have died under mysterious circumstances thought to be associated with abuse of EPO. Because of the widespread abuse of EPO, new methods of detection have been put in place to limit its impact on organized sports and its participants.

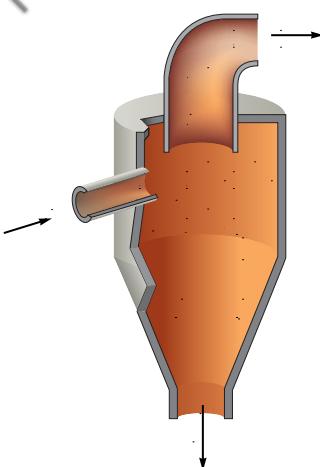
The advantage that Eero Mäenpää gained in the 1964 Olympics was the result of a disorder that he had lived with for his entire life. His body had become accustomed to operating with elevated levels of hemoglobin, and it became a natural advantage. Synthetic EPO holds much promise for those suffering conditions that result in hemoglobin deficiency. But as a performance-enhancing drug, EPO's advantages come with enormous risk.



The 1998 Tour de France.

**TABLE 21.19 Common Minerals Found in Ores**

Anion	Examples
None (free metal)	Au, Ag, Pt, Pd, Rh, Ir, Ru
Oxide	Fe <sub>2</sub> O <sub>3</sub> (hematite) Fe <sub>3</sub> O <sub>4</sub> (magnetite) Al <sub>2</sub> O <sub>3</sub> (bauxite) SnO <sub>2</sub> (cassiterite)
Sulfide	PbS (galena) ZnS (sphalerite) FeS <sub>2</sub> (pyrite) HgS (cinnabar) Cu <sub>2</sub> S (chalococite)
Chloride	NaCl (rock salt) KCl (sylvite) KCl · MgCl <sub>2</sub> (carnalite)
Carbonate	FeCO <sub>3</sub> (siderite) CaCO <sub>3</sub> (limestone) MgCO <sub>3</sub> (magnesite) MgCO <sub>3</sub> · CaCO <sub>3</sub> (dolomite)
Sulfate	CaSO <sub>4</sub> · 2H <sub>2</sub> O (gypsum) BaSO <sub>4</sub> (barite)
Silicate	Be <sub>3</sub> Al <sub>2</sub> Si <sub>6</sub> O <sub>18</sub> (beryl) Al <sub>2</sub> (Si <sub>2</sub> O <sub>8</sub> )(OH) <sub>4</sub> (kaolinite) LiAl(SiO <sub>3</sub> ) <sub>2</sub> (spondumene)

**FIGURE 21.34**

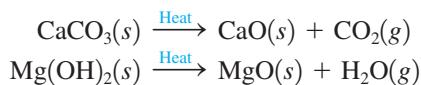
A schematic diagram of a cyclone separator. The ore is pulverized and blown into the separator. The more dense mineral particles are thrown toward the walls by centrifugal force and fall down the funnel. The lighter particles (gangue) tend to stay closer to the center and are drawn out through the top by the stream of air.

very hard and difficult to process, making metal extraction relatively expensive. Therefore, other ores are used when available.

After mining, an ore must be treated to remove the gangue and to concentrate the mineral. The ore is first pulverized and then processed in a variety of devices, including cyclone separators (see Fig. 21.34), inclined vibrating tables, and flotation tanks.

In the **flotation process**, the crushed ore is fed into a tank containing a water–oil–detergent mixture. Because of the difference in the surface characteristics of the mineral particles and the silicate rock particles, the oil wets the mineral particles. A stream of air blown through the mixture causes tiny bubbles to form on the oil-covered pieces, which then float to the surface, where they can be skimmed off.

After the mineral has been concentrated, it is often chemically altered in preparation for the reduction step. For example, nonoxide minerals are often converted to oxides before reduction. Carbonates and hydroxides can be converted by simple heating:



Sulfide minerals can be converted to oxides by heating in air at temperatures below their melting points, a process called **roasting**:



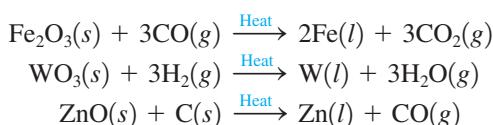
As we have seen earlier, sulfur dioxide causes severe problems if released into the atmosphere, and modern roasting operations collect this gas and use it in the manufacture of sulfuric acid.

The method chosen to reduce the metal ion to the free metal, a process called **smelting**, depends on the affinity of the metal ion for electrons. Some metals are good enough oxidizing agents that the free metal is produced in the roasting process. For example, the roasting reaction for cinnabar is



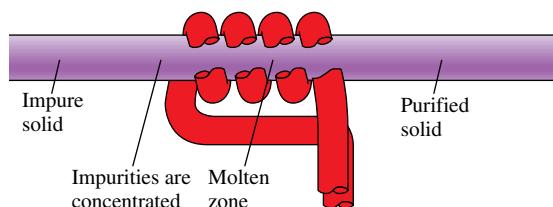
where the  $\text{Hg}^{2+}$  is reduced by electrons donated by the  $\text{S}^{2-}$  ion, which is then further oxidized by  $\text{O}_2$  to form  $\text{SO}_2$ .

The roasting of a more active metal produces the metal oxide, which must be reduced to obtain the free metal. The most common reducing agents are coke (impure carbon), carbon monoxide, and hydrogen. The following are some common examples of the reduction process:



The most active metals, such as aluminum and the alkali metals, must be reduced electrolytically, usually from molten salts (see Section 17.8).

The metal obtained in the reduction step is invariably impure and must be refined. The methods of refining include electrolytic refining (see Section 17.8), oxidation of impurities (as for iron, see below), and distillation of low-boiling metals such as mercury and zinc. One process used when highly pure metals are needed is **zone refining**. In this process a bar of the impure metal travels through a heater (see Fig. 21.35), which causes melting and recrystallizing of the metal as the bar cools. Purification of the metal occurs because as the crystal re-forms, the metal ions are likely to fit much better in the crystal lattice than are the atoms of impurities. Thus the impurities tend to be excluded and carried to the end of the bar. Several repetitions of this process give a very pure metal bar.

**FIGURE 21.35**

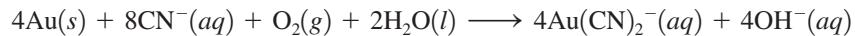
A schematic representation of zone refining.

## Hydrometallurgy

The metallurgical processes we have considered so far are usually called **pyrometallurgy** (*pyro* means “at high temperatures”). These traditional methods require large quantities of energy and have two other serious problems: atmospheric pollution (mainly by sulfur dioxide) and relatively high costs that make treatment of low-grade ores economically unfeasible.

In the past hundred years, a different process, **hydrometallurgy** (*hydro* means “water”), has been employed to extract metals from ores by use of aqueous chemical solutions, a process called **leaching**. The first two uses of hydrometallurgy were for the extraction of gold from low-grade ores and for the production of aluminum oxide, or alumina, from bauxite, an aluminum-bearing ore.

Gold is sometimes found in ores in the elemental state, but it usually occurs in relatively small concentrations. A process called **cyanidation** treats the crushed ore with an aqueous cyanide solution in the presence of air to dissolve the gold by forming the complex ion  $\text{Au}(\text{CN})_2^-$ :



Pure gold is then recovered by reaction of the solution of  $\text{Au}(\text{CN})_2^-$  with zinc powder to reduce  $\text{Au}^+$  to  $\text{Au}$ :



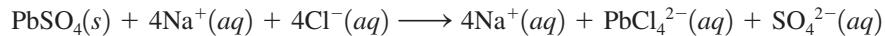
The extraction of alumina from bauxite (the Bayer process) leaches the ore with sodium hydroxide at high temperatures and pressures to dissolve the amphoteric aluminum oxide:



This process leaves behind solid impurities such as  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{TiO}_2$ , which are not appreciably soluble in basic solution. After the solid impurities are removed, the pH of the solution is lowered, causing the pure aluminum oxide to re-form. It is then electrolyzed to produce aluminum metal (see Section 17.8).

As illustrated by these processes, hydrometallurgy involves two distinct steps: *selective leaching* of a given metal ion from the ore and recovery of the metal ion from the solution by *selective precipitation* as an ionic compound.

The leaching agent can simply be water if the metal-containing compound is a water-soluble chloride or sulfate. However, most commonly, the metal is present in a water-insoluble substance that must somehow be dissolved. The leaching agents used in such cases are usually aqueous solutions containing acids, bases, oxidizing agents, salts, or some combination of these. Often the dissolving process involves the formation of complex ions. For example, when an ore containing water-insoluble lead sulfate is treated with an aqueous sodium chloride solution, the soluble complex ion  $\text{PbCl}_4^{2-}$  is formed:



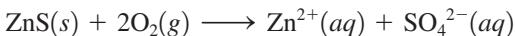
Precipitation reactions are discussed in Section 15.7.

**TABLE 21.20 Examples of Methods for Recovery of Metal Ions from Leaching Solutions**

Method	Examples
Precipitation of a salt	$\text{Cu}^{2+}(aq) + \text{S}^{2-}(aq) \longrightarrow \text{CuS}(s)$
Reduction	$\text{Cu}^+(aq) + \text{HCN}(aq) \longrightarrow \text{CuCN}(s) + \text{H}^+(aq)$
	$\left\{ \begin{array}{l} \text{Au}^+(aq) + \text{Fe}^{2+}(aq) \longrightarrow \text{Au}(s) + \text{Fe}^{3+}(aq) \\ \text{Cu}^{2+}(aq) + \text{Fe}(s) \longrightarrow \text{Cu}(s) + \text{Fe}^{2+}(aq) \\ \text{Ni}^{2+}(aq) + \text{H}_2(g) \longrightarrow \text{Ni}(s) + 2\text{H}^+(aq) \\ \text{Cu}^{2+}(aq) + 2\text{e}^- \longrightarrow \text{Cu}(s) \\ \text{Al}^{3+}(aq) + 3\text{e}^- \longrightarrow \text{Al}(s) \end{array} \right.$
Reduction plus precipitation	$2\text{Cu}^{2+}(aq) + 2\text{Cl}^-(aq) + \text{H}_2\text{SO}_3(aq) + \text{H}_2\text{O}(l) \longrightarrow 2\text{CuCl}(s) + 3\text{H}^+(aq) + \text{HSO}_4^-(aq)$

Formation of a complex ion also occurs in the cyanidation process for the recovery of gold. However, since the gold is present in the ore as particles of metal, it must first be oxidized by oxygen to produce  $\text{Au}^+$ , which then reacts with  $\text{CN}^-$  to form the soluble  $\text{Au}(\text{CN})_2^-$  species. Thus, in this case, the leaching process involves a combination of oxidation and complexation.

Sometimes just oxidation is used. For example, insoluble zinc sulfide can be converted to soluble zinc sulfate by pulverizing the ore and suspending it in water to form a slurry through which oxygen is bubbled:



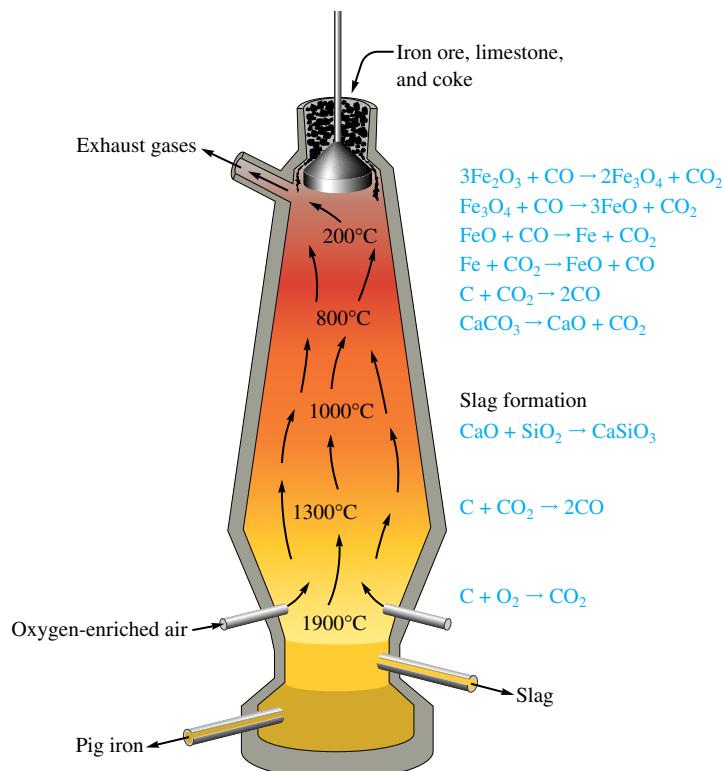
One advantage of hydrometallurgy over the traditional processes is that sometimes the leaching agent can be pumped directly into the ore deposits in the earth. For example, aqueous sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) can be injected into uranium-bearing ores to form water-soluble complex carbonate ions.

Recovering the metal ions from the leaching solution involves forming an insoluble solid containing the metal ion to be recovered. This step may involve addition of an anion to form an insoluble salt, reduction to the solid metal, or a combination of reduction and precipitation of a salt. Examples of these processes are shown in Table 21.20. Because of its suitability for treating low-grade ores economically and without significant pollution, hydrometallurgy is becoming more popular for recovering many important metals such as copper, nickel, zinc, and uranium.

## The Metallurgy of Iron

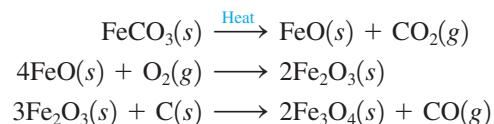
Iron is present in the earth's crust in many types of minerals. *Iron pyrite* ( $\text{FeS}_2$ ) is widely distributed but is not suitable for production of metallic iron and steel because it is almost impossible to remove the last traces of sulfur. The presence of sulfur makes the resulting steel too brittle to be useful. *Siderite* ( $\text{FeCO}_3$ ) is a valuable iron mineral that can be converted to iron oxide by heating. The iron oxide minerals are *hematite* ( $\text{Fe}_2\text{O}_3$ ), the more abundant, and *magnetite* ( $\text{Fe}_3\text{O}_4$ , really  $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ ). *Taconite* ores contain iron oxides mixed with silicates and are more difficult to process than the others. However, taconite ores are being increasingly used as the more desirable ores are consumed.

To concentrate the iron in iron ores, advantage is taken of the natural magnetism of  $\text{Fe}_3\text{O}_4$  (hence its name, *magnetite*). The  $\text{Fe}_3\text{O}_4$  particles can be separated from the gangue by magnets. The ores that are not magnetic are often converted to  $\text{Fe}_3\text{O}_4$ ; hematite is partially reduced to magnetite, while siderite is first converted to  $\text{FeO}$  thermally, then

**FIGURE 21.36**

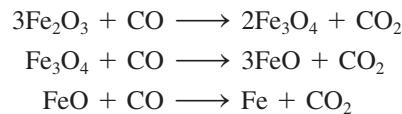
The blast furnace used in the production of iron.

oxidized to  $\text{Fe}_2\text{O}_3$ , and then reduced to  $\text{Fe}_3\text{O}_4$ :

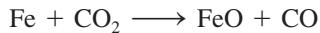


Sometimes the nonmagnetic ores are concentrated by flotation processes.

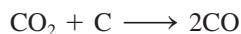
The most commonly used reduction process for iron takes place in the **blast furnace** (Fig. 21.36). The raw materials required are concentrated iron ore, coke, and limestone (which serves as a *flux* to trap impurities). The furnace, which is approximately 25 feet in diameter, is charged from the top with a mixture of iron ore, coke, and limestone. A very strong blast ( $\sim 350 \text{ mi/h}$ ) of hot air is injected at the bottom, where the oxygen reacts with the carbon in the coke to form carbon monoxide, the reducing agent for the iron. The temperature of the charge increases as it travels down the furnace, with reduction of the iron to iron metal occurring in steps:



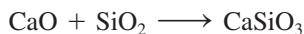
Iron can reduce carbon dioxide,



so complete reduction of the iron occurs only if the carbon dioxide is destroyed by adding excess coke:



The limestone ( $\text{CaCO}_3$ ) in the charge loses carbon dioxide, or *calcines*, in the hot furnace and combines with silica and other impurities to form **slag**, which is mostly molten calcium silicate,  $\text{CaSiO}_3$ ,



and alumina ( $\text{Al}_2\text{O}_3$ ). The slag floats on the molten iron and is skimmed off. The gas that escapes from the top of the furnace contains carbon monoxide, which is combined with air to form carbon dioxide. The energy released in this exothermic reaction is collected in a heat exchanger and used in heating the furnace.

The iron collected from the blast furnace, called **pig iron**, is quite impure. It contains ~90% iron, ~5% carbon, ~2% manganese, ~1% silicon, ~0.3% phosphorus, and ~0.04% sulfur (from impurities in the coke). The production of 1 ton of pig iron requires approximately 1.7 tons of iron ore, 0.5 ton of coke, 0.25 ton of limestone, and 2 tons of air.

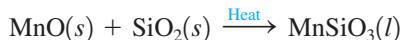
Iron oxide also can be reduced in a **direct reduction furnace**, which operates at much lower temperatures (1300–2000°F) than a blast furnace and produces a solid “sponge iron” rather than molten iron. Because of the milder reaction conditions, the direct reduction furnace requires a higher grade of iron ore (with fewer impurities) than that used in a blast furnace. The iron from the direct reduction furnace is called *DRI* (*directly reduced iron*) and contains ~95% iron, with the balance mainly silica and alumina.

## Production of Steel

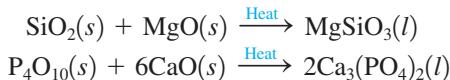
Steel is an alloy and can be classified as **carbon steel**, which contains up to about 1.5% carbon, or **alloy steel**, which contains carbon plus other metals such as Cr, Co, Mn, and Mo. The wide range of mechanical properties associated with steel is determined by its chemical composition and by the heat treatment of the final product.

The production of iron from its ore is fundamentally a reduction process, but the conversion of iron to steel is basically an oxidation process in which unwanted impurities are eliminated. Oxidation is carried out in various ways, but the two most common are the open hearth process and the basic oxygen process.

In the oxidation reactions of steelmaking, the manganese, phosphorus, and silicon in the impure iron react with oxygen to form oxides, which in turn react with appropriate fluxes to form slag. Sulfur enters the slag primarily as sulfides, and excess carbon forms carbon monoxide or carbon dioxide. The flux chosen depends on the major impurities present. If manganese is the chief impurity, an acidic flux of silica is used:

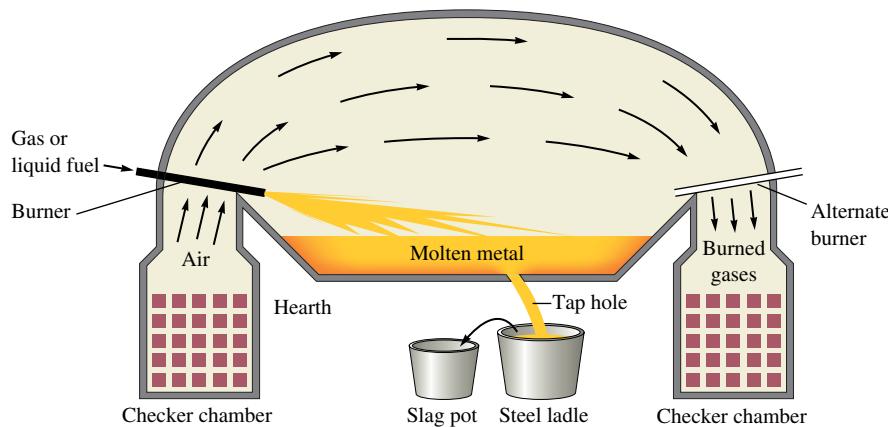


If the main impurity is silicon or phosphorus, a basic flux, usually lime ( $\text{CaO}$ ) or magnesia ( $\text{MgO}$ ), is needed to give reactions such as



Whether an acidic or a basic slag will be needed is a factor that must be considered when a furnace is constructed so that its refractory linings will be compatible with the slag. Silica bricks would deteriorate quickly in the presence of basic slag, and magnesia or lime bricks would dissolve in acid slag.

The **open hearth process** (Fig. 21.37) uses a dishlike container that holds 100 to 200 tons of molten iron. An external heat source is required to keep the iron molten, and a concave roof over the container reflects heat back toward the iron surface. A blast of air or oxygen is passed over the surface of the iron to react with impurities. Silicon

**FIGURE 21.37**

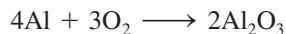
A schematic diagram of the open hearth process for steelmaking. The checker chambers contain bricks that absorb heat from gases passing over the molten charge. The flow of air and gases is reversed periodically.

and manganese are oxidized first and enter the slag, followed by oxidation of carbon to carbon monoxide, which causes agitation and foaming of the molten bath. The exothermic oxidation of carbon raises the temperature of the bath, causing the limestone flux to calcine:



The resulting lime floats to the top of the molten mixture (an event called the *lime boil*), where it combines with phosphates, sulfates, and silicates. Next comes the refining process, which involves continued oxidation of carbon and other impurities. Because the melting point increases as the carbon content decreases, the bath temperatures must be increased during this phase of the operation. If the carbon content falls below that desired in the final product, coke or pig iron may be added.

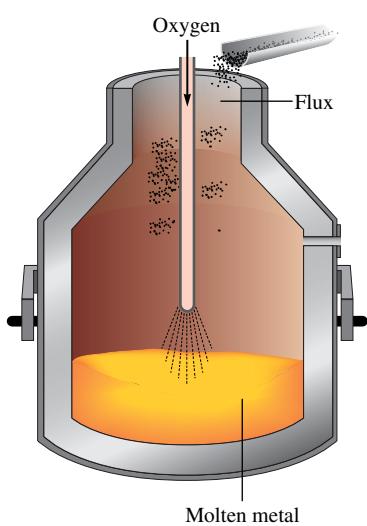
The final composition of the steel is “fine-tuned” after the charge is poured. For example, aluminum is sometimes added at this stage to remove trace amounts of oxygen via the reaction



Alloying metals such as vanadium, chromium, titanium, manganese, and nickel are also added to give the steel the properties needed for a specific application.

The processing of a batch of steel by the open hearth process is quite slow, taking up to 8 hours. The **basic oxygen process** is much faster. Molten pig iron and scrap iron are placed in a barrel-shaped container (Fig. 21.38) that can hold as much as 300 tons of material. A high-pressure blast of oxygen is directed at the surface of the molten iron, oxidizing impurities in a manner very similar to that used in the open hearth process. Fluxes are added after the oxygen blow begins. One advantage of this process is that the exothermic oxidation reactions proceed so rapidly that they produce enough heat to raise the temperature nearly to the boiling point of iron without an external heat source. Also, at these high temperatures only about an hour is needed to complete the oxidation processes.

The **electric arc method**, which was once used only for small batches of specialty steels, is being utilized more and more in the steel industry. In this process an electric arc between carbon electrodes is used to melt the charge. This means that no fuel-borne impurities are added to the steel, since no fuel is needed. Also, higher temperatures are possible than in the open hearth or basic oxygen processes, and this leads to more effective removal of sulfur and phosphorus impurities. Oxygen is added in this process so that the oxide impurities in the steel can be controlled effectively.

**FIGURE 21.38**

The basic oxygen process for steelmaking.

**TABLE 21.21 Percent Composition and Uses of Various Types of Steel**

Type of Steel	% Carbon	% Manganese	% Phosphorus	% Sulfur	% Silicon	% Nickel	% Chromium	% Other	Uses
Plain carbon	≤1.35	≤1.65	≤0.04	≤0.05	≤0.60	—	—	—	Sheet steel, tools
High-strength (low-alloy)	≤0.25	≤1.65	≤0.04	≤0.05	0.15–0.9	0.4–1	0.3–1.3	Cu (0.2–0.6) Sb (0.01–0.08) V (0.01–0.08)	Transportation equipment, structural beams
Alloy	≤1.00	≤3.50	≤0.04	≤0.05	0.15–2.0	0.25–10.0	0.25–4.0	Mo (0.08–4.0) V (0–0.2) W (0–18) Co (0–5)	Automobile and aircraft engine parts
Stainless	0.03–1.2	1.0–10	0.04–0.06	≤0.03	1–3	1–22	4.0–27	—	Engine parts, steam turbine parts, kitchen utensils
Silicon	—	—	—	—	0.5–5.0	—	—	—	Electric motors and transformers

## Heat Treatment of Steel

Refer to Section 10.3 for a review of packing and crystal lattices.

One way of producing the desired physical properties in steel is by controlling the chemical composition (see Table 21.21). Another method for tailoring the properties of steel involves heat treatment. Pure iron exists in two different crystalline forms, depending on the temperature. At any temperature below 912°C, iron has a body-centered cubic structure and is called *α-iron*. Between 912°C and 1394°C, iron has a face-centered cubic structure called *austenite*, or *γ-iron*. At 1394°C, iron changes to *δ-iron*, a body-centered cubic structure identical to *α-iron*.

When iron is alloyed with carbon, which fits into holes among the iron atoms to form the interstitial alloy *carbon steel*, the situation becomes even more complex. For example, the temperature at which *α-iron* changes to austenite is lowered by about 200°C. Also, at high temperatures iron and carbon react by an endothermic reversible reaction to form an iron carbide called *cementite*:



By Le Châtelier's principle, we can predict that cementite will become more stable relative to iron and carbon as the temperature is increased. This is the observed result.

Thus steel is really a mixture of iron metal in one of its crystal forms, carbon, and cementite. The proportions of these components are very important in determining the physical properties of steel.

When steel is heated to temperatures in the region of 1000°C, much of the carbon is converted to cementite. If the steel is then allowed to cool slowly, the equilibrium shown above shifts to the left, and small crystals of carbon precipitate, giving a steel that is relatively ductile. If the cooling is very rapid, the equilibrium does not have time to adjust. The cementite is trapped, and the steel has a high cementite content, making it quite brittle. The proportions of carbon crystals and cementite can be "fine-tuned" to give the desired properties by heating to intermediate temperatures followed by rapid cooling, a process called **tempering**. The rate of heating and cooling determines not only the amounts of cementite present but also the size of its crystals and the form of crystalline iron present.

## Key Terms

### Section 21.1

complex ion  
first-row transition metals  
lanthanide contraction  
lanthanide series

### Section 21.3

coordination compound  
counterion  
oxidation state  
coordination number  
ligand  
coordinate covalent bond  
monodentate (unidentate) ligand  
chelating ligand (chelate)  
bidentate ligand

### Section 21.4

isomers  
structural isomerism  
stereoisomerism  
coordination isomerism  
linkage isomerism  
geometrical (*cis-trans*) isomerism  
*trans* isomer  
*cis* isomer  
optical isomerism  
chiral  
enantiomers

### Section 21.6

crystal field model  
*d*-orbital splitting  
strong-field (low-spin) case  
weak-field (high-spin) case  
spectrochemical series

### Section 21.7

cytochromes  
heme  
porphyrin  
myoglobin  
hemoglobin  
carboxyhemoglobin

### Section 21.8

metallurgy  
minerals  
gangue  
flotation process  
roasting  
smelting  
zone refining  
pyrometallurgy  
hydrometallurgy  
leaching  
cyanidation  
blast furnace  
slag  
pig iron

## For Review

### First-row transition metals (scandium–zinc)

- All have one or more electrons in the 4s orbital and various numbers of 3*d* electrons
- All exhibit metallic properties
  - A particular element often shows more than one oxidation state in its compounds
- Most compounds are colored, and many are paramagnetic
- Most commonly form coordination compounds containing a complex ion involving ligands (Lewis bases) attached to a central transition metal ion
  - The number of attached ligands (called the coordination number) can vary from 2 to 8, with 4 and 6 being most common
- Many transition metal ions have major biologic importance in molecules such as enzymes and those that transport and store oxygen
- Chelating ligands form more than one bond to the transition metal ion

### Isomerism

- Isomers: two or more compounds with the same formula but different properties
  - Coordination isomerism: the composition of the coordination sphere varies
  - Linkage isomerism: the point of attachment of one or more ligands varies
  - Stereoisomerism: isomers have identical bonds but different spatial arrangements
  - Geometric isomerism: ligands assume different relative positions in the coordination sphere; examples are *cis* and *trans* isomers
  - Optical isomerism: molecules with nonsuperimposable mirror images rotate plane-polarized light in opposite directions

### Spectral and magnetic properties

- Usually explained in terms of the crystal field model
- Model assumes the ligands are point charges that split the energies of the 3*d* orbitals
- Color and magnetism are explained in terms of how the 3*d* electrons occupy the split 3*d* energy levels
  - Strong-field case: relatively large orbital splitting
  - Weak-field case: relatively small orbital splitting

### Metallurgy

- The processes connected with separating a metal from its ore
  - The minerals in ores are often converted to oxides (roasting) before being reduced to the metal (smelting)
- The metallurgy of iron: most common method for reduction uses a blast furnace; process involves iron ore, coke, and limestone
  - Impure product (~90% iron) is called pig iron
- Steel is manufactured by oxidizing the impurities in pig iron

### REVIEW QUESTIONS

1. What two first-row transition metals have unexpected electron configurations? A statement in the text says that first-row transition metal ions do not have 4s electrons. Why not? Why do transition metal ions often have several oxidation states, whereas representative metals generally have only one?
2. Define each of the following terms:
  - a. coordination compound
  - b. complex ion
  - c. counterions
  - d. coordination number

## 988 Chapter Twenty-One Transition Metals and Coordination Chemistry

direct reduction furnace  
carbon steel  
alloy steel  
open hearth process  
basic oxygen process  
electric arc method  
tempering

- e. ligand
- f. chelate
- g. bidentate

How would transition metal ions be classified using the Lewis definition of acids and bases? What must a ligand have to bond to a metal? What do we mean when we say that a bond is a “coordinate covalent bond”?

3. When a metal ion has a coordination number of 2, 4, or 6, what are the observed geometries and associated bond angles? For each of the following, give the correct formulas for the complex ions.

- a. linear  $\text{Ag}^+$  complex ions having  $\text{CN}^-$  ligands
- b. tetrahedral  $\text{Cu}^+$  complex ions having  $\text{H}_2\text{O}$  ligands
- c. tetrahedral  $\text{Mn}^{2+}$  complex ions having oxalate ligands
- d. square planar  $\text{Pt}^{2+}$  complex ions having  $\text{NH}_3$  ligands
- e. octahedral  $\text{Fe}^{3+}$  complex ions having EDTA ligands
- f. octahedral  $\text{Co}^{2+}$  complex ions having  $\text{Cl}^-$  ligands
- g. octahedral  $\text{Cr}^{3+}$  complex ions having ethylenediamine ligands

What is the electron configuration for the metal ion in each of the complex ions in a–g?

4. What is wrong with the following formula–name combinations? Give the correct names for each.

- |  |  |
|--|--|
| a. $[\text{Cu}(\text{NH}_3)_4]\text{Cl}_2$                   | copperammine chloride                      |
| b. $[\text{Ni}(\text{en})_2]\text{SO}_4$                     | bis(ethylenediamine)nickel(IV) sulfate     |
| c. $\text{K}[\text{Cr}(\text{H}_2\text{O})_2\text{Cl}_4]$    | potassium tetrachlorodiaquachromium(III)   |
| d. $\text{Na}_4[\text{Co}(\text{CN})_4\text{C}_2\text{O}_4]$ | tetrasodium tetracyanooxalatocobaltate(II) |

5. Define each of the following and give examples of each.

- a. isomer
- b. structural isomer
- c. stereoisomer
- d. coordination isomer
- e. linkage isomer
- f. geometrical isomer
- g. optical isomer

Consider the *cis* and *trans* forms of the octahedral complex  $\text{Cr}(\text{en})_2\text{Cl}_2$ . Are both of these isomers optically active? Explain.

Another way to determine whether a substance is optically active is to look for a plane of symmetry in the molecule. If a substance has a plane of symmetry, then it will not exhibit optical activity (the mirror image will be superimposable). Show the plane of symmetry in the *trans* isomer and prove to yourself that the *cis* isomer does not have a plane of symmetry.

6. What is the major focus of the crystal field model? Why are the *d* orbitals split into two sets for an octahedral complex? What are the two sets of orbitals?

Define each of the following.

- a. weak-field ligand
- b. strong-field ligand
- c. low-spin complex
- d. high-spin complex

Why is  $\text{Co}(\text{NH}_3)_6^{3+}$  diamagnetic whereas  $\text{CoF}_6^{3-}$  is paramagnetic? Some octahedral complex ions have the same *d*-orbital splitting diagrams whether they are high-spin or low-spin. For which of the following is this true?

- a.  $\text{V}^{3+}$
- b.  $\text{Ni}^{2+}$
- c.  $\text{Ru}^{2+}$

7. The crystal field model predicts magnetic properties of complex ions and explains the colors of these complex ions. How? Solutions of  $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$  are yellow, but  $\text{Cr}(\text{NH}_3)_6^{3+}$  does not absorb yellow light. Why? What color light is absorbed by  $\text{Cr}(\text{NH}_3)_6^{3+}$ ? What is the spectrochemical series, and how can the study of light absorbed by various complex ions be used to develop this series? Would you expect  $\text{Co}(\text{NH}_3)_6^{2+}$  to absorb light of a longer or shorter wavelength than  $\text{Co}(\text{NH}_3)_6^{3+}$ ? Explain. Compounds of copper(II) are generally colored, but compounds of copper(I) are not colored. Explain. Would you expect  $\text{Cd}(\text{NH}_3)_4\text{Cl}_2$  to be colored? Explain. Compounds of  $\text{Sc}^{3+}$  are not colored, but those of  $\text{Ti}^{3+}$  and  $\text{V}^{3+}$  are colored. Explain.
8. Why do tetrahedral complex ions have a different crystal field diagram than octahedral complex ions? What is the tetrahedral crystal field diagram? Why are virtually all tetrahedral complex ions “high spin”?
- Explain the crystal field diagram for square planar complex ions and for linear complex ions.
9. Review Table 21.18, which lists some important biological functions associated with different first-row transition metals. The transport of  $\text{O}_2$  in the blood is carried out by hemoglobin. Briefly explain how hemoglobin transports  $\text{O}_2$  in the blood. Why are  $\text{CN}^-$  and CO toxic to humans and animals?
10. Define and give an example of each of the following.
- roasting
  - smelting
  - flotation
  - leaching
  - gangue

What are the advantages and disadvantages of hydrometallurgy? Describe the process by which a metal is purified by zone refining.

## Active Learning Questions

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

- You isolate a compound with the formula  $\text{PtCl}_4 \cdot 2\text{KCl}$ . From electrical conductance tests of an aqueous solution of the compound, you find that three ions per formula unit are present, and you also notice that addition of  $\text{AgNO}_3$  does not cause a precipitate. Give the formula for this compound that shows the complex ion present. Explain your findings. Name this compound.
- Both  $\text{Ni}(\text{NH}_3)_4^{2+}$  and  $\text{Ni}(\text{CN})_4^{2-}$  have four ligands. The first is paramagnetic, and the second is diamagnetic. Are the complex ions tetrahedral or square planar? Explain.
- Which is more likely to be paramagnetic,  $\text{Fe}(\text{CN})_6^{4-}$  or  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ ? Explain.
- A metal ion in a high-spin octahedral complex has two more unpaired electrons than the same ion does in a low-spin octahedral complex. Name some possible metal ions for which this would be true.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

## Questions

- Oxalic acid is often used to remove rust stains. What properties of oxalic acid allow it to do this?
- Four different octahedral chromium coordination compounds exist that all have the same oxidation state for chromium and have  $\text{H}_2\text{O}$  and  $\text{Cl}^-$  as the ligands and counterions. When 1 mol of each of the four compounds is dissolved in water, how many mol of silver chloride will precipitate upon addition of excess  $\text{AgNO}_3$ ?
- Figure 21.17 shows that the *cis* isomer of  $\text{Co}(\text{en})_2\text{Cl}_2^+$  is optically active while the *trans* isomer is not optically active. Is the same true for  $\text{Co}(\text{NH}_3)_4\text{Cl}_2^+$ ? Explain.
- A certain first-row transition metal ion forms many different colored solutions. When four coordination compounds of this metal, each having the same coordination number, are dissolved in water, the colors of the solutions are red, yellow, green, and blue. Further experiments reveal that two of the complex ions are paramagnetic with four unpaired electrons and the other two are diamagnetic. What can be deduced from this information about the four coordination compounds?

## Chapter Twenty-One Transition Metals and Coordination Chemistry

**9.**  $\text{CoCl}_4^{2-}$  forms a tetrahedral complex ion and  $\text{Co}(\text{CN})_6^{3-}$  forms an octahedral complex ion. What is wrong about the following statements concerning each complex ion and the *d* orbital splitting diagrams?

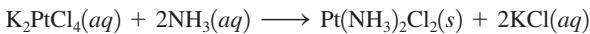
- a.  $\text{CoCl}_4^{2-}$  is an example of a strong-field case having two unpaired electrons.
- b. Because  $\text{CN}^-$  is a weak field ligand,  $\text{Co}(\text{CN})_6^{3-}$  will be a low spin case having four unpaired electrons.

**10.** The following statements discuss some coordination compounds. For each coordination compound, give the complex ion and the counterions, the electron configuration of the transition metal, and the geometry of the complex ion.

- a.  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  is a compound used in novelty devices that predict rain.
- b. During the developing process of black-and-white film, silver bromide is removed from photographic film by the fixer. The major component of the fixer is sodium thiosulfate. The equation for the reaction is:

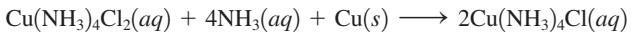


- c. The compound cisplatin,  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ , has been studied extensively as an antitumor agent. The reaction for the synthesis of cisplatin is:



Assume these platinum complex ions have a square planar geometry.

- d. In the production of printed circuit boards for the electronics industry, a thin layer of copper is laminated onto an insulating plastic board. Next, a circuit pattern made of a chemically resistant polymer is printed on the board. The unwanted copper is removed by chemical etching, and the protective polymer is finally removed by solvents. One etching reaction is:



Assume these copper complex ions have tetrahedral geometry.

- 11.** What causes high-altitude sickness and what is high-altitude acclimatization?
- 12.** Almost all metals in nature are found as ionic compounds in ores instead of being in the pure state. Why? What must be done to a sample of ore to obtain a metal substance that has desirable properties?

### Exercises

In this section similar exercises are paired.

#### Transition Metals and Coordination Compounds

- 13.** Write electron configurations for the following metals.

- a. Ni    b. Cd    c. Zr    d. Os

- 14.** Write electron configurations for the following ions.

- a.  $\text{Ni}^{2+}$     c.  $\text{Zr}^{3+}$  and  $\text{Zr}^{4+}$
- b.  $\text{Cd}^{2+}$     d.  $\text{Os}^{2+}$  and  $\text{Os}^{3+}$

- 15.** Write electron configurations for each of the following.

- a. Ti,  $\text{Ti}^{2+}$ ,  $\text{Ti}^{4+}$
- b. Re,  $\text{Re}^{2+}$ ,  $\text{Re}^{3+}$
- c. Ir,  $\text{Ir}^{2+}$ ,  $\text{Ir}^{3+}$

- 16.** Write electron configurations for each of the following.

- a. Cr,  $\text{Cr}^{2+}$ ,  $\text{Cr}^{3+}$
- b. Cu,  $\text{Cu}^+$ ,  $\text{Cu}^{2+}$
- c. V,  $\text{V}^{2+}$ ,  $\text{V}^{3+}$

- 17.** What is the electron configuration for the transition metal ion in each of the following compounds?

- a.  $\text{K}_3[\text{Fe}(\text{CN})_6]$
- b.  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$
- c.  $[\text{Ni}(\text{H}_2\text{O})_6]\text{Br}_2$
- d.  $[\text{Cr}(\text{H}_2\text{O})_4(\text{NO}_2)_2]\text{I}$

- 18.** What is the electron configuration for the transition metal ion(s) in each of the following compounds?

- a.  $(\text{NH}_4)_2[\text{Fe}(\text{H}_2\text{O})_2\text{Cl}_4]$
- b.  $[\text{Co}(\text{NH}_3)_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2]\text{I}_2$
- c.  $\text{Na}_2[\text{TaF}_7]$
- d.  $[\text{Pt}(\text{NH}_3)_4\text{I}_2][\text{PtI}_4]$

Pt forms +2 and +4 oxidation states in compounds.

- 19.** Molybdenum is obtained as a by-product of copper mining or is mined directly (primary deposits are in the Rocky Mountains in Colorado). In both cases it is obtained as  $\text{MoS}_2$ , which is then converted to  $\text{MoO}_3$ . The  $\text{MoO}_3$  can be used directly in the production of stainless steel for high-speed tools (which accounts for about 85% of the molybdenum used). Molybdenum can be purified by dissolving  $\text{MoO}_3$  in aqueous ammonia and crystallizing ammonium molybdate. Depending on conditions, either  $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$  or  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  is obtained.

a. Give names for  $\text{MoS}_2$  and  $\text{MoO}_3$ .

b. What is the oxidation state of Mo in each of the compounds mentioned above?

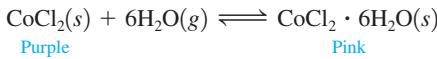
- 20.** Iron is present in the earth's crust in many types of minerals. The iron oxide minerals are hematite ( $\text{Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ). What is the oxidation state of iron in each mineral? The iron ions in magnetite are a mixture of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions. What is the ratio of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  ions in magnetite? The formula for magnetite is usually written as  $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ . Does this make sense? Explain.

- 21.** What is the lanthanide contraction? How does the lanthanide contraction affect the properties of the 4*d* and 5*d* transition metals?

- 22.** We expect the atomic radius to increase down a group in the periodic table. Can you suggest why the atomic radius of hafnium breaks this rule? (See the following data.)

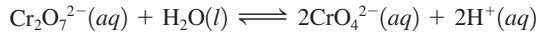
Element	Atomic Radius (Å)	Element	Atomic Radius (Å)
Sc	1.57	Ti	1.477
Y	1.693	Zr	1.593
La	1.915	Hf	1.476

- 23.** Novelty devices for predicting rain contain cobalt(II) chloride and are based on the following equilibrium:

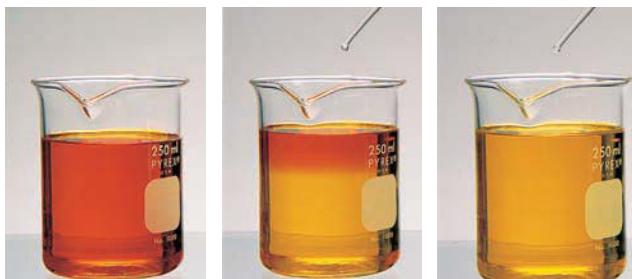


What color will such an indicator be if rain is imminent?

- 24.** Chromium(VI) forms two different oxyanions, the orange dichromate ion,  $\text{Cr}_2\text{O}_7^{2-}$ , and the yellow chromate ion,  $\text{CrO}_4^{2-}$ . The equilibrium reaction between the two ions is

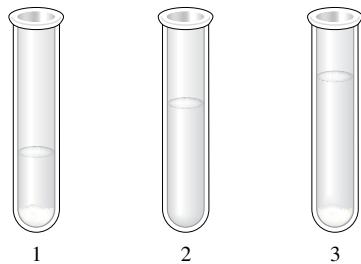


The following pictures show what happens when sodium hydroxide is added to a dichromate solution.



Explain what happened.

- 25.** A series of chemicals was added to some  $\text{AgNO}_3(aq)$ .  $\text{NaCl}(aq)$  was added first to the silver nitrate solution with the end result shown below in test tube 1,  $\text{NH}_3(aq)$  was then added with the end result shown in test tube 2, and  $\text{HNO}_3(aq)$  was added last with the end result shown in test tube 3.



Explain the results shown in each test tube. Include a balanced equation for the reaction(s) taking place.

- 26.** When an aqueous solution of  $\text{KCN}$  is added to a solution containing  $\text{Ni}^{2+}$  ions, a precipitate forms, which redissolves on addition of more  $\text{KCN}$  solution. Write reactions describing what happens in this solution. (*Hint:*  $\text{CN}^-$  is a Brønsted–Lowry base [ $K_b \approx 10^{-5}$ ] and a Lewis base.)

- 27.** Consider aqueous solutions of the following coordination compounds:  $\text{Co}(\text{NH}_3)_6\text{I}_3$ ,  $\text{Pt}(\text{NH}_3)_4\text{I}_4$ ,  $\text{Na}_2\text{PtI}_6$ , and  $\text{Cr}(\text{NH}_3)_4\text{I}_3$ . If aqueous  $\text{AgNO}_3$  is added to separate beakers containing solutions of each coordination compound, how many moles of  $\text{AgI}$  will precipitate per mole of transition metal present? Assume that each transition metal ion forms an octahedral complex.

- 28.** A coordination compound of cobalt(III) contains four ammonia molecules, one sulfate ion, and one chloride ion. Addition of aqueous  $\text{BaCl}_2$  solution to an aqueous solution of the compound gives no precipitate. Addition of aqueous  $\text{AgNO}_3$  to an aqueous solution of the compound produces a white precipitate. Propose a structure for this coordination compound.

- 29.** Name the following complex ions.  
 a.  $\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+}$       c.  $\text{Mn}(\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_2)_3^{2+}$   
 b.  $\text{Fe}(\text{CN})_6^{4-}$       d.  $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$

- 30.** Name the following complex ions.  
 a.  $\text{Ni}(\text{CN})_4^{2-}$       c.  $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$   
 b.  $\text{Cr}(\text{NH}_3)_4\text{Cl}_2^+$       d.  $\text{Co}(\text{SCN})_2(\text{H}_2\text{O})_4^+$

- 31.** Name the following coordination compounds.

- a.  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$       d.  $\text{K}_4[\text{PtCl}_6]$   
 b.  $[\text{Co}(\text{H}_2\text{O})_6]\text{I}_3$       e.  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$   
 c.  $\text{K}_2[\text{PtCl}_4]$       f.  $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$

- 32.** Name the following coordination compounds.

- a.  $[\text{Cr}(\text{H}_2\text{O})_5\text{Br}]\text{Br}_2$       c.  $[\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2(\text{NO}_2)_2]\text{Cl}$   
 b.  $\text{Na}_3[\text{Co}(\text{CN})_6]$       d.  $[\text{Pt}(\text{NH}_3)_4\text{I}_2][\text{PtI}_4]$

- 33.** Give formulas for the following.

- a. potassium tetrachlorocobaltate(II)  
 b. aquatricarbonylplatinum(II) bromide  
 c. sodium dicyanobis(oxalato)ferrate(III)  
 d. triamminechloroethylenediaminechromium(III) iodide

- 34.** Give formulas for the following complex ions.

- a. tetrachloroferrate(III) ion  
 b. pentaammineaquaruthenium(III) ion  
 c. tetracarbonyldihydroxochromium(III) ion  
 d. amminetrichloroplatinate(II) ion

- 35.** Draw geometrical isomers of each of the following complex ions.

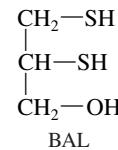
- a.  $[\text{Co}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$       c.  $[\text{Ir}(\text{NH}_3)_3\text{Cl}_3]^+$   
 b.  $[\text{Pt}(\text{NH}_3)_4\text{I}_2]^{2+}$       d.  $[\text{Cr}(\text{en})(\text{NH}_3)_2\text{I}_2]^+$

- 36.** Draw structures of each of the following.

- a. *cis*-dichloroethylenediamineplatinum(II)  
 b. *trans*-dichlorobis(ethylenediamine)cobalt(II)  
 c. *cis*-tetraamminechloronitrocobalt(III) ion  
 d. *trans*-tetraamminechloronitrocobalt(III) ion  
 e. *trans*-diaquabis(ethylenediamine)copper(II) ion

- 37.** Amino acids can act as ligands toward transition metal ions. The simplest amino acid is glycine ( $\text{NH}_2\text{CH}_2\text{CO}_2\text{H}$ ). Draw a structure of the glycinate anion ( $\text{NH}_2\text{CH}_2\text{CO}_2^-$ ) acting as a bidentate ligand. Draw the structural isomers of the square planar complex  $\text{Cu}(\text{NH}_2\text{CH}_2\text{CO}_2)_2$ .

- 38.** BAL is a chelating agent used in treating heavy metal poisoning. It acts as a bidentate ligand. What type of linkage isomers are possible when BAL coordinates to a metal ion?

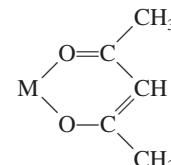


- 39.** Which of the following ligands are capable of linkage isomerism? Explain your answer.



- 40.** Draw all geometrical and linkage isomers of  $\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2$ .

- 41.** Acetylacetone, abbreviated acacH, is a bidentate ligand. It loses a proton and coordinates as  $\text{acac}^-$ , as shown below, where M is a transition metal:



## Chapter Twenty-One Transition Metals and Coordination Chemistry

- Which of the following complexes are optically active: *cis*-Cr(acac)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>, *trans*-Cr(acac)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>, and Cr(acac)<sub>3</sub>?
42. Draw all geometrical isomers of Pt(CN)<sub>2</sub>Br<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>. Which of these isomers has an optical isomer? Draw the various optical isomers.

### Bonding, Color, and Magnetism in Coordination Compounds

43. Draw the *d*-orbital splitting diagrams for the octahedral complex ions of each of the following.
- Fe<sup>2+</sup> (high and low spin)
  - Fe<sup>3+</sup> (high spin)
  - Ni<sup>2+</sup>
44. Draw the *d*-orbital splitting diagrams for the octahedral complex ions of each of the following.
- Zn<sup>2+</sup>
  - Co<sup>2+</sup> (high and low spin)
  - Ti<sup>3+</sup>
45. The CrF<sub>6</sub><sup>4-</sup> ion is known to have four unpaired electrons. Does the F<sup>-</sup> ligand produce a strong or weak field?
46. The Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> ion is diamagnetic, but Fe(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> is paramagnetic. Explain.

47. How many unpaired electrons are in the following complex ions?
- Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> (low-spin case)
  - Ni(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>
  - V(en)<sub>3</sub><sup>3+</sup>
48. The complex ion Fe(CN)<sub>6</sub><sup>3-</sup> is paramagnetic with one unpaired electron. The complex ion Fe(SCN)<sub>6</sub><sup>3-</sup> has five unpaired electrons. Where does SCN<sup>-</sup> lie in the spectrochemical series relative to CN<sup>-</sup>?

49. Rank the following complex ions in order of increasing wavelength of light absorbed.

- [Co(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>, [Co(CN)<sub>6</sub>]<sup>3-</sup>, [Co(I<sub>6</sub>)]<sup>3-</sup>, [Co(en)<sub>3</sub>]<sup>3+</sup>
50. The complex ion [Cu(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> has an absorption maximum at around 800 nm. When four ammonias replace water, [Cu(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>, the absorption maximum shifts to around 600 nm. What do these results signify in terms of the relative field splittings of NH<sub>3</sub> and H<sub>2</sub>O? Explain.
51. The following test tubes each contain a different chromium complex ion.



For each compound, predict the predominant color of light absorbed. If the complex ions are Cr(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>, Cr(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>, and Cr(H<sub>2</sub>O)<sub>4</sub>Cl<sub>2</sub><sup>+</sup>, what is the identity of the complex ion in each test tube? Hint: Reference the spectrochemical series.

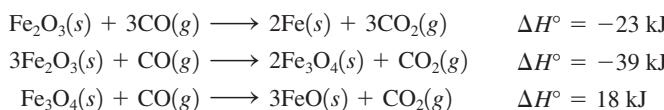
52. Consider the complex ions Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>, Co(CN)<sub>6</sub><sup>3-</sup>, and CoF<sub>6</sub><sup>3-</sup>. The wavelengths of absorbed electromagnetic radiation for these compounds (in no specific order) are 770 nm, 440 nm, and 290 nm. Match the complex ion to the wavelength of absorbed electromagnetic radiation.
53. The wavelength of absorbed electromagnetic radiation for CoBr<sub>4</sub><sup>2-</sup> is  $3.4 \times 10^{-6}$  m. Will the complex ion CoBr<sub>6</sub><sup>4-</sup> absorb electromagnetic radiation having a wavelength longer or shorter than  $3.4 \times 10^{-6}$  m? Explain.
54. Tetrahedral complexes of Co<sup>2+</sup> are quite common. Use a *d*-orbital splitting diagram to rationalize the stability of Co<sup>2+</sup> tetrahedral complex ions.

55. How many unpaired electrons are present in the tetrahedral ion FeCl<sub>4</sub><sup>-</sup>?

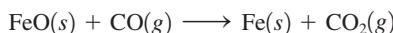
56. The complex ion PdCl<sub>4</sub><sup>2-</sup> is diamagnetic. Propose a structure for PdCl<sub>4</sub><sup>2-</sup>.

### Metallurgy

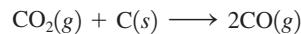
57. A blast furnace is used to reduce iron oxides to elemental iron. The reducing agent for this reduction process is carbon monoxide.
- Given the following data:



determine  $\Delta H^\circ$  for the reaction

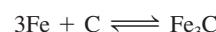


- The CO<sub>2</sub> produced in a blast furnace during the reduction process actually can oxidize iron into FeO. To eliminate this reaction, excess coke is added to convert CO<sub>2</sub> into CO by the reaction

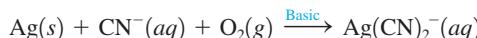


Using data from Appendix 4, determine  $\Delta H^\circ$  and  $\Delta S^\circ$  for this reaction. Assuming  $\Delta H^\circ$  and  $\Delta S^\circ$  do not depend on temperature, at what temperature is the conversion reaction of CO<sub>2</sub> into CO spontaneous at standard conditions?

58. What roles do kinetics and thermodynamics play in the effect that the following reaction has on the properties of steel?



59. Silver is sometimes found in nature as large nuggets; more often it is found mixed with other metals and their ores. Cyanide ion is often used to extract the silver by the following reaction that occurs in basic solution:



Balance this equation by using the half-reaction method.

- 60.** One of the classic methods for the determination of the manganese content in steel involves converting all the manganese to the deeply colored permanganate ion and then measuring the absorption of light. The steel is first dissolved in nitric acid, producing the manganese(II) ion and nitrogen dioxide gas. This solution is then reacted with an acidic solution containing periodate ion; the products are the permanganate and iodate ions. Write balanced chemical equations for both of these steps.

## Additional Exercises

- 61.** Ammonia and potassium iodide solutions are added to an aqueous solution of  $\text{Cr}(\text{NO}_3)_3$ . A solid is isolated (compound A), and the following data are collected:

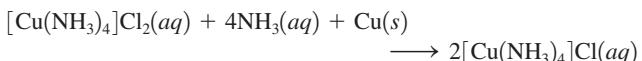
- When 0.105 g of compound A was strongly heated in excess  $\text{O}_2$ , 0.0203 g of  $\text{CrO}_3$  was formed.
- In a second experiment it took 32.93 mL of 0.100 M HCl to titrate completely the  $\text{NH}_3$  present in 0.341 g of compound A.
- Compound A was found to contain 73.53% iodine by mass.
- The freezing point of water was lowered by  $0.64^\circ\text{C}$  when 0.601 g of compound A was dissolved in 10.00 g of  $\text{H}_2\text{O}$  ( $K_f = 1.86^\circ\text{C} \cdot \text{kg/mol}$ ).

What is the formula of the compound? What is the structure of the complex ion present? (Hints:  $\text{Cr}^{3+}$  is expected to be six-coordinate, with  $\text{NH}_3$  and possibly  $\text{I}^-$  as ligands. The  $\text{I}^-$  ions will be the counterions if needed.)

- 62.** A transition metal compound contains a cobalt ion, chloride ions, and water molecules. The  $\text{H}_2\text{O}$  molecules are the ligands in the complex ion and the  $\text{Cl}^-$  ions are the counterions. A 0.256-g sample of the compound was dissolved in water, and excess silver nitrate was added. The silver chloride was filtered, dried, and weighed, and it had a mass of 0.308 g. A second sample of 0.416 g of the compound was dissolved in water, and an excess of sodium hydroxide was added. The hydroxide salt was filtered and heated in a flame, forming cobalt(III) oxide. The mass of cobalt(III) oxide formed was 0.145 g. What is the oxidation state of cobalt in the complex ion and what is the formula of the compound?

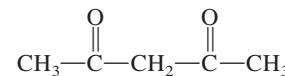
- 63.** When aqueous KI is added gradually to mercury(II) nitrate, an orange precipitate forms. Continued addition of KI causes the precipitate to dissolve. Write balanced equations to explain these observations. (Hint:  $\text{Hg}^{2+}$  reacts with  $\text{I}^-$  to form  $\text{HgI}_4^{2-}$ . Would you expect  $\text{HgI}_4^{2-}$  to form colored solutions? Explain.)

- 64.** In the production of printed circuit boards for the electronics industry, a 0.60-mm layer of copper is laminated onto an insulating plastic board. Next, a circuit pattern made of a chemically resistant polymer is printed on the board. The unwanted copper is removed by chemical etching, and the protective polymer is finally removed by solvents. One etching reaction is



- Is this reaction an oxidation-reduction process? Explain.
- A plant needs to manufacture 10,000 printed circuit boards, each  $8.0 \times 16.0$  cm in area. An average of 80.0% of the copper is removed from each board (density of copper =  $8.96 \text{ g/cm}^3$ ). What masses of  $[\text{Cu}(\text{NH}_3)_4]\text{Cl}_2$  and  $\text{NH}_3$  are needed to do this? Assume 100% yield.
- How many bonds could each of the following chelates form with a metal ion?

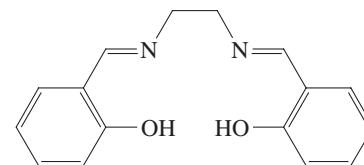
- a. acetylacetone(acacH)



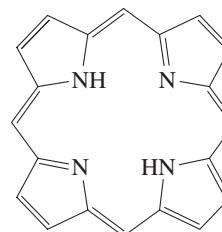
- b. diethylenetriamine



- c. salen

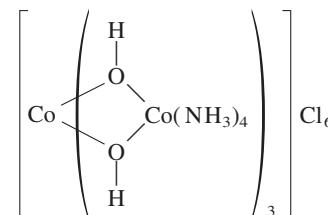


- d. porphine



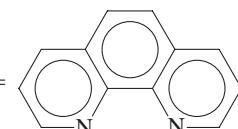
- 66.** Until the discoveries of Werner, it was thought that carbon had to be present in a compound for it to be optically active. Werner prepared the following compound containing  $\text{OH}^-$  ions as bridging groups and separated the optical isomers.

- Draw structures of the two optically active isomers of this compound.
- What are the oxidation states of the cobalt ions?
- How many unpaired electrons are present if the complex is the low-spin case?



- 67.** The complex ion  $\text{Ru}(\text{phen})_3^{2+}$  has been used as a probe for the structure of DNA. (Phen is a bidentate ligand.)

- What type of isomerism is found in  $\text{Ru}(\text{phen})_3^{2+}$ ?
- $\text{Ru}(\text{phen})_3^{2+}$  is diamagnetic (as are all complex ions of  $\text{Ru}^{2+}$ ). Draw the crystal field diagram for the  $d$  orbitals in this complex ion.



Phen = 1,10-phenanthroline =

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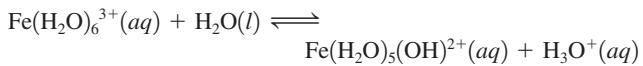
68. A compound related to acetylacetone is 1,1,1-trifluoroacetylacetone (abbreviated Htfa):



Htfa forms complexes in a manner similar to acetylacetone. (See Exercise 41.) Both  $\text{Be}^{2+}$  and  $\text{Cu}^{2+}$  form complexes with  $\text{tfa}^-$  having the formula  $\text{M}(\text{tfa})_2$ . Two isomers are formed for each metal complex.

- The  $\text{Be}^{2+}$  complexes are tetrahedral. Draw the two isomers of  $\text{Be}(\text{tfa})_2$ . What type of isomerism is exhibited by  $\text{Be}(\text{tfa})_2$ ?
  - The  $\text{Cu}^{2+}$  complexes are square planar. Draw the two isomers of  $\text{Cu}(\text{tfa})_2$ . What type of isomerism is exhibited by  $\text{Cu}(\text{tfa})_2$ ?
69. Would it be better to use octahedral  $\text{Ni}^{2+}$  complexes or octahedral  $\text{Cr}^{2+}$  complexes to determine whether a given ligand is a strong-field or weak-field ligand by measuring the number of unpaired electrons? How else could the relative ligand field strengths be determined?

70. The equilibrium constant,  $K_a$ , for the reaction



is  $6.0 \times 10^{-3}$ .

- Calculate the pH of a 0.10 M solution of  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ .
  - Will a 1.0 M solution of iron(II) nitrate have a higher or lower pH than a 1.0 M solution of iron(III) nitrate? Explain.
71. Ethylenediaminetetraacetate ( $\text{EDTA}^{4-}$ ) is used as a complexing agent in chemical analysis with the structure shown in Figure 21.7. Solutions of  $\text{EDTA}^{4-}$  are used to treat heavy metal poisoning by removing the heavy metal in the form of a soluble complex ion. The complex ion virtually eliminates the heavy metal ions from reacting with biochemical systems. The reaction of  $\text{EDTA}^{4-}$  with  $\text{Pb}^{2+}$  is



Consider a solution with 0.010 mol  $\text{Pb}(\text{NO}_3)_2$  added to 1.0 L of an aqueous solution buffered at pH = 13.00 and containing 0.050 M  $\text{Na}_4\text{EDTA}$ . Does  $\text{Pb}(\text{OH})_2$  precipitate from this solution? ( $K_{sp}$  for  $\text{Pb}(\text{OH})_2 = 1.2 \times 10^{-15}$ .)

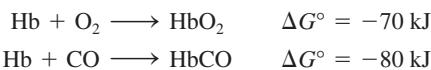
72. Hemoglobin (abbreviated Hb) is a protein that is responsible for the transport of oxygen in the blood of mammals. Each hemoglobin molecule contains four iron atoms that serve as the binding sites for  $\text{O}_2$  molecules. The oxygen binding is pH dependent. The relevant equilibrium reaction is



Use Le Châtelier's principle to answer the following.

- What form of hemoglobin,  $\text{HbH}_4^{4+}$  or  $\text{Hb}(\text{O}_2)_4$ , is favored in the lungs? What form is favored in the cells?
- When a person hyperventilates, the concentration of  $\text{CO}_2$  in the blood decreases. How does this affect the oxygen-binding equilibrium? How does breathing into a paper bag help to counteract this effect?
- When a person has suffered a cardiac arrest, an injection of a sodium bicarbonate solution is given. Why is this step necessary?

73. Carbon monoxide is toxic because it binds more strongly to iron in hemoglobin (Hb) than does  $\text{O}_2$ . Consider the following reactions and approximate standard free energy changes:



Using these data, estimate the equilibrium constant value at 25°C for the following reaction:



74. For the process

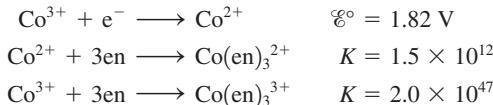


what would be the expected ratio of *cis* to *trans* isomers in the product?

### Challenge Problems

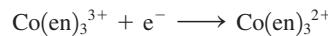
75. The complex *trans*-[ $\text{NiA}_2\text{B}_4$ ] $^{2+}$ , where A and B represent neutral ligands, is known to be diamagnetic. Do A and B produce very similar or very different crystal fields? Explain.
76. Impure nickel, refined by smelting sulfide ores in a blast furnace, can be converted into metal from 99.90% to 99.99% purity by the Mond process. The primary reaction involved in the Mond process is
- $$\text{Ni}(s) + 4\text{CO}(g) \rightleftharpoons \text{Ni}(\text{CO})_4(g)$$
- Without referring to Appendix 4, predict the sign of  $\Delta S^\circ$  for the preceding reaction. Explain.
  - The spontaneity of the preceding reaction is temperature dependent. Predict the sign of  $\Delta S_{\text{surv}}$  for this reaction. Explain.
  - For  $\text{Ni}(\text{CO})_4(g)$ ,  $\Delta H_f^\circ = -607 \text{ kJ/mol}$  and  $S^\circ = 417 \text{ J/K} \cdot \text{mol}$  at 298 K. Using these values and data in Appendix 4, calculate  $\Delta H^\circ$  and  $\Delta S^\circ$  for the preceding reaction.
  - Calculate the temperature at which  $\Delta G^\circ = 0$  ( $K = 1$ ) for the preceding reaction, assuming that  $\Delta H^\circ$  and  $\Delta S^\circ$  do not depend on temperature.
  - The first step of the Mond process involves equilibrating impure nickel with  $\text{CO}(g)$  and  $\text{Ni}(\text{CO})_4(g)$  at about 50°C. The purpose of this step is to convert as much nickel as possible into the gas phase. Calculate the equilibrium constant for the preceding reaction at 50°C.
  - In the second step of the Mond process, the gaseous  $\text{Ni}(\text{CO})_4$  is isolated and heated at 227°C. The purpose of this step is to deposit as much nickel as possible as pure solid (the reverse of the preceding reaction). Calculate the equilibrium constant for the above reaction at 227°C.
  - Why is temperature increased for the second step of the Mond process?

77. Consider the following data:



where en = ethylenediamine.

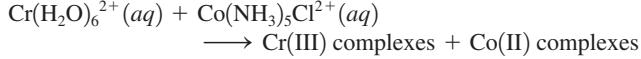
- Calculate  $\mathcal{E}^\circ$  for the half-reaction



- b.** Based on your answer to part a, which is the stronger oxidizing agent,  $\text{Co}^{3+}$  or  $\text{Co}(\text{en})_3^{3+}$ ?

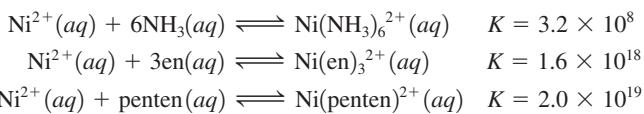
**c.** Use the crystal field model to rationalize the result in part b.

**78.** Henry Taube, 1983 Nobel Prize winner in chemistry, has studied the mechanisms of the oxidation-reduction reactions of transition metal complexes. In one experiment he and his students studied the following reaction:

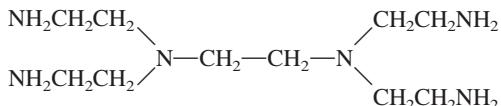


Chromium(III) and cobalt(III) complexes are substitutionally inert (no exchange of ligands) under conditions of the experiment. Chromium(II) and cobalt(II) complexes can exchange ligands very rapidly. One of the products of the reaction is  $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ . Is this consistent with the reaction proceeding through formation of  $(\text{H}_2\text{O})_5\text{Cr}-\text{Cl}-\text{Co}(\text{NH}_3)_5$  as an intermediate? Explain.

79. Chelating ligands often form more stable complex ions than the corresponding monodentate ligands with the same donor atoms. For example,



where en is ethylenediamine and penten is



This increased stability is called the *chelate effect*. Based on bond energies, would you expect the enthalpy changes for the above reactions to be very different? What is the order (from least favorable to most favorable) of the entropy changes for the above reactions? How do the values of the formation constants correlate with  $\Delta S^\circ$ ? How can this be used to explain the chelate effect?

80. Qualitatively draw the crystal field splitting of the  $d$  orbitals in a trigonal planar complex ion. (Let the  $z$  axis be perpendicular to the plane of the complex.)

81. Qualitatively draw the crystal field splitting for a trigonal bipyramidal complex ion. (Let the  $z$  axis be perpendicular to the trigonal plane.)

82. Sketch a  $d$ -orbital energy diagram for the following.

  - a linear complex with ligands on the  $x$  axis
  - a linear complex with ligands on the  $y$  axis

83. Sketch and explain the most likely pattern for the crystal field diagram for the complex ion *trans*-diamminetetracyanonickelate(II), where  $\text{CN}^-$  produces a *much* stronger crystal field than  $\text{NH}_3$ . Explain completely and label the  $d$  orbitals in your diagram. Assume the  $\text{NH}_3$  ligands lie on the axis.

84. a. Calculate the molar solubility of  $\text{AgBr}$  in pure water.  $K_{\text{sp}}$  for  $\text{AgBr}$  is  $5.0 \times 10^{-13}$ .

b. Calculate the molar solubility of  $\text{AgBr}$  in  $3.0\text{ M } \text{NH}_3$ . The overall formation constant for  $\text{Ag}(\text{NH}_3)_2^+$  is  $1.7 \times 10^7$ , that is,

$$\text{Ag}^+(aq) + 2\text{NH}_3(aq) \longrightarrow \text{Ag}(\text{NH}_3)_2^+(aq) \quad K = 1.7 \times 10^7.$$

c. Compare the calculated solubilities from parts a and b. Explain any differences.

- d. What mass of AgBr will dissolve in 250.0 mL of 3.0 M  $\text{NH}_3$ ?
  - e. What effect does adding  $\text{HNO}_3$  have on the solubilities calculated in parts a and b?

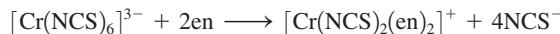
## Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

- 85.** The ferrate ion,  $\text{FeO}_4^{2-}$ , is such a powerful oxidizing agent that in acidic solution, aqueous ammonia is reduced to elemental nitrogen along with the formation of the iron(III) ion.

  - What is the oxidation state of iron in  $\text{FeO}_4^{2-}$ , and what is the electron configuration of iron in this polyatomic ion?
  - If 25.0 mL of a 0.243 M  $\text{FeO}_4^{2-}$  solution is allowed to react with 55.0 mL of 1.45 M aqueous ammonia, what volume of nitrogen gas can form at 25°C and 1.50 atm?

**86.** a. In the absorption spectrum of the complex ion  $[\text{Cr}(\text{NCS})_6]^{3-}$ , there is a band corresponding to the absorption of a photon of light with an energy of  $1.75 \times 10^4 \text{ cm}^{-1}$ . Given  $1 \text{ cm}^{-1} = 1.986 \times 10^{-23} \text{ J}$ , what is the wavelength of this photon?  
b. The Cr—N—C bond angle in  $[\text{Cr}(\text{NCS})_6]^{3-}$  is predicted to be 180°. What is the hybridization of the N atom in the  $\text{NCS}^-$  ligand when a Lewis acid–base reaction occurs between  $\text{Cr}^{3+}$  and  $\text{NCS}^-$  that would give a 180° Cr—N—C bond angle?  $[\text{Cr}(\text{NCS})_6]^{3-}$  undergoes substitution by ethylenediammine (en) according to the equation



Does  $[\text{Cr}(\text{NCS})_2(\text{en})_2]^+$  exhibit geometric isomerism? Does  $[\text{Cr}(\text{NCS})_2(\text{en})_2]^+$  exhibit optical isomerism?

## Marathon Problem

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

87. There are three salts that contain complex ions of chromium and have the molecular formula  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ . Treating 0.27 g of the first salt with a strong dehydrating agent resulted in a mass loss of 0.036 g. Treating 270 mg of the second salt with the same dehydrating agent resulted in a mass loss of 18 mg. The third salt did not lose any mass when treated with the same dehydrating agent. Addition of excess aqueous silver nitrate to 100.0-mL portions of 0.100 M solutions of each salt resulted in the formation of different masses of silver chloride; one solution yielded 1430 mg  $\text{AgCl}$ ; another, 2870 mg  $\text{AgCl}$ ; the third, 4300 mg  $\text{AgCl}$ . Two of the salts are green and one is violet.

Suggest probable structural formulas for these salts, defending your answer on the basis of the preceding observations. State which salt is most likely to be violet. Would a study of the magnetic properties of the salts be helpful in determining the structural formulas? Explain.



Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving by visiting the Online Study Center at [college.hmco.com/PIC/zumdahl7e](http://college.hmco.com/PIC/zumdahl7e).

# 22 Organic and Biological Molecules

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### 22.5 Polymers

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- Proteins
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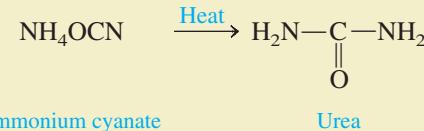


Polarized light micrograph of crystals of phenylalanine, one of the essential amino acids that the body cannot synthesize.

**T**wo Group 4A elements, carbon and silicon, form the basis of most natural substances. Silicon, with its great affinity for oxygen, forms chains and rings containing Si—O—Si bridges to produce the silica and silicates that form the basis for most rocks, sands, and soils. What silicon is to the geological world, carbon is to the biological world. Carbon has the unusual ability of bonding strongly to itself to form long chains or rings of carbon atoms. In addition, carbon forms strong bonds to other nonmetals such as hydrogen, nitrogen, oxygen, sulfur, and the halogens. Because of these bonding properties, there are a myriad of carbon compounds; several million are now known, and the number continues to grow rapidly. Among these many compounds are the **biomolecules**, those responsible for maintaining and reproducing life.

The study of carbon-containing compounds and their properties is called **organic chemistry**. Although a few compounds involving carbon, such as its oxides and carbonates, are considered to be inorganic substances, the vast majority are organic compounds that typically contain chains or rings of carbon atoms.

Originally, the distinction between inorganic and organic substances was based on whether a compound was produced by living systems. For example, until the early nineteenth century it was believed that organic compounds had some sort of “life force” and could be synthesized only by living organisms. This view was dispelled in 1828 when the German chemist Friedrich Wöhler (1800–1882) prepared urea from the inorganic salt ammonium cyanate by simple heating:



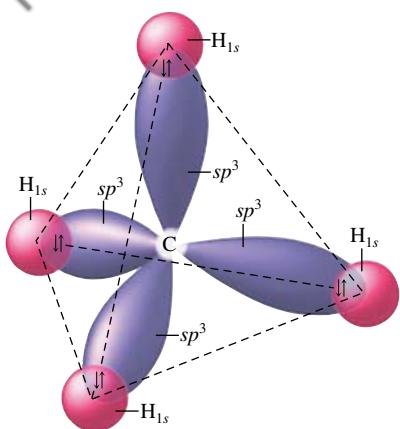
Urea is a component of urine, so it is clearly an organic material; yet here was clear evidence that it could be produced in the laboratory as well as by living things.

Organic chemistry plays a vital role in our quest to understand living systems. Beyond that, the synthetic fibers, plastics, artificial sweeteners, and drugs that are such an accepted part of modern life are products of industrial organic chemistry. In addition, the energy on which we rely so heavily to power our civilization is based mostly on the organic materials found in coal and petroleum.

Because organic chemistry is such a vast subject, we can provide only a brief introduction to it in this book. We will begin with the simplest class of organic compounds, the hydrocarbons, and then show how most other organic compounds can be considered to be derivatives of hydrocarbons.

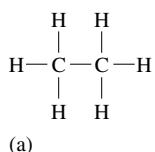
## 22.1 Alkanes: Saturated Hydrocarbons

As the name indicates, **hydrocarbons** are compounds composed of carbon and hydrogen. Those compounds whose carbon–carbon bonds are all single bonds are said to be **saturated**, because each carbon is bound to four atoms, the maximum number. Hydrocarbons containing carbon–carbon multiple bonds are described as being **unsaturated**.

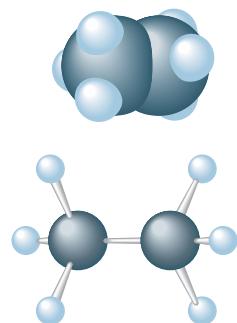


## **FIGURE 22.1**

The C—H bonds in methane.



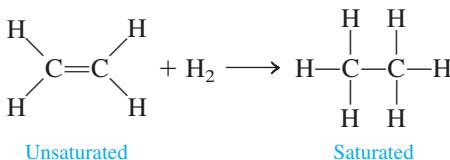
(b)



## FIGURE 22.2

- (a) The Lewis structure of ethane ( $C_2H_6$ ).
- (b) The molecular structure of ethane represented by space-filling and ball-and-stick models.

since the carbon atoms involved in a multiple bond can react with additional atoms, as shown by the *addition* of hydrogen to ethylene:

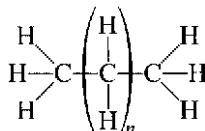


Note that each carbon in ethylene is bonded to three atoms (one carbon and two hydrogens) but that each can bond to one additional atom if one bond of the carbon–carbon double bond is broken.

The simplest member of the saturated hydrocarbons, which are also called the **alkanes**, is *methane* ( $\text{CH}_4$ ). As discussed in Section 9.1, methane has a tetrahedral structure and can be described in terms of a carbon atom using an  $sp^3$  hybrid set of orbitals to bond to the four hydrogen atoms (see Fig. 22.1). The next alkane, the one containing two carbon atoms, is *ethane* ( $\text{C}_2\text{H}_6$ ), as shown in Fig. 22.2. Each carbon in ethane is surrounded by four atoms and thus adopts a tetrahedral arrangement and  $sp^3$  hybridization, as predicted by the localized electron model.

The next two members of the series are *propane* ( $C_3H_8$ ) and *butane* ( $C_4H_{10}$ ), shown in Fig. 22.3. Again, each carbon is bonded to four atoms and is described as  $sp^3$  hybridized.

Alkanes in which the carbon atoms form long “strings” or chains are called **normal**, **straight-chain**, or **unbranched hydrocarbons**. As can be seen from Fig. 22.3, the chains in normal alkanes are not really straight but zig-zag, since the tetrahedral C—C—C angle is  $109.5^\circ$ . The normal alkanes can be represented by the structure



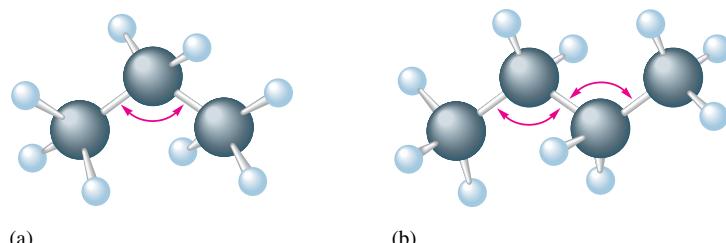
where  $n$  is an integer. Note that each member is obtained from the previous one by inserting a *methylene* ( $\text{CH}_2$ ) group. We can condense the structural formulas by omitting some of the C—H bonds. For example, the general formula for normal alkanes shown above can be condensed to



The first ten normal alkanes and some of their properties are listed in Table 22.1. Note that all alkanes can be represented by the general formula  $C_nH_{2n+2}$ . For example, nonane, which has nine carbon atoms, is represented by  $C_9H_{(2 \times 9) + 2}$ , or  $C_9H_{20}$ . Also note from Table 22.1 that the melting points and boiling points increase as the molar masses increase, as we would expect.

## Isomerism in Alkanes

Butane and all succeeding members of the alkanes exhibit **structural isomerism**. Recall from Section 21.4 that structural isomerism occurs when two molecules have the same atoms

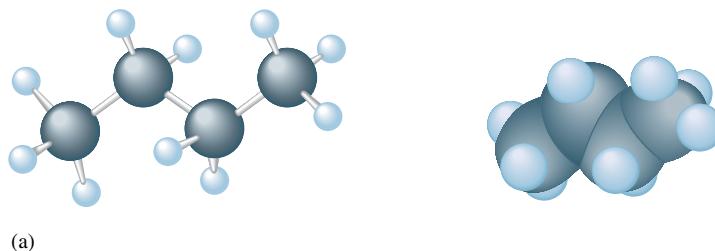


### FIGURE 22.3

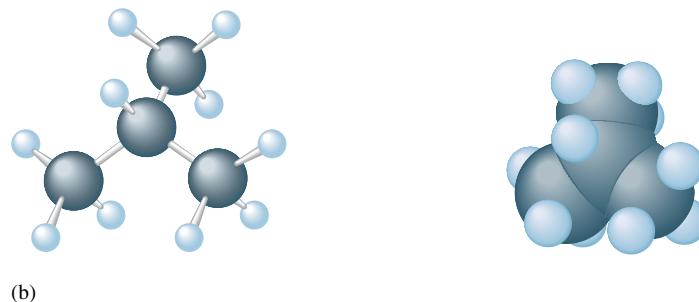
The structures of (a) propane ( $\text{CH}_3\text{CH}_2\text{CH}_3$ ) and (b) butane ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ ). Each angle shown in red is  $109.5^\circ$ .

**TABLE 22.1 Selected Properties of the First Ten Normal Alkanes**

Name	Formula	Molar Mass	Melting Point (°C)	Boiling Point (°C)	Number of Structural Isomers
Methane	CH <sub>4</sub>	16	-182	-162	1
Ethane	C <sub>2</sub> H <sub>6</sub>	30	-183	-89	1
Propane	C <sub>3</sub> H <sub>8</sub>	44	-187	-42	1
Butane	C <sub>4</sub> H <sub>10</sub>	58	-138	0	2
Pentane	C <sub>5</sub> H <sub>12</sub>	72	-130	36	3
Hexane	C <sub>6</sub> H <sub>14</sub>	86	-95	68	5
Heptane	C <sub>7</sub> H <sub>16</sub>	100	-91	98	9
Octane	C <sub>8</sub> H <sub>18</sub>	114	-57	126	18
Nonane	C <sub>9</sub> H <sub>20</sub>	128	-54	151	35
Decane	C <sub>10</sub> H <sub>22</sub>	142	-30	174	75

**FIGURE 22.4**

(a) Normal butane (abbreviated *n*-butane).  
 (b) The branched isomer of butane (called isobutane).



but different bonds. For example, butane can exist as a straight-chain molecule (normal butane, or *n*-butane) or with a branched-chain structure (called isobutane), as shown in Fig. 22.4. Because of their different structures, these molecules exhibit different properties. For example, the boiling point of *n*-butane is  $-0.5^{\circ}\text{C}$ , whereas that of isobutane is  $-12^{\circ}\text{C}$ .

### Sample Exercise 22.1

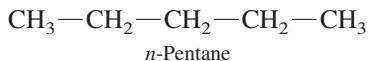
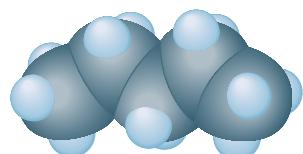
### Structural Isomerism

Draw the isomers of pentane.

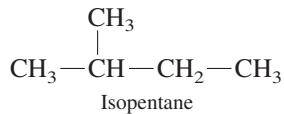
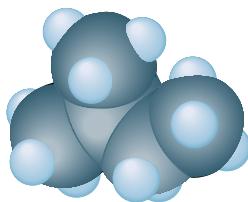
#### Solution

Pentane ( $\text{C}_5\text{H}_{12}$ ) has the following isomeric structures:

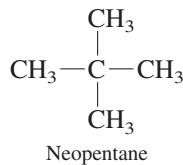
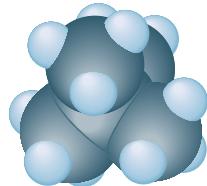
1.



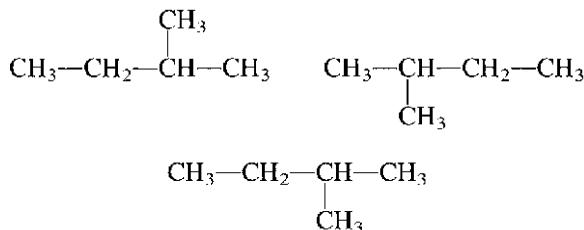
2.



3.



Note that the structures



which might appear to be other isomers, are actually identical to structure 2.

*See Exercise 22.13.*

**TABLE 22.2 The Most Common Alkyl Substituents and Their Names**

Structure*	Name†
$-\text{CH}_3$	Methyl
$-\text{CH}_2\text{CH}_3$	Ethyl
$-\text{CH}_2\text{CH}_2\text{CH}_3$	Propyl
$\begin{array}{c}   \\ \text{CH}_3\text{CHCH}_3 \end{array}$	Isopropyl
$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Butyl
$\begin{array}{c}   \\ \text{CH}_3\text{CHCH}_2\text{CH}_3 \end{array}$	<i>sec</i> -Butyl
$\begin{array}{c} \text{H} \\   \\ \text{---CH}_2-\text{C}-\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$	Isobutyl
$\begin{array}{c} \text{CH}_3 \\   \\ \text{---C}-\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$	<i>tert</i> -Butyl

\*The bond with one end open shows the point of attachment of the substituent to the carbon chain.

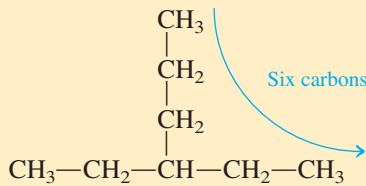
†For the butyl groups, *sec*- indicates attachment to the chain through a secondary carbon, a carbon atom attached to two other carbon atoms. The designation *tert*- signifies attachment through a tertiary carbon, a carbon attached to three other carbon atoms.

## Nomenclature

Because there are literally millions of organic compounds, it would be impossible to remember common names for all of them. We must have a systematic method for naming them. The following rules are used in naming alkanes.

### Rules for Naming Alkanes

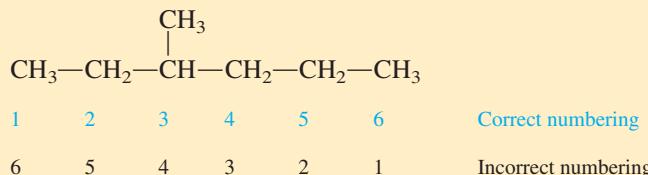
- The names of the alkanes beyond butane are obtained by adding the suffix *-ane* to the Greek root for the number of carbon atoms (*pent-* for five, *hex-* for six, and so on). For a branched hydrocarbon, the longest continuous chain of carbon atoms determines the root name for the hydrocarbon. For example, in the alkane



the longest chain contains six carbon atoms, and this compound is named as a hexane.

- When alkane groups appear as substituents, they are named by dropping the *-ane* and adding *-yl*. For example,  $-\text{CH}_3$  is obtained by removing a hydrogen from methane and is called *methyl*,  $-\text{C}_2\text{H}_5$  is called *ethyl*,  $-\text{C}_3\text{H}_7$  is called *propyl*, and so on. The compound above is therefore an ethylhexane. (See Table 22.2.)

3. The positions of substituent groups are specified by numbering the longest chain of carbon atoms sequentially, starting at the end closest to the branching. For example, the compound



is called 3-methylhexane. Note that the top set of numbers is correct since the left end of the molecule is closest to the branching, and this gives the smallest number for the position of the substituent. Also, note that a hyphen is written between the number and the substituent name.

4. The location and name of each substituent are followed by the root alkane name. The substituents are listed in alphabetical order, and the prefixes *di-*, *tri-*, and so on, are used to indicate multiple, identical substituents.

### Sample Exercise 22.2

### Isomerism and Nomenclature

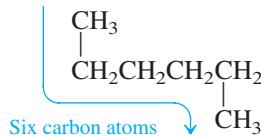
Draw the structural isomers for the alkane  $\text{C}_6\text{H}_{14}$  and give the systematic name for each one.

#### Solution

We will proceed systematically, starting with the longest chain and then rearranging the carbons to form the shorter, branched chains.

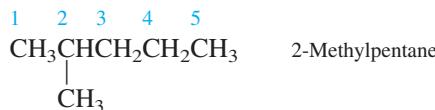


Note that although a structure such as



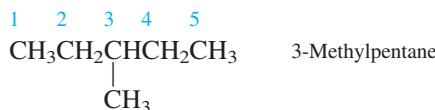
may look different it is still hexane, since the longest carbon chain has six atoms.

2. We now take one carbon out of the chain and make it a methyl substituent.



Since the longest chain consists of five carbons, this is a substituted pentane: 2-methylpentane. The 2 indicates the position of the methyl group on the chain. Note that if we numbered the chain from the right end, the methyl group would be on carbon 4. Because we want the smallest possible number, the numbering shown is correct.

3. The methyl substituent can also be on carbon 3 to give



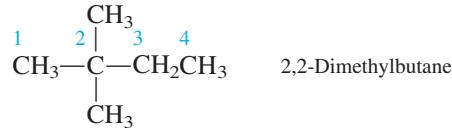
Note that we have now exhausted all possibilities for placing a single methyl group on pentane.

4. Next, we can take two carbons out of the original six-member chain:

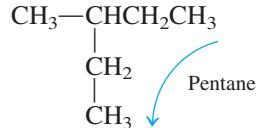


Since the longest chain now has four carbons, the root name is butane. Since there are two methyl groups, we use the prefix *di-*. The numbers denote that the two methyl groups are positioned on the second and third carbons in the butane chain. Note that when two or more numbers are used, they are separated by a comma.

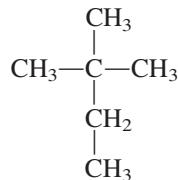
5. The two methyl groups can also be attached to the same carbon atom as shown here:



We might also try ethyl-substituted butanes, such as



However, note that this is instead a pentane (3-methylpentane), since the longest chain has five carbon atoms. Thus it is not a new isomer. Trying to reduce the chain to three atoms provides no further isomers either. For example, the structure



is actually 2,2-dimethylbutane.

Thus there are only five distinct structural isomers of C<sub>6</sub>H<sub>14</sub>: hexane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, and 2,2-dimethylbutane.

*See Exercises 22.15 and 22.16.*

### Sample Exercise 22.3

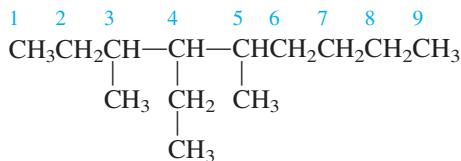
### Structures from Names

Determine the structure for each of the following compounds.

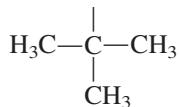
- a. 4-ethyl-3,5-dimethylnonane      b. 4-*tert*-butylheptane

#### Solution

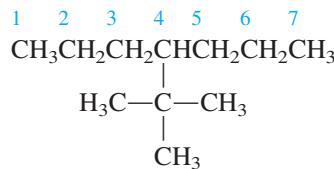
- a. The root name *nonane* signifies a nine-carbon chain. Thus we have



- b. Heptane signifies a seven-carbon chain, and the *tert*-butyl group is



Thus we have

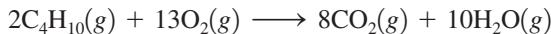


*See Exercises 22.19 and 22.20.*

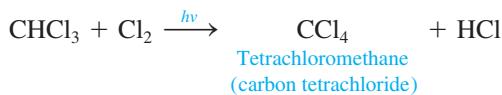
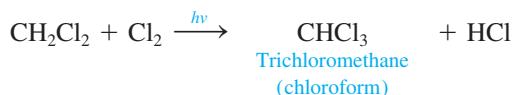
## Reactions of Alkanes

Because they are saturated compounds and because the C—C and C—H bonds are relatively strong, the alkanes are fairly unreactive. For example, at 25°C they do not react with acids, bases, or strong oxidizing agents. This chemical inertness makes them valuable as lubricating materials and as the backbone for structural materials such as plastics.

At a sufficiently high temperature alkanes do react vigorously and exothermically with oxygen, and these **combustion reactions** are the basis for their widespread use as fuels. For example, the reaction of butane with oxygen is



The alkanes can also undergo **substitution reactions**, primarily where halogen atoms replace hydrogen atoms. For example, methane can be successively chlorinated as follows:



Note that the products of the last two reactions have two names; the systematic name is given first, followed by the common name in parentheses. (This format will be used throughout this chapter for compounds that have common names.) Also, note that ultraviolet light ( $h\nu$ ) furnishes the energy to break the Cl—Cl bond to produce chlorine atoms:



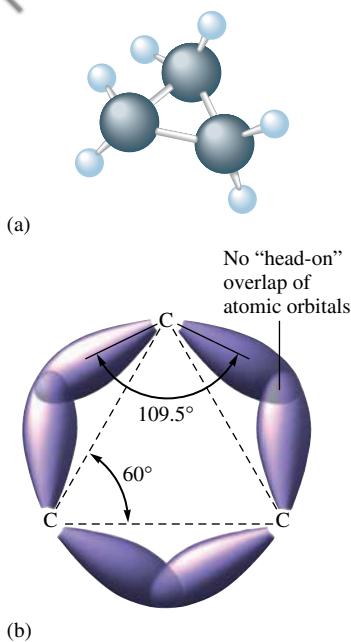
A chlorine atom has an unpaired electron, as indicated by the dot, which makes it very reactive and able to attack the C—H bond.

Substituted methanes with the general formula  $\text{CF}_x\text{Cl}_{4-x}$  containing both chlorine and fluorine as substituents are called chlorofluorocarbons (CFCs) and are also known as *Freons*. These substances are very unreactive and have been extensively used as coolant fluids in refrigerators and air conditioners. Unfortunately, their chemical inertness allows



A butane lighter used for camping.

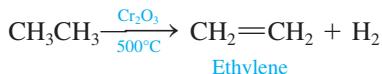
The  $h\nu$  above the arrow represents ultraviolet light.



**FIGURE 22.5**  
(a) The molecular structure of cyclopropane ( $C_3H_6$ ). (b) The overlap of the  $sp^3$  orbitals that form the C—C bonds in cyclopropane.

Freons to remain in the atmosphere so long that they eventually reach altitudes where they are a threat to the protective ozone layer (see Section 12.8), and the use of these compounds is being rapidly phased out.

Alkanes can also undergo **dehydrogenation reactions** in which hydrogen atoms are removed and the product is an unsaturated hydrocarbon. For example, in the presence of chromium(III) oxide at high temperatures, ethane can be dehydrogenated, yielding ethylene:



### Cyclic Alkanes

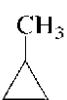
Besides forming chains, carbon atoms also form rings. The simplest of the **cyclic alkanes** (general formula  $C_nH_{2n}$ ) is cyclopropane ( $C_3H_6$ ), shown in Fig. 22.5(a). Since the carbon atoms in cyclopropane form an equilateral triangle with  $60^\circ$  bond angles, their  $sp^3$  hybrid orbitals do not overlap head-on as in normal alkanes [Fig. 22.5(b)]. This results in unusually weak, or *strained*, C—C bonds; thus the cyclopropane molecule is much more reactive than straight-chain propane. The carbon atoms in cyclobutane ( $C_4H_8$ ) form a square with  $88^\circ$  bond angles, and cyclobutane is also quite reactive.

The next two members of the series, cyclopentane ( $C_5H_{10}$ ) and cyclohexane ( $C_6H_{12}$ ), are quite stable, because their rings have bond angles very close to the tetrahedral angles, which allows the  $sp^3$  hybrid orbitals on adjacent carbon atoms to overlap head-on and form normal C—C bonds, which are quite strong. To attain the tetrahedral angles, the cyclohexane ring must “pucker”—that is, become nonplanar. Cyclohexane can exist in two forms, the *chair* and the *boat* forms, as shown in Fig. 22.6. The two hydrogen atoms above the ring in the boat form are quite close to each other, and the resulting repulsion between these atoms causes the chair form to be preferred. At  $25^\circ C$  more than 99% of cyclohexane exists in the chair form.

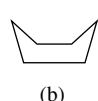
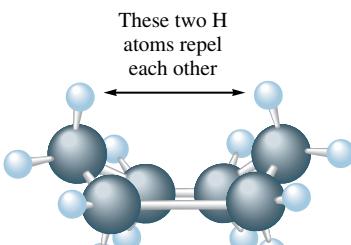
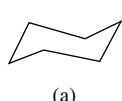
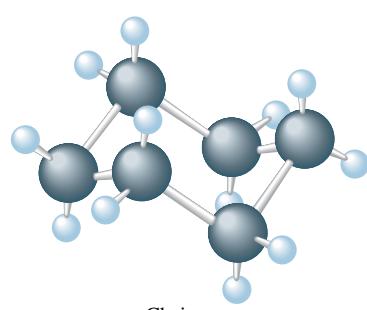
For simplicity, the cyclic alkanes are often represented by the following structures:



Thus the structure



represents methylcyclopropane.



**FIGURE 22.6**

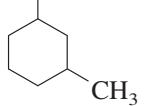
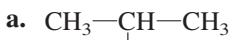
The (a) chair and (b) boat forms of cyclohexane.

The nomenclature for cycloalkanes follows the same rules as for the other alkanes except that the root name is preceded by the prefix *cyclo*- . The ring is numbered to yield the smallest substituent numbers possible.

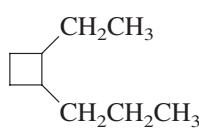
### Sample Exercise 22.4

### Naming Cyclic Alkanes

Name each of the following cyclic alkanes.

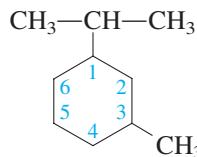


b.



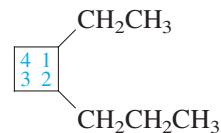
#### Solution

- a. The six-carbon cyclohexane ring is numbered as follows:



There is an isopropyl group at carbon 1 and a methyl group at carbon 3. The name is 1-isopropyl-3-methylcyclohexane, since the alkyl groups are named in alphabetical order.

- b. This is a cyclobutane ring, which is numbered as follows:

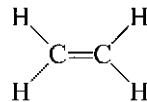


The name is 1-ethyl-2-propylcyclobutane.

*See Exercise 22.22.*

## 22.2 Alkenes and Alkynes

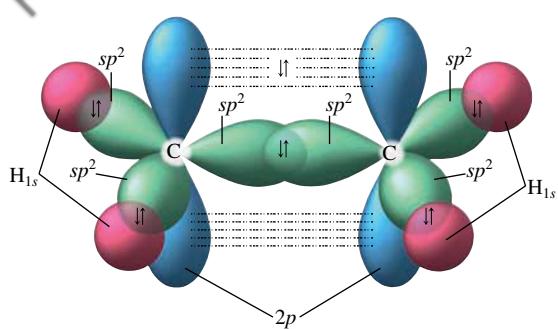
Multiple carbon–carbon bonds result when hydrogen atoms are removed from alkanes. Hydrocarbons that contain at least one carbon–carbon double bond are called **alkenes** and have the general formula  $\text{C}_n\text{H}_{2n}$ . The simplest alkene ( $\text{C}_2\text{H}_4$ ), commonly known as *ethylene*, has the Lewis structure



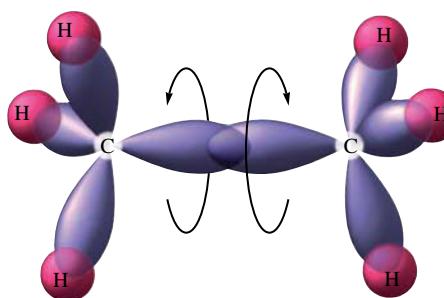
As discussed in Section 9.1, each carbon in ethylene can be described as  $sp^2$  hybridized. The C–C  $\sigma$  bond is formed by sharing an electron pair between  $sp^2$  orbitals, and the  $\pi$  bond is formed by sharing a pair of electrons between  $p$  orbitals (Fig. 22.7).

The systematic nomenclature for alkenes is quite similar to that for alkanes.

1. The root hydrocarbon name ends in *-ene* rather than *-ane*. Thus the systematic name for  $\text{C}_2\text{H}_4$  is *ethene* and the name for  $\text{C}_3\text{H}_6$  is *propene*.
2. In alkenes containing more than three carbon atoms, the location of the double bond is indicated by the lowest-numbered carbon atom involved in the bond. Thus  $\text{CH}_2=\text{CHCH}_2\text{CH}_3$  is called 1-butene, and  $\text{CH}_3\text{CH}=\text{CHCH}_3$  is called 2-butene.

**FIGURE 22.7**

The bonding in ethylene.

**FIGURE 22.8**

The bonding in ethane.

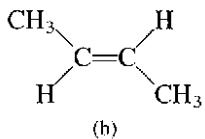
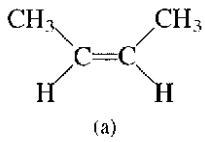
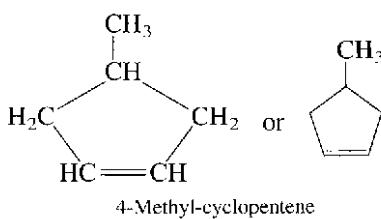
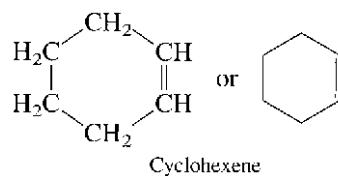
Note from Fig. 22.7 that the  $p$  orbitals on the two carbon atoms in ethylene must be lined up (parallel) to allow formation of the  $\pi$  bond. This prevents rotation of the two  $\text{CH}_2$  groups relative to each other at ordinary temperatures, in contrast to alkanes, where free rotation is possible (see Fig. 22.8). The restricted rotation around doubly bonded carbon atoms means that alkenes exhibit **cis-trans isomerism**. For example, there are two stereoisomers of 2-butene (Fig. 22.9). Identical substituents on the same side of the double bond are designated *cis* and those on opposite sides are labeled *trans*.

**Alkynes** are unsaturated hydrocarbons containing at least one triple carbon–carbon bond. The simplest alkyne is  $\text{C}_2\text{H}_2$  (commonly called *acetylene*), which has the systematic name *ethyne*. As discussed in Section 9.1, the triple bond in acetylene can be described as one  $\sigma$  bond between two  $sp$  hybrid orbitals on the two carbon atoms and two  $\pi$  bonds involving two  $2p$  orbitals on each carbon atom (Fig. 22.10).

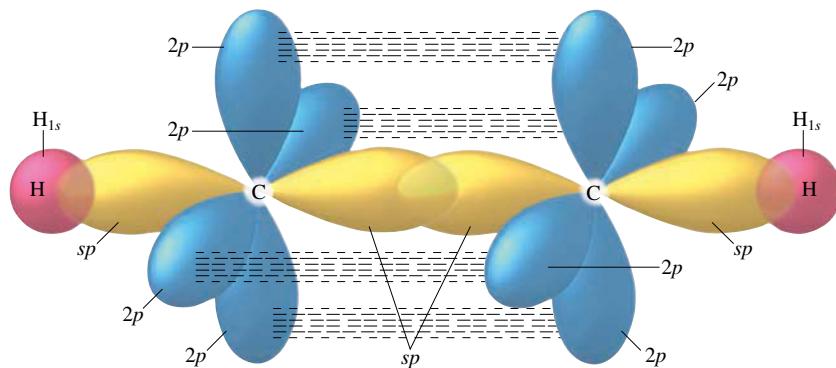
The nomenclature for alkynes involves the use of *-yne* as a suffix to replace the *-ane* of the parent alkane. Thus the molecule  $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CCH}_3$  has the name 2-pentyne.

Like alkanes, unsaturated hydrocarbons can exist as ringed structures, for example,

For cyclic alkenes, number through the double bond toward the substituent.

**FIGURE 22.9**The two stereoisomers of 2-butene: (a) *cis*-2-butene and (b) *trans*-2-butene.**FIGURE 22.10**

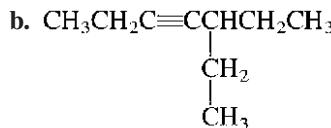
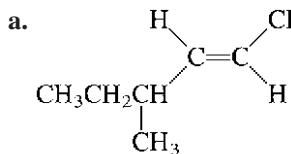
The bonding in acetylene.



### **Sample Exercise 22.5**

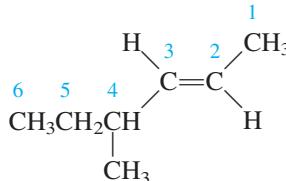
# Naming Alkenes and Alkynes

Name each of the following molecules.



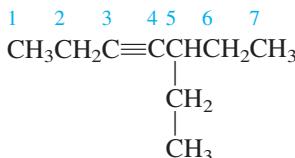
### *Solution*

- a. The longest chain, which contains six carbon atoms, is numbered as follows:



Thus the hydrocarbon is a 2-hexene. Since the hydrogen atoms are located on opposite sides of the double bond, this molecule corresponds to the *trans* isomer. The name is 4-methyl-*trans*-2-hexene.

- b. The longest chain, consisting of seven carbon atoms, is numbered as shown (giving the triple bond the lowest possible number):

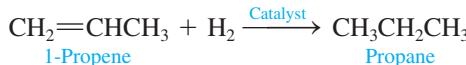


The hydrocarbon is a 3-heptyne. The full name is 5-ethyl-3-heptyne, where the position of the triple bond is indicated by the lower-numbered carbon atom involved in this bond.

*See Exercises 22.25 through 22.28 and 22.44.*

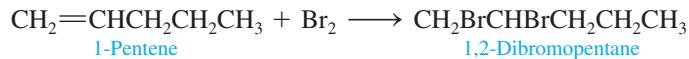
## Reactions of Alkenes and Alkynes

Because alkenes and alkynes are unsaturated, their most important reactions are **addition reactions**. In these reactions  $\pi$  bonds, which are weaker than the C—C  $\sigma$  bonds, are broken, and new  $\sigma$  bonds are formed to the atoms being added. For example, **hydrogenation reactions** involve the addition of hydrogen atoms:



For this reaction to proceed rapidly at normal temperatures, a catalyst of platinum, palladium, or nickel is used. The catalyst serves to help break the relatively strong H—H bond, as was discussed in Section 12.8. Hydrogenation of alkenes is an important industrial process, particularly in the manufacture of solid shortenings where unsaturated fats (fats containing double bonds), which are generally liquid, are converted to solid saturated fats.

**Halogenation** of unsaturated hydrocarbons involves addition of halogen atoms. For example,

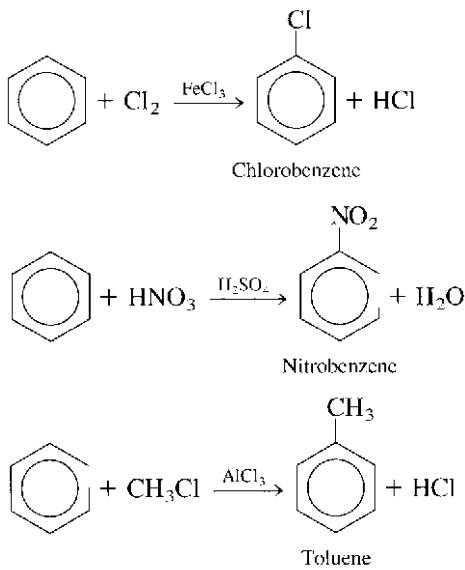


Another important reaction involving certain unsaturated hydrocarbons is **polymerization**, a process in which many small molecules are joined together to form a large molecule. Polymerization will be discussed in Section 22.5.

## 22.3 Aromatic Hydrocarbons

A special class of cyclic unsaturated hydrocarbons is known as the **aromatic hydrocarbons**. The simplest of these is benzene ( $\text{C}_6\text{H}_6$ ), which has a planar ring structure, as shown in Fig. 22.11(a). In the localized electron model of the bonding in benzene, resonance structures of the type shown in Fig. 22.11(b) are used to account for the known equivalence of all the carbon–carbon bonds. But as we discussed in Section 9.5, the best description of the benzene molecule assumes that  $sp^2$  hybrid orbitals on each carbon are used to form the C—C and C—H  $\sigma$  bonds, while the remaining  $2p$  orbital on each carbon is used to form  $\pi$  molecular orbitals. The delocalization of these  $\pi$  electrons is usually indicated by a circle inside the ring [Fig. 22.11(c)].

The delocalization of the  $\pi$  electrons makes the benzene ring behave quite differently from a typical unsaturated hydrocarbon. As we have seen previously, unsaturated hydrocarbons generally undergo rapid addition reactions. However, benzene does not. Instead, it undergoes substitution reactions in which *hydrogen atoms are replaced by other atoms*. For example,

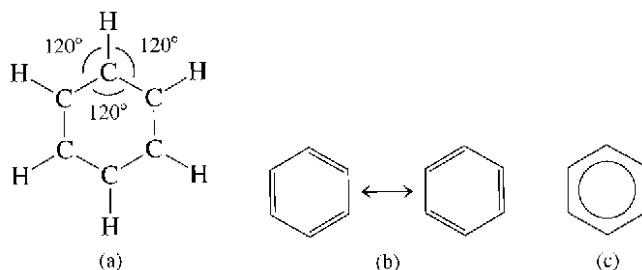


In each case the substance shown over the arrow is needed to catalyze these substitution reactions.

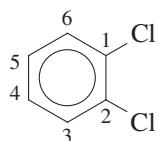
Substitution reactions are characteristic of saturated hydrocarbons, and addition reactions are characteristic of unsaturated ones. The fact that benzene reacts more like a saturated hydrocarbon indicates the great stability of the delocalized  $\pi$  electron system.

**FIGURE 22.11**

(a) The structure of benzene, a planar ring system in which all bond angles are  $120^\circ$ .  
 (b) Two of the resonance structures of benzene. (c) The usual representation of benzene. The circle represents the electrons in the delocalized  $\pi$  system. All C—C bonds in benzene are equivalent.

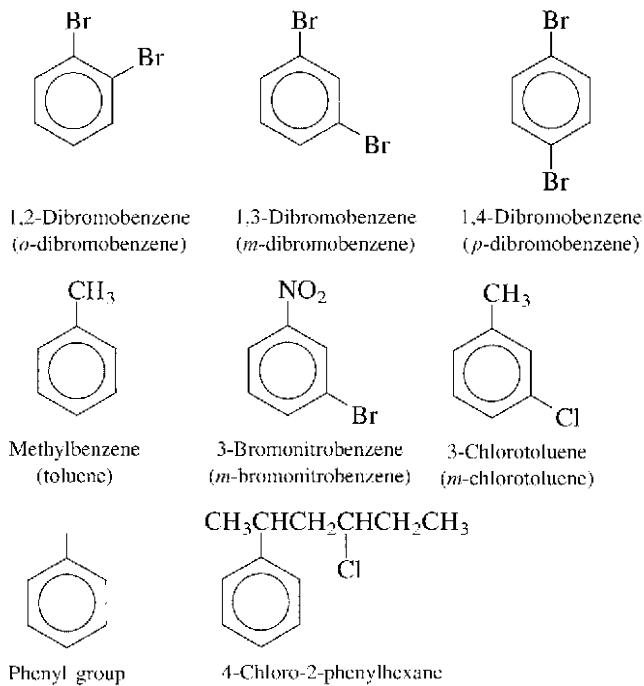


The nomenclature of benzene derivatives is similar to the nomenclature for saturated ring systems. If there is more than one substituent present, numbers are used to indicate substituent positions. For example, the compound



is named 1,2-dichlorobenzene. Another nomenclature system uses the prefix *ortho*- (*o*-) for two adjacent substituents, *meta*- (*m*-) for two substituents with one carbon between them, and *para*- (*p*-) for two substituents opposite each other. When benzene is used as a substituent, it is called the **phenyl group**. Examples of some aromatic compounds are shown in Fig. 22.12.

Benzene is the simplest aromatic molecule. More complex aromatic systems can be viewed as consisting of a number of “fused” benzene rings. Some examples are given in Table 22.3.

**FIGURE 22.12**

Some selected substituted benzenes and their names. Common names are given in parentheses.

**TABLE 22.3 More Complex Aromatic Systems**

Structural Formula	Name	Use or Effect
	Naphthalene	Formerly used in mothballs
	Anthracene	Dyes
	Phenanthrene	Dyes, explosives, and synthesis of drugs
	3,4-Benzpyrene	Active carcinogen found in smoke and smog

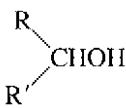
## 22.4 Hydrocarbon Derivatives

The vast majority of organic molecules contain elements in addition to carbon and hydrogen. However, most of these substances can be viewed as **hydrocarbon derivatives**, molecules that are fundamentally hydrocarbons but that have additional atoms or groups of atoms called **functional groups**. The common functional groups are listed in Table 22.4. Because each functional group exhibits characteristic chemistry, we will consider the groups separately.

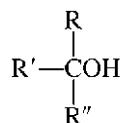
### Alcohols



*Primary alcohol*  
(one R group)



*Secondary alcohol*  
(two R groups)



*Tertiary alcohol*  
(three R groups)

**Alcohols** are characterized by the presence of the hydroxyl group ( $-\text{OH}$ ). Some common alcohols are shown in Table 22.5. The systematic name for an alcohol is obtained by replacing the final *-e* of the parent hydrocarbon with *-ol*. The position of the  $-\text{OH}$  group is specified by a number (where necessary) chosen so that it is the smallest of the substituent numbers. Alcohols are classified according to the number of hydrocarbon fragments bonded to the carbon where the  $-\text{OH}$  group is attached (see margin), where R, R', and R'' (which may be the same or different) represent hydrocarbon fragments.

Alcohols usually have much higher boiling points than might be expected from their molar masses. For example, both methanol and ethane have a molar mass of 30, but the boiling point for methanol is  $65^\circ\text{C}$  while that for ethane is  $-89^\circ\text{C}$ . This difference can be understood if we consider the types of intermolecular attractions that occur in these liquids. Ethane molecules are nonpolar and exhibit only weak London dispersion interactions. However, the polar  $-\text{OH}$  group of methanol produces extensive hydrogen bonding similar to that found in water (see Section 10.1), which results in the relatively high boiling point.

Although there are many important alcohols, the simplest ones, methanol and ethanol, have the greatest commercial value. Methanol, also known as *wood alcohol* because it was formerly obtained by heating wood in the absence of air, is prepared industrially

**TABLE 22.4** The Common Functional Groups

Class	Functional Group	General Formula*	Example
Halohydrocarbons	$-X$ (F, Cl, Br, I)	R—X	CH <sub>3</sub> I Iodomethane (methyl iodide)
Alcohols	—OH	R—OH	CH <sub>3</sub> OH Methanol (methyl alcohol)
Ethers	—O—	R—O—R'	CH <sub>3</sub> OCH <sub>3</sub> Dimethyl ether
Aldehydes	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}—\text{H} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}—\text{C}—\text{H} \end{array}$	CH <sub>2</sub> O Methanal (formaldehyde)
Ketones	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R—C—R'} \end{array}$	CH <sub>3</sub> COCH <sub>3</sub> Propanone (dimethyl ketone or acetone)
Carboxylic acids	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—OH} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R—C—OH} \end{array}$	CH <sub>3</sub> COOH Ethanoic acid (acetic acid)
Esters	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—O—} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R—C—O—R'} \end{array}$	CH <sub>3</sub> COOCH <sub>2</sub> CH <sub>3</sub> Ethyl acetate
Amines	—NH <sub>2</sub>	R—NH <sub>2</sub>	CH <sub>3</sub> NH <sub>2</sub> Aminomethane (methylamine)

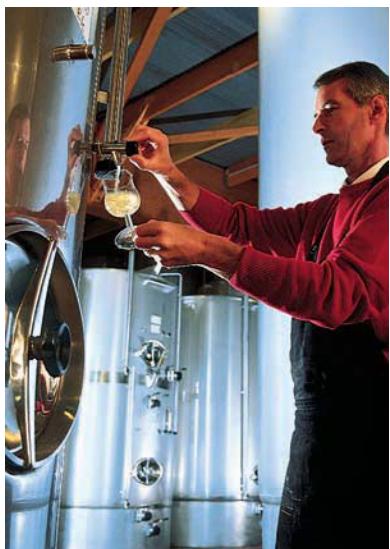
\*R and R' represent hydrocarbon fragments.

(approximately 4 million tons annually in the United States) by the hydrogenation of carbon monoxide:



Methanol is used as a starting material for the synthesis of acetic acid and for many types of adhesives, fibers, and plastics. It is also used (and such use may increase) as a motor fuel. Methanol is highly toxic to humans and can lead to blindness and death if ingested.

Ethanol is the alcohol found in beverages such as beer, wine, and whiskey; it is produced by the fermentation of glucose in corn, barley, grapes, and so on:



A winemaker drawing off a glass of wine in a modern wine cellar.

**TABLE 22.5** Some Common Alcohols

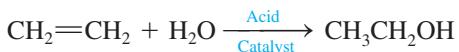
Formula	Systematic Name	Common Name
CH <sub>3</sub> OH	Methanol	Methyl alcohol
CH <sub>3</sub> CH <sub>2</sub> OH	Ethanol	Ethyl alcohol
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	1-Propanol	n-Propyl alcohol
CH <sub>3</sub> CH(OH)CH <sub>3</sub>	2-Propanol	Isopropyl alcohol



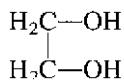
Ethanol is being tested in selected areas as a fuel for automobiles.

The reaction is catalyzed by the enzymes found in yeast. This reaction can proceed only until the alcohol content reaches about 13% (the percentage found in most wines), at which point the yeast can no longer survive. Beverages with higher alcohol content are made by distilling the fermentation mixture.

Ethanol, like methanol, can be burned in the internal combustion engines of automobiles and is now commonly added to gasoline to form gasohol (see Section 6.6). It is also used in industry as a solvent and for the preparation of acetic acid. The commercial production of ethanol (500,000 tons per year in the United States) is carried out by reaction of water with ethylene:

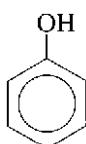


Many polyhydroxyl (more than one —OH group) alcohols are known, the most important being *1,2-ethanediol* (ethylene glycol),



a toxic substance that is the major constituent of most automobile antifreeze solutions.

The simplest aromatic alcohol is



which is commonly called **phenol**. Most of the 1 million tons of phenol produced annually in the United States is used to make polymers for adhesives and plastics.

### Sample Exercise 22.6

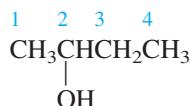
### Naming and Classifying Alcohols

For each of the following alcohols, give the systematic name and specify whether the alcohol is primary, secondary, or tertiary.

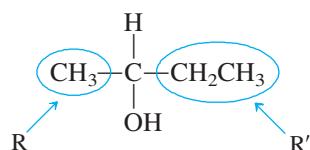


#### Solution

a. The chain is numbered as follows:



The compound is called 2-butanol, since the —OH group is located at the number 2 position of a four-carbon chain. Note that the carbon to which the —OH is attached also has —CH<sub>3</sub> and —CH<sub>2</sub>CH<sub>3</sub> groups attached:

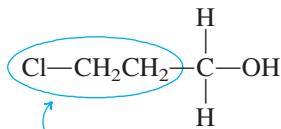


Therefore, this is a *secondary* alcohol.

b. The chain is numbered as follows:

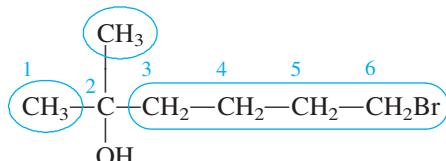


The name is 3-chloro-1-propanol. This is a *primary* alcohol:



One R group attached to the carbon with the —OH group

c. The chain is numbered as follows:



The name is 6-bromo-2-methyl-2-hexanol. This is a *tertiary* alcohol since the carbon where the —OH is attached also has three other R groups attached.

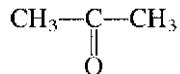
*See Exercises 22.51 and 22.52.*

## Aldehydes and Ketones

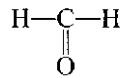
Aldehydes and ketones contain the **carbonyl group**,



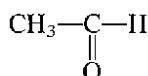
In **ketones** this group is bonded to two carbon atoms, as in acetone,



In **aldehydes** the carbonyl group is bonded to at least one hydrogen atom, as in formaldehyde,



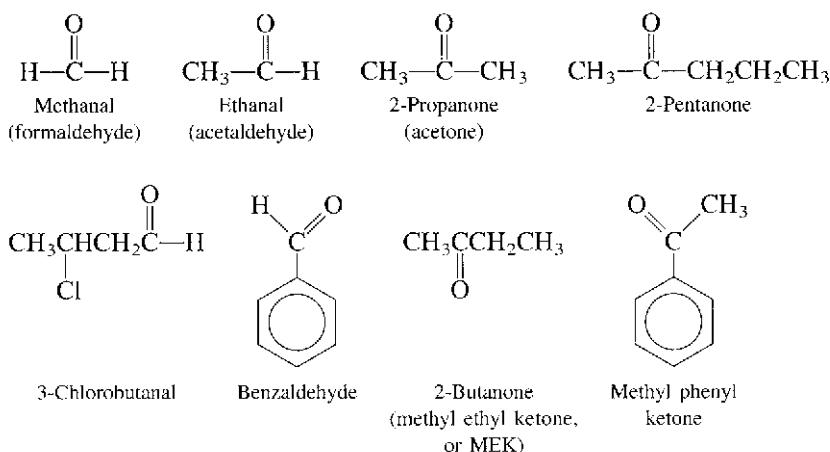
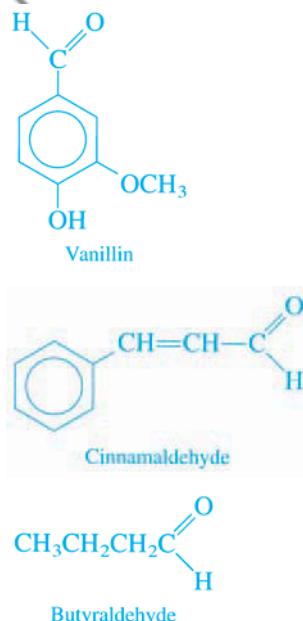
or acetaldehyde,



Cinnamaldehyde produces the characteristic odor of cinnamon.

The systematic name for an aldehyde is obtained from the parent alkane by removing the final *-e* and adding *-al*. For ketones the final *-e* is replaced by *-one*, and a number indicates the position of the carbonyl group where necessary. Examples of common aldehydes and ketones are shown in Fig. 22.13. Note that since the aldehyde functional group always occurs at the end of the carbon chain, the aldehyde carbon is assigned the number 1 when substituent positions are listed in the name.

Ketones often have useful solvent properties (acetone is found in nail polish remover, for example) and are frequently used in industry for this purpose. Aldehydes typically have strong odors. Vanillin is responsible for the pleasant odor in vanilla beans; cinnamaldehyde

**FIGURE 22.13**

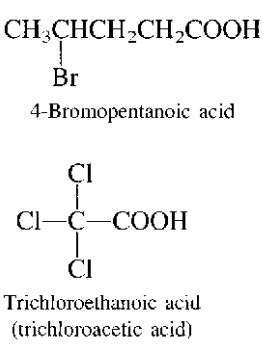
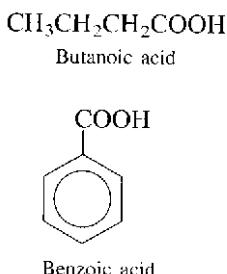
Some common ketones and aldehydes. Note that since the aldehyde functional group always appears at the end of a carbon chain, carbon is assigned the number 1 when the compound is named.

produces the characteristic odor of cinnamon. On the other hand, the unpleasant odor in rancid butter arises from the presence of butyraldehyde.

Aldehydes and ketones are most often produced commercially by the oxidation of alcohols. For example, oxidation of a *primary* alcohol yields the corresponding aldehyde:

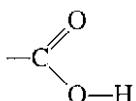


Oxidation of a *secondary* alcohol results in a ketone:



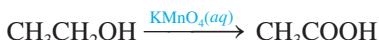
## Carboxylic Acids and Esters

**Carboxylic acids** are characterized by the presence of the **carboxyl group**



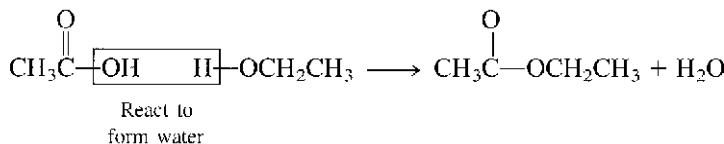
that gives an acid of the general formula RCOOH. Typically, these molecules are weak acids in aqueous solution (see Section 14.5). Organic acids are named from the parent alkane by dropping the final *-e* and adding *-oic*. Thus CH<sub>3</sub>COOH, commonly called acetic acid, has the systematic name ethanoic acid, since the parent alkane is ethane. Other examples of carboxylic acids are shown in Fig. 22.14.

Many carboxylic acids are synthesized by oxidizing primary alcohols with a strong oxidizing agent. For example, ethanol can be oxidized to acetic acid by using potassium permanganate:



**FIGURE 22.14**  
Some carboxylic acids.

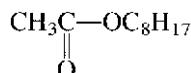
A carboxylic acid reacts with an alcohol to form an **ester** and a water molecule. For example, the reaction of acetic acid with ethanol produces ethyl acetate and water:



Esters often have a sweet, fruity odor that is in contrast to the often pungent odors of the parent carboxylic acids. For example, the odor of bananas is caused by *n*-amyl acetate,

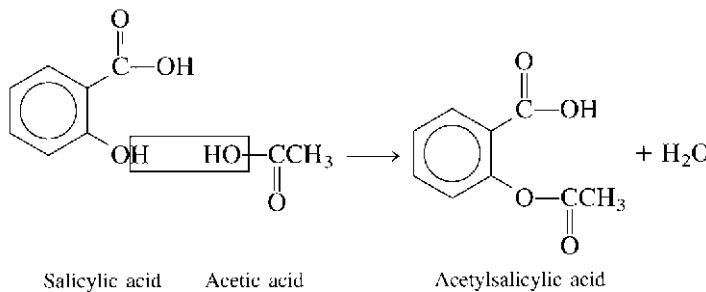


and that of oranges is caused by *n*-octyl acetate,

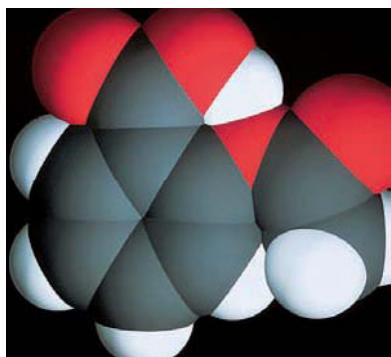


The systematic name for an ester is formed by changing the *-oic* ending of the parent acid to *-oate*. The parent alcohol chain is named first with a *-yl* ending. For example, the systematic name for *n*-octyl acetate is *n*-octylethanoate (from ethanoic acid).

A very important ester is formed from the reaction of salicylic acid and acetic acid:



Aspirin tablets.



Computer-generated space-filling model of acetylsalicylic acid (aspirin).

The product is acetylsalicylic acid, commonly known as *aspirin*, which is used in huge quantities as an analgesic (painkiller).

## Amines

**Amines** are probably best viewed as derivatives of ammonia in which one or more N—H bonds are replaced by N—C bonds. The resulting amines are classified as *primary* if one N—C bond is present, *secondary* if two N—C bonds are present, and *tertiary* if all three N—H bonds in NH<sub>3</sub> have been replaced by N—C bonds (Fig. 22.15). Examples of some common amines are given in Table 22.6.

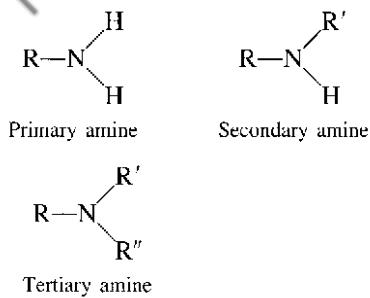
Common names are often used for simple amines; the systematic nomenclature for more complex molecules uses the name *amino-* for the —NH<sub>2</sub> functional group. For example, the molecule



is named 2-aminobutane.

Many amines have unpleasant “fishlike” odors. For example, the odors associated with decaying animal and human tissues are caused by amines such as putrescine (H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>) and cadaverine (H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>).

Aromatic amines are primarily used to make dyes. Since many of them are carcinogenic, they must be handled with great care.

**FIGURE 22.15**

The general formulas for primary, secondary, and tertiary amines. R, R', and R'' represent carbon-containing substituents.

**TABLE 22.6 Some Common Amines**

Formula	Common Name	Type
$\text{CH}_3\text{NH}_2$	Methylamine	Primary
$\text{CH}_3\text{CH}_2\text{NH}_2$	Ethylamine	Primary
$(\text{CH}_3)_2\text{NH}$	Dimethylamine	Secondary
$(\text{CH}_3)_3\text{N}$	Trimethylamine	Tertiary
	Aniline	Primary
	Diphenylamine	Secondary

## 22.5 Polymers

**Polymers** are large, usually chainlike molecules that are built from small molecules called *monomers*. Polymers form the basis for synthetic fibers, rubbers, and plastics and have played a leading role in the revolution that has been brought about in daily life by chemistry. It has been estimated that about 50% of the industrial chemists in the United States work in some area of polymer chemistry, a fact that illustrates just how important polymers are to our economy and standard of living.

### The Development and Properties of Polymers

The development of the polymer industry provides a striking example of the importance of serendipity in the progress of science. Many discoveries in polymer chemistry arose from accidental observations that scientists followed up.

The age of plastics might be traced to a day in 1846 when Christian Schoenbein, a chemistry professor at the University of Basel in Switzerland, spilled a flask containing nitric and sulfuric acids. In his hurry to clean up the spill, he grabbed his wife's cotton apron, which he then rinsed out and hung up in front of a hot stove to dry. Instead of drying, the apron flared and burned.

Very interested in this event, Schoenbein repeated the reaction under more controlled conditions and found that the new material, which he correctly concluded to be nitrated cellulose, had some surprising properties. As he had experienced, the nitrated cellulose is extremely flammable and, under certain circumstances, highly explosive. In addition, he found that it could be molded at moderate temperatures to give objects that were, upon cooling, tough but elastic. Predictably, the explosive nature of the substance was initially of more interest than its other properties, and cellulose nitrate rapidly became the basis for smokeless gun powder. Although Schoenbein's discovery cannot be described as a truly synthetic polymer (because he simply found a way to modify the natural polymer cellulose), it formed the basis for a large number of industries that grew up to produce photographic films, artificial fibers, and molded objects of all types.

The first synthetic polymers were produced as by-products of various organic reactions and were regarded as unwanted contaminants. Thus the first preparations of many of the polymers now regarded as essential to our modern lifestyle were thrown away in



The soybeans on the left are coated with a red acrylic polymer to delay soybean emergence. This allows farmers to plant their crops more efficiently.

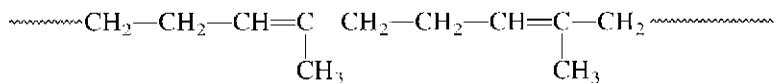
disgust. One chemist who refused to be defeated by the “tarry” products obtained when he reacted phenol with formaldehyde was the Belgian-American chemist Leo H. Baekeland (1863–1944). Baekeland’s work resulted in the first completely synthetic plastic (called Bakelite), a substance that when molded to a certain shape under high pressure and temperature cannot be softened again or dissolved. Bakelite is a **thermoset polymer**. In contrast, cellulose nitrate is a **thermoplastic polymer**; that is, it can be remelted after it has been molded.

The discovery of Bakelite in 1907 spawned a large plastics industry, producing telephones, billiard balls, and insulators for electrical devices. During the early days of polymer chemistry, there was a great deal of controversy over the nature of these materials. Although the German chemist Hermann Staudinger speculated in 1920 that polymers were very large molecules held together by strong chemical bonds, most chemists of the time assumed that these materials were much like colloids, in which small molecules are aggregated into large units by forces weaker than chemical bonds.

One chemist who contributed greatly to the understanding of polymers as giant molecules was Wallace H. Carothers of the DuPont Chemical Company. Among his accomplishments was the preparation of nylon. The nylon story further illustrates the importance of serendipity in scientific research. When nylon is first prepared, the resulting product is a sticky material with little structural integrity. Because of this, it was initially put aside as having no apparently useful characteristics. However, Julian Hill, a chemist in the Carothers research group, one day put a small ball of this nylon on the end of a stirring rod and drew it away from the remaining sticky mass, forming a string. He noticed the silky appearance and strength of this thread and realized that nylon could be drawn into useful fibers.

The reason for this behavior of nylon is now understood. When nylon is first formed, the individual polymer chains are oriented randomly, like cooked spaghetti, and the substance is highly amorphous. However, when drawn out into a thread, the chains tend to line up (the nylon becomes more crystalline), which leads to increased hydrogen bonding between adjacent chains. This increase in crystallinity, along with the resulting increase in hydrogen-bonding interactions, leads to strong fibers and thus to a highly useful material. Commercially, nylon is produced by forcing the raw material through a *spinneret*, a plate containing small holes, which forces the polymer chains to line up.

Another property that adds strength to polymers is **crosslinking**, the existence of covalent bonds between adjacent chains. The structure of Bakelite is highly crosslinked, which accounts for the strength and toughness of this polymer. Another example of crosslinking occurs in the manufacture of rubber. Raw natural rubber consists of chains of the type

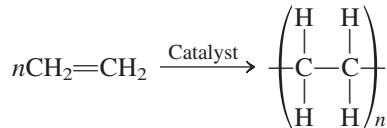


Charles Goodyear tried for many years to change natural rubber into a useful product. In 1839 he accidentally dropped some rubber containing sulfur on a hot stove. Noting that the rubber did not melt as expected, Goodyear pursued this lead and developed vulcanization.

and is a soft, sticky material unsuitable for tires. However, in 1839 Charles Goodyear (1800–1860), an American chemist, accidentally found that if sulfur is added to rubber and the resulting mixture is heated (a process called **vulcanization**), the resulting rubber is still elastic (reversibly stretchable) but is much stronger. This change in character occurs because sulfur atoms become bonded between carbon atoms on different chains. These sulfur atoms form bridges between the polymer chains, thus linking the chains together.

## Types of Polymers

The simplest and one of the best-known polymers is *polyethylene*, which is constructed from ethylene monomers:



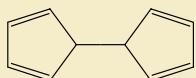


## CHEMICAL IMPACT

### Heal Thyself

One major problem with structural materials is that they crack and weaken as they age. The human body has mechanisms for healing itself if the skin is cut or a bone is broken. However, inanimate materials have had no such mechanisms—until now. Scientists at the University of Illinois at Urbana–Champaign (UIUC) have invented a plastic that automatically heals microscopic cracks before they can develop into large cracks that would degrade the usefulness of the material. This accomplishment was achieved by an interdisciplinary team of scientists including aeronautical engineering professors Scott White and Philippe Geubelle, applied mechanics professor Nancy Sottos, and chemistry professor Jeffrey Moore.

The self-healing system is based on microcapsules containing liquid dicyclopentadiene



Dicyclopentadiene

that are blended into the plastic. When a microscopic crack develops, it encounters and breaks a microcapsule. The dicyclopentadiene then leaks out, where it encounters a catalyst (blended into the plastic when it was formulated) that mediates a repair polymerization process. This process involves opening the cyclopentadiene rings, which leads to a highly cross-linked repair of the crack.

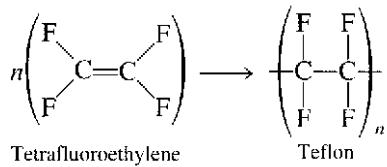
The trickiest part of the repair mechanism is to get the microcapsules to be the correct size and to have the appropriate wall strength. They must be small enough not to degrade the strength of the plastic. The walls must also be thick enough to survive the molding of the plastic but thin enough to burst as the lengthening crack reaches them.

Self-healing materials should have many applications. The U.S. Air Force, which partially funded the research at UIUC, is interested in using the materials in tanks that hold gases and liquids under pressure. The current materials used for these tanks are subject to microcracks that eventually grow, causing the tanks to leak. Self-healing materials would



Cross-linking gives the rubber in these tires strength and toughness.

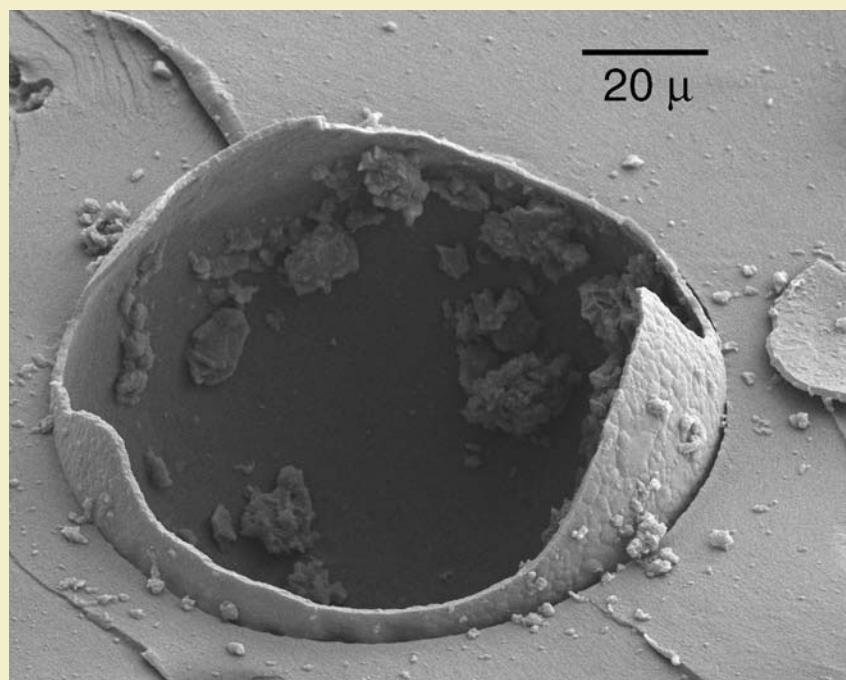
where  $n$  represents a large number (usually several thousand). Polyethylene is a tough, flexible plastic used for piping, bottles, electrical insulation, packaging films, garbage bags, and many other purposes. Its properties can be varied by using substituted ethylene monomers. For example, when tetrafluoroethylene is the monomer, the polymer Teflon is obtained:



The discovery of Teflon, a very important substituted polyethylene, is another illustration of the role of chance in chemical research. In 1938 a DuPont chemist named Roy Plunkett was studying the chemistry of gaseous tetrafluoroethylene. He synthesized about 100 pounds of the chemical and stored it in steel cylinders. When one of the cylinders failed to produce perfluoroethylene gas when the valve was opened, the cylinder was cut open to reveal a white powder. This powder turned out to be a polymer of perfluoroethylene, which was eventually developed into Teflon. Because of the resistance of the strong C—F bonds to chemical attack, Teflon is an inert, tough, and nonflammable material widely used for electrical insulation, nonstick coatings on cooking utensils, and bearings for low-temperature applications.

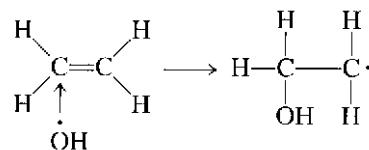
Other polyethylene-type polymers are made from monomers containing chloro, methyl, cyano, and phenyl substituents, as summarized in Table 22.7 on page 1020. In each case the double carbon–carbon bond in the substituted ethylene monomer becomes a single bond in the polymer. The different substituents lead to a wide variety of properties.

also be valuable in situations where repair is impossible or impractical, such as electronic circuit boards, components of deep space probes, and implanted medical devices.

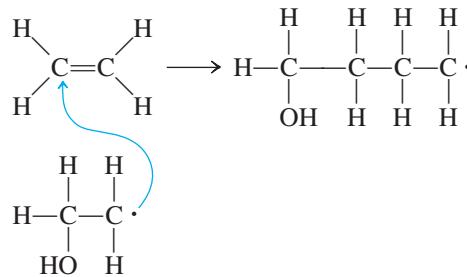


A scanning electron microscope image showing the fractured plane of a self-healing material with a ruptured microcapsule in a thermosetting matrix.

The polyethylene polymers illustrate one of the major types of polymerization reactions, called **addition polymerization**, in which the monomers simply “add together” to produce the polymer. No other products are formed. The polymerization process is initiated by a **free radical** (a species with an unpaired electron) such as the hydroxyl radical ( $\text{HO}\cdot$ ). The free radical attacks and breaks the  $\pi$  bond of an ethylene molecule to form a new free radical,

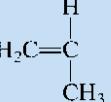
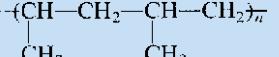
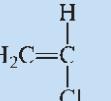
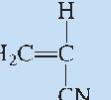
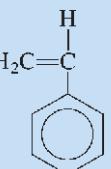
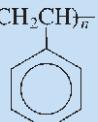
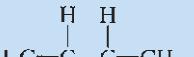
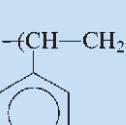


which is then available to attack another ethylene molecule:



Repetition of this process thousands of times creates a long-chain polymer. Termination of the growth of the chain occurs when *two radicals* react to form a bond, a process that consumes two radicals without producing any others.

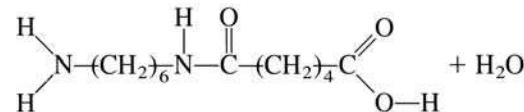
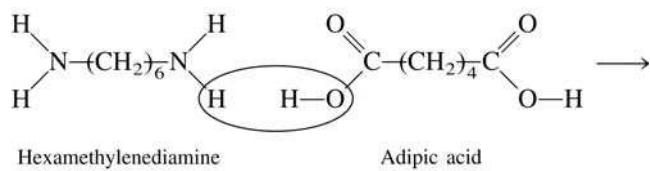
**TABLE 22.7 Some Common Synthetic Polymers, Their Monomers and Applications**

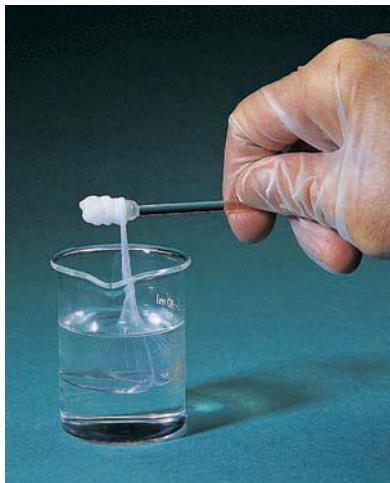
Monomer		Polymer		
Name	Formula	Name	Formula	Uses
Ethylene	$\text{H}_2\text{C}=\text{CH}_2$	Polyethylene	$-(\text{CH}_2-\text{CH}_2)_n-$	Plastic piping, bottles, electrical insulation, toys
Propylene		Polypropylene	$-(\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2)_n-$ 	Film for packaging, carpets, lab wares, toys
Vinyl chloride		Polyvinyl chloride (PVC)	$(\text{CH}_2-\overset{\text{CH}}{\underset{\text{Cl}}{ }})_n-$	Piping, siding, floor tile, clothing, toys
Acrylonitrile		Polyacrylonitrile (PAN)	$-(\text{CH}_2-\overset{\text{CH}}{\underset{\text{CN}}{ }})_n-$	Carpets, fabrics
Tetrafluoroethylene	$\text{F}_2\text{C}=\text{CF}_2$	Teflon	$-(\text{CF}_2-\text{CF}_2)_n-$	Cooking utensils, electrical insulation, bearings
Styrene		Polystyrene	$-(\text{CH}_2\text{CH})_n-$ 	Containers, thermal insulation, toys
Butadiene		Polybutadiene	$-(\text{CH}_2\text{CH}=\text{CHCH}_2)_n-$	Tire tread, coating resin
Butadiene and styrene	(See above.)	Styrene-butadiene rubber	$-(\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2)_n-$ 	Synthetic rubber



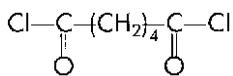
## Visualization: Synthesis of

Another common type of polymerization is **condensation polymerization**, in which a small molecule, such as water, is formed for each extension of the polymer chain. The most familiar polymer produced by condensation is *nylon*. Nylon is a **copolymer**, since two different types of monomers combine to form the chain; a **homopolymer** is the result of polymerizing a single type of monomer. One common form of nylon is produced when hexamethylenediamine and adipic acid react by splitting out a water molecule to form a C—N bond:



**FIGURE 22.16**

The reaction to form nylon can be carried out at the interface of two immiscible liquid layers in a beaker. The bottom layer contains adipoyl chloride,



dissolved in  $\text{CCl}_4$ , and the top layer contains hexamethylenediamine,



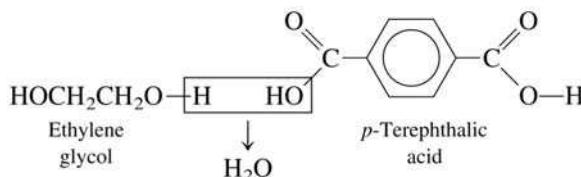
dissolved in water. A molecule of  $\text{HCl}$  is formed as each  $\text{C}-\text{N}$  bond forms.

The molecule formed, called a **dimer** (two monomers joined), can undergo further condensation reactions since it has an amino group at one end and a carboxyl group at the other. Thus both ends are free to react with another monomer. Repetition of this process leads to a long chain of the type

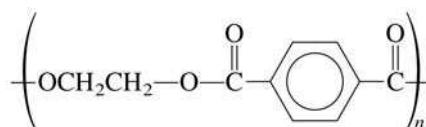


which is the basic structure of nylon. The reaction to form nylon occurs quite readily and is often used as a lecture demonstration (see Fig. 22.16). The properties of nylon can be varied by changing the number of carbon atoms in the chain of the acid or amine monomer.

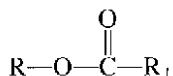
More than 1 million tons of nylon is produced annually in the United States for use in clothing, carpets, rope, and so on. Many other types of condensation polymers are also produced. For example, Dacron is a copolymer formed from the condensation reaction of ethylene glycol (a dialcohol) and *p*-terephthalic acid (a dicarboxylic acid):



The repeating unit of Dacron is



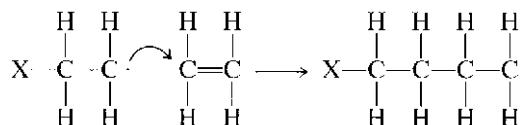
Note that this polymerization involves a carboxylic acid and an alcohol forming an ester group:



Thus Dacron is called a **polyester**. By itself or blended with cotton, Dacron is widely used in fibers for the manufacture of clothing.

### Polymers Based on Ethylene

A large section of the polymer industry involves the production of macromolecules from ethylene or substituted ethylenes. As discussed previously, ethylene molecules polymerize by addition after the double bond has been broken by some initiator:



This process continues by adding new ethylene molecules to eventually give polyethylene, a thermoplastic material.

There are two forms of polyethylene: low-density polyethylene (LDPE) and high-density polyethylene (HDPE). The chains in LDPE contain many branches and thus do not pack as tightly as those in HDPE, which consist of mostly straight-chain molecules.

Traditionally, LDPE has been manufactured under conditions of high pressure ( $\approx 20,000$  psi) and high temperature ( $500^\circ\text{C}$ ). These severe reaction conditions require specially designed equipment, and for safety reasons the reaction usually has been run behind a reinforced concrete barrier. More recently, lower reaction pressures and

psi is the abbreviation for pounds per square inch:  $15 \text{ psi} \approx 1 \text{ atm}$ .



## CHEMICAL IMPACT

### Wallace Hume Carothers

Wallace H. Carothers, a brilliant organic chemist who was principally responsible for the development of nylon and the first synthetic rubber (Neoprene), was born in 1896 in Burlington, Iowa. As a youth, Carothers was fascinated by tools and mechanical devices and spent many hours experimenting. In 1915 he entered Tarkio College in Missouri. Carothers so excelled in chemistry that even before his graduation, he was made a chemistry instructor.

Carothers eventually moved to the University of Illinois at Urbana-Champaign, where he was appointed to the faculty when he completed his Ph.D. in organic chemistry in 1924. He moved to Harvard University in 1926, and then to DuPont in 1928 to participate in a new program in fundamental research. At DuPont, Carothers headed the organic chemistry division, and during his ten years there played a prominent role in laying the foundations of polymer chemistry.

By the age of 33, Carothers had become a world-famous chemist whose advice was sought by almost everyone working in polymers. He was the first industrial chemist to be elected to the prestigious National Academy of Sciences.

Carothers was an avid reader of poetry and a lover of classical music. Unfortunately, he also suffered from severe bouts of depression that finally led to his suicide in 1937 in a Philadelphia hotel room, where he drank a cyanide



Wallace H. Carothers.

solution. He was 41 years old. Despite the brevity of his career, Carothers was truly one of the finest American chemists of all time. His great intellect, his love of chemistry, and his insistence on perfection produced his special genius.

temperatures have become possible through the use of catalysts. One catalytic system using triethylaluminum,  $\text{Al}(\text{C}_2\text{H}_5)_3$ , and titanium(IV) chloride was developed by Karl Ziegler in Germany and Giulio Natta in Italy. Although this catalyst is very efficient, it catches fire on contact with air and must be handled very carefully. A safer catalytic system was developed at Phillips Petroleum Company. It uses a chromium(III) oxide ( $\text{Cr}_2\text{O}_3$ ) and aluminosilicate catalyst and has mainly taken over in the United States. The product of the catalyzed reaction is highly linear (unbranched) and is often called *linear low-density polyethylene*. It is very similar to HDPE.

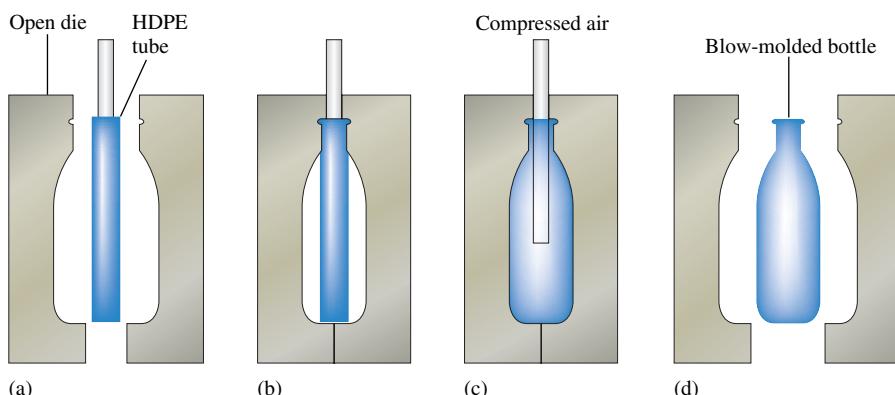
The major use of LDPE is in the manufacture of the tough transparent film that is used in packaging so many consumer goods. Two-thirds of the approximately 10 billion pounds of LDPE produced annually in the United States are used for this purpose. The major use of HDPE is for blow-molded products, such as bottles for consumer products (see Fig. 22.17).

The useful properties of polyethylene are due primarily to its high molecular weight (molar mass). Although the strengths of the interactions between specific points on the nonpolar chains are quite small, the chains are so long that these small attractions accumulate to a very significant value, so that the chains stick together very tenaciously. There is also a great deal of physical tangling of the lengthy chains. The combination of these interactions gives the polymer strength and toughness. However, a material like polyethylene can be melted and formed into a new shape (thermoplastic behavior), because in the melted state the molecules can readily flow past one another.

Molecular weight (not molar mass) is the common terminology in the polymer industry.

**FIGURE 22-17**

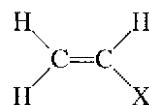
A major use of HDPE is for blow-molded objects such as bottles for soft drinks, shampoos, bleaches, and so on. (a) A tube composed of HDPE is inserted into the mold (die). (b) The die closes, sealing the bottom of the tube. (c) Compressed air is forced into the warm HDPE tube, which then expands to take the shape of the die. (d) The molded bottle is removed from the die.



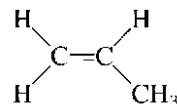
Since a high molecular weight gives a polymer useful properties, one might think that the goal would be to produce polymers with chains as long as possible. However, this is not the case—polymers become much more difficult to process as the molecular weights increase. Most industrial operations require that the polymer flow through pipes as it is processed. But as the chain lengths increase, viscosity also increases. In practice, the upper limit of a polymer's molecular weight is set by the flow requirements of the manufacturing process. Thus the final product often reflects a compromise between the optimal properties for the application and those needed for ease of processing.

Although many polymer properties are greatly influenced by molecular weight, some other important properties are not. For example, chain length does not affect a polymer's resistance to chemical attack. Physical properties such as color, refractive index, hardness, density, and electrical conductivity are also not greatly influenced by molecular weight.

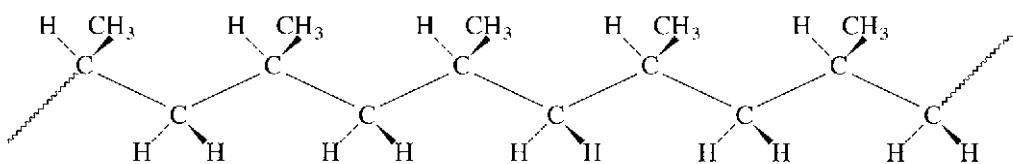
We have already seen that one way of altering the strength of a polymeric materials is to vary the chain length. Another method for modifying polymer behavior involves varying the substituents. For example, if we use a monomer of the type



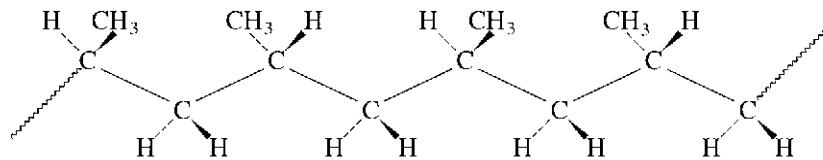
the properties of the resulting polymer depend on the identity of X. The simplest example is polypropylene, whose monomer is



and that has the form



The  $\text{CH}_3$  groups can be arranged on the same side of the chain (called an **isotactic chain**) as shown above, can alternate (called a **syndiotactic chain**) as shown below,



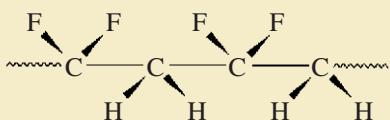
or can be randomly distributed (called an **atactic chain**).



## CHEMICAL IMPACT

### Plastic That Talks and Listens

**I**magine a plastic so “smart” that it can be used to sense a baby’s breath, measure the force of a karate punch, sense the presence of a person 100 feet away, or make a balloon that sings. There is a plastic film capable of doing all these things. It’s called polyvinylidene difluoride (PVDF), which has the structure



When this polymer is processed in a particular way, it becomes piezoelectric and pyroelectric. A piezoelectric substance produces an electric current when it is physically deformed or alternatively undergoes a deformation caused by the application of a current. A pyroelectric material is one that develops an electrical potential in response to a change in its temperature.

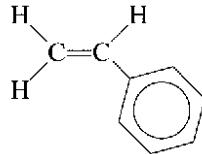
Because PVDF is piezoelectric, it can be used to construct a paper-thin microphone; it responds to sound by producing a current proportional to the deformation caused by the sound waves. A ribbon of PVDF plastic one-quarter of

an inch wide could be strung along a hallway and used to listen to all the conversations going on as people walk through. On the other hand, electric pulses can be applied to the PVDF film to produce a speaker. A strip of PVDF film glued to the inside of a balloon can play any song stored on a microchip attached to the film—hence a balloon that can sing “Happy Birthday” at a party. The PVDF film can also be used to construct a sleep apnea monitor, which, when placed beside the mouth of a sleeping infant, will set off an alarm if the breathing stops, thus helping to prevent sudden infant death syndrome (SIDS). The same type of film is used by the U.S. Olympic karate team to measure the force of kicks and punches as the team trains. Also, gluing two strips of film together gives a material that curls in response to a current, creating an artificial muscle. In addition, because the PVDF film is pyroelectric, it responds to the infrared (heat) radiation emitted by a human as far away as 100 feet, making it useful for burglar alarm systems.

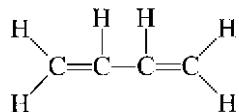
Making the PVDF polymer piezoelectric and pyroelectric requires some very special processing, which makes it costly (\$10 per square foot). This expense seems a small price to pay for its near-magical properties.

The chain arrangement has a significant effect on the polymer’s properties. Most polypropylene is made using the Ziegler-Natta catalyst,  $\text{Al}(\text{C}_2\text{H}_5)_3 \cdot \text{TiCl}_4$ , which produces highly isotactic chains that pack together quite closely. As a result, polypropylene is more crystalline, and therefore stronger and harder, than polyethylene. The major uses of polypropylene are for molded parts (40%), fibers (35%), and packaging films (10%). Polypropylene fibers are especially useful for athletic wear because they do not absorb water from perspiration, as cotton does. Rather, the moisture is drawn away from the skin to the surface of the polypropylene garment, where it can evaporate. The annual U.S. production of polypropylene is about 7 billion pounds.

Another related polymer, **polystyrene**, is constructed from the monomer styrene,



Pure polystyrene is too brittle for many uses, so most polystyrene-based polymers are actually *copolymers* of styrene and butadiene,

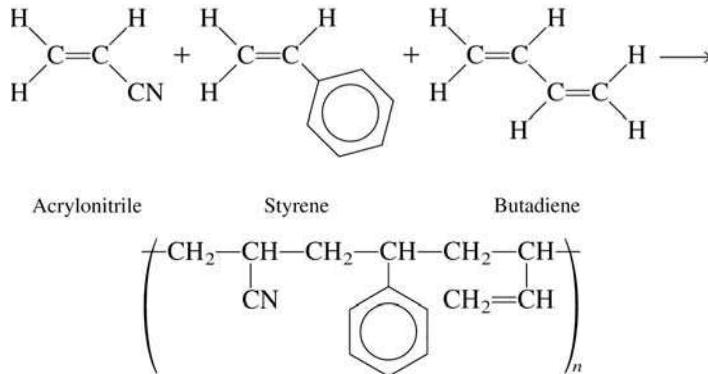


thus incorporating bits of butadiene rubber into the polystyrene matrix. The resulting polymer is very tough and is often used as a substitute for wood in furniture.

Another polystyrene-based product is acrylonitrile-butadiene-styrene (ABS), a tough, hard, and chemically resistant plastic used for pipes and for items such as radio housings, telephone cases, and golf club heads, for which shock resistance is an essential property. Originally, ABS was produced by copolymerization of the three monomers:

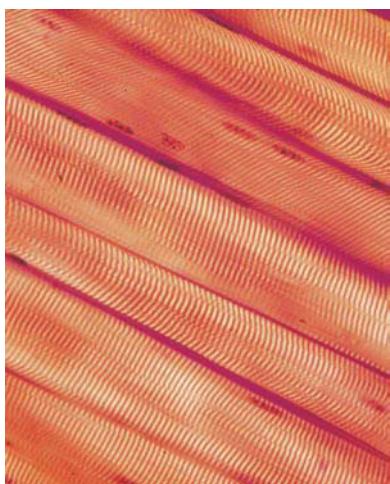
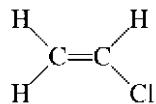


PVC pipe is widely used in industry.



It is now prepared by a special process called *grafting*, in which butadiene is polymerized first, and then the cyanide and phenyl substituents are added chemically.

Another high-volume polymer, **polyvinyl chloride (PVC)**, is constructed from the monomer vinyl chloride,



The protein in muscles enables them to contract.

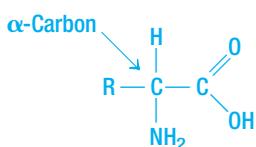
## 22.6 Natural Polymers

### Proteins

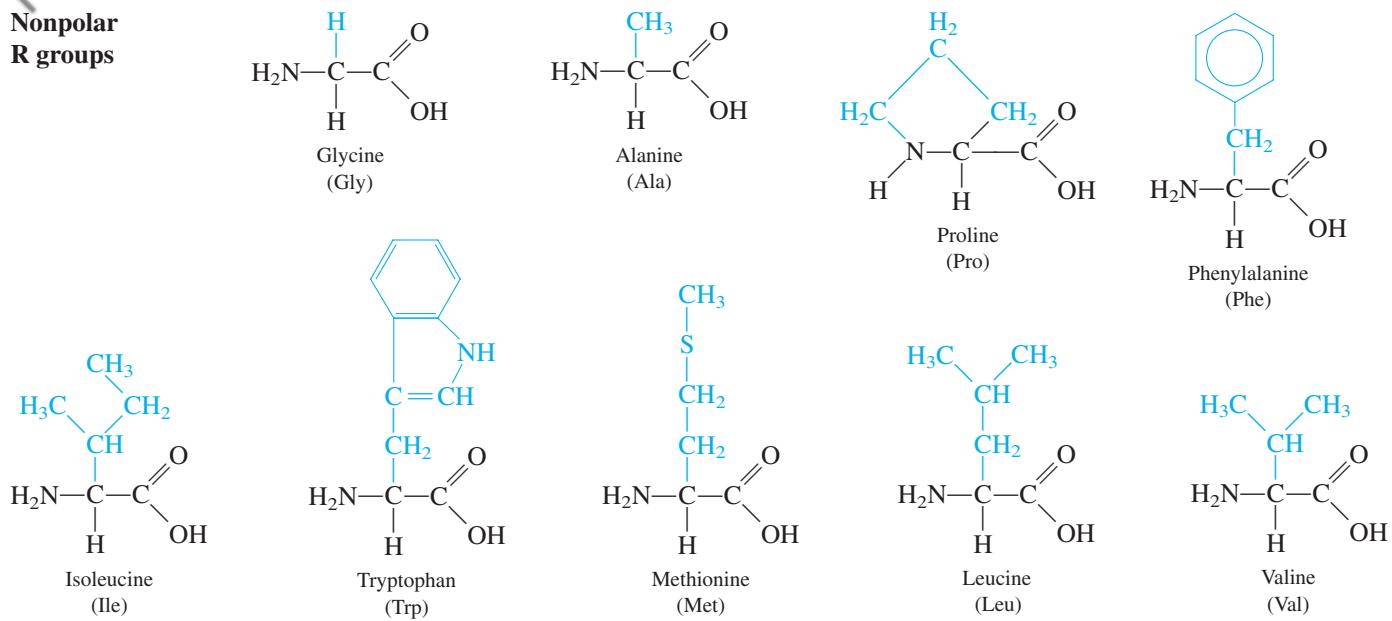
We have seen that many useful synthetic materials are polymers. Thus it should not be surprising that a great many natural materials are also polymers: starch, hair, silicate chains in soil and rocks, silk and cotton fibers, and the cellulose in woody plants, to name only a few.

In this section we consider a class of natural polymers, the **proteins**, which make up about 15% of our bodies and have molecular weights (molar masses) that range from about 6000 to over 1,000,000 grams per mole. Proteins perform many functions in the human body. **Fibrous proteins** provide structural integrity and strength for many types of tissue and are the main components of muscle, hair, and cartilage. Other proteins, usually called **globular proteins** because of their roughly spherical shape, are the “worker” molecules of the body. These proteins transport and store oxygen and nutrients, act as catalysts for the thousands of reactions that make life possible, fight invasion by foreign objects, participate in the body’s many regulatory systems, and transport electrons in the complex process of metabolizing nutrients.

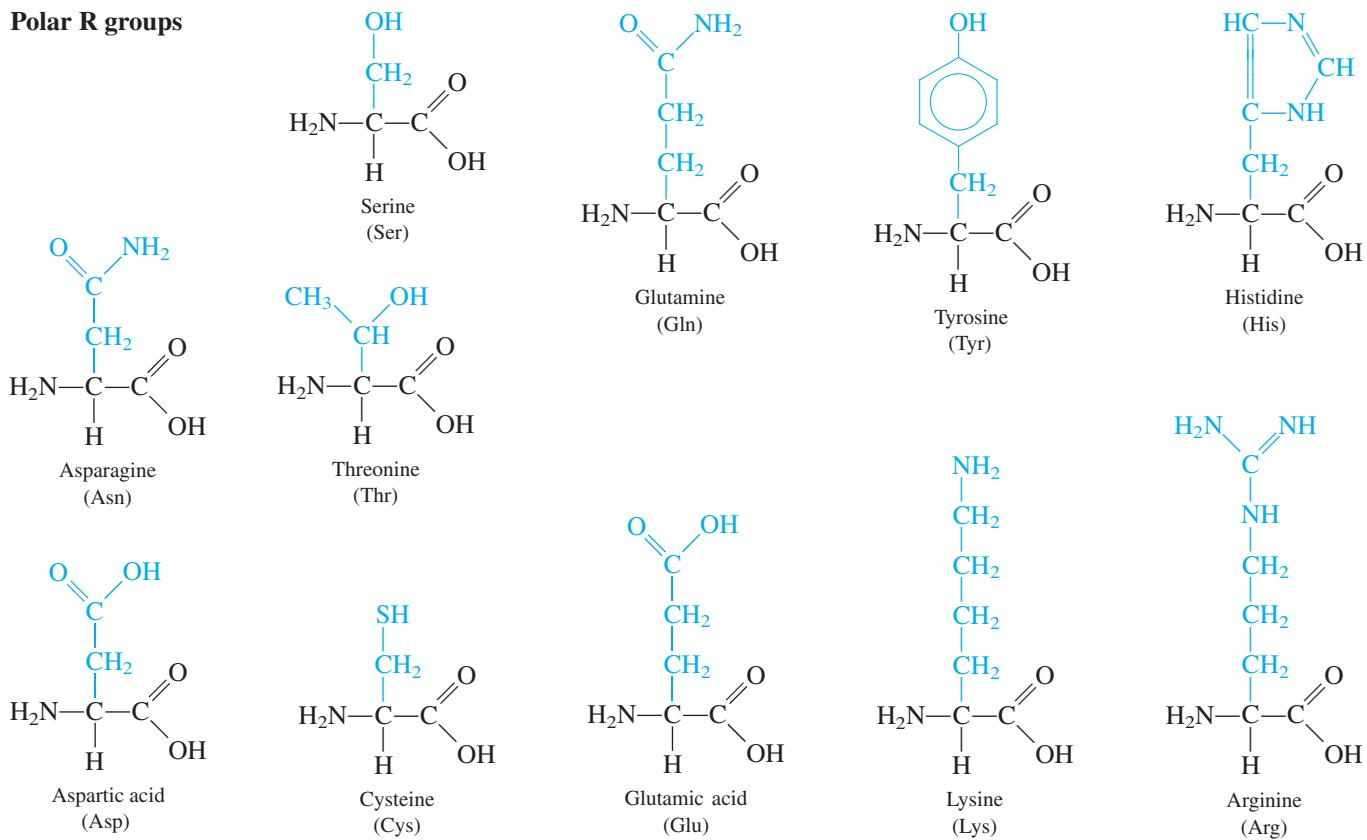
The building blocks of all proteins are the  **$\alpha$ -amino acids**, where R may represent H, CH<sub>3</sub>, or a more complex substituent. These molecules are called  $\alpha$ -amino acids because the amino group ( $-\text{NH}_2$ ) is always attached to the  $\alpha$ -carbon, the one next to the carboxyl group ( $-\text{CO}_2\text{H}$ ). The 20 amino acids most commonly found in proteins are shown in Fig. 22.18.



**Nonpolar R groups**



**Polar R groups**



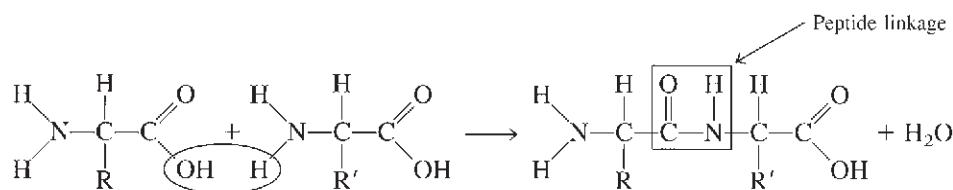
**FIGURE 22.18**

The 20  $\alpha$ -amino acids found in most proteins. The R group is shown in color.

At the pH in biological fluids, the amino acids shown in Fig. 22.18 exist in a different form, with the proton of the  $\text{—COOH}$  group transferred to the  $\text{—NH}_2$  group. For example, glycine would be in the form  $\text{H}_3^+ \text{NCH}_2\text{COO}^-$ .

Note from Fig. 22.18 that the amino acids are grouped into polar and nonpolar classes, determined by the R groups, or **side chains**. Nonpolar side chains contain mostly carbon and hydrogen atoms, whereas polar side chains contain large numbers of nitrogen and oxygen atoms. This difference is important, because polar side chains are *hydrophilic* (water-loving), but nonpolar side chains are *hydrophobic* (water-fearing), and this characteristic greatly affects the three-dimensional structure of the resulting protein.

The protein polymer is built by condensation reactions between amino acids. For example,



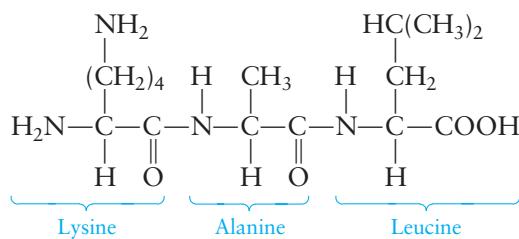
The product shown above is called a **dipeptide**. This name is used because the structure



is called a **peptide linkage** by biochemists. (The same grouping is called an amide by organic chemists.) Additional condensation reactions lengthen the chain to produce a **polypeptide**, eventually yielding a protein.

You can imagine that with 20 amino acids, which can be assembled in any order, there is essentially an infinite variety possible in the construction of proteins. This flexibility allows an organism to tailor proteins for the many types of functions that must be carried out.

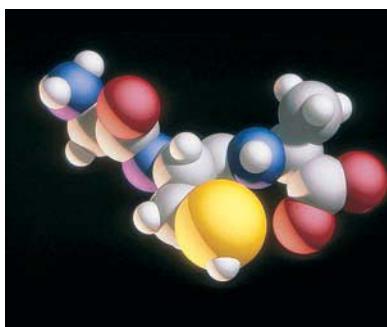
The order, or sequence, of amino acids in the protein chain is called the **primary structure**, conveniently indicated by using three-letter codes for the amino acids (see Fig. 22.18), where it is understood that the terminal carboxyl group is on the right and the terminal amino group is on the left. For example, one possible sequence for a tripeptide containing the amino acids lysine, alanine, and leucine is



which is represented in the shorthand notation by

lys-ala-leu

Note from Sample Exercise 22.7 that there are six sequences possible for a polypeptide with three given amino acids. There are three possibilities for the first amino acid (any one of the three given amino acids), there are two possibilities for the second amino acid (one has already been accounted for), but there is only one possibility left for the third amino acid. Thus the number of sequences is  $3 \times 2 \times 1 = 6$ . The product  $3 \times 2 \times 1$  is often written  $3!$  (and is called 3 factorial). Similar reasoning shows that for a polypeptide with four amino acids, there are  $4!$ , or  $4 \times 3 \times 2 \times 1 = 24$ , possible sequences.



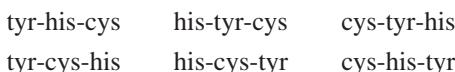
A tripeptide containing glycine, cysteine, and alanine.

**Sample Exercise 22.7****Tripeptide Sequences**

Write the sequences of all possible tripeptides composed of the amino acids tyrosine, histidine, and cysteine.

**Solution**

There are six possible sequences:



*See Exercise 22.89.*

**Sample Exercise 22.8****Polypeptide Sequences**

(a) cys-tyr-[ile]-gln-asn-cys-pro-[leu]-gly

(b) cys-tyr-[phe]-gln-asn-cys-pro-[arg]-gly

**FIGURE 22.19**

The amino acid sequences in (a) oxytocin and (b) vasopressin. The differing amino acids are boxed.

What number of possible sequences exists for a polypeptide composed of 20 different amino acids?

**Solution**

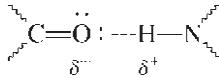
The answer is  $20!$ , or

$$20 \times 19 \times 18 \times 17 \times 16 \times \dots \times 5 \times 4 \times 3 \times 2 \times 1 = 2.43 \times 10^{18}$$

*See Exercise 22.90.*

A striking example of the importance of the primary structure of polypeptides can be seen in the differences between *oxytocin* and *vasopressin*. Both of these molecules are nine-unit polypeptides that differ by only two amino acids (Fig. 22.19), yet they perform completely different functions in the human body. Oxytocin is a hormone that triggers contraction of the uterus and milk secretion. Vasopressin raises blood pressure levels and regulates kidney function.

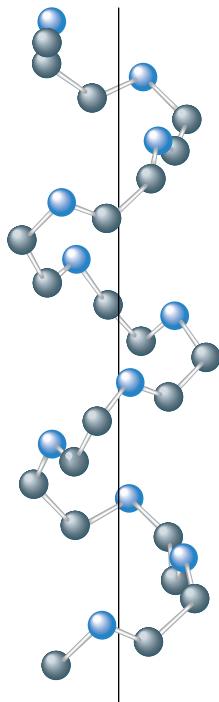
A second level of structure in proteins, beyond the sequence of amino acids, is the arrangement of the chain of the long molecule. The **secondary structure** is determined to a large extent by hydrogen bonding between lone pairs on an oxygen atom in the carbonyl group of an amino acid and a hydrogen atom attached to a nitrogen of another amino acid:



Such interactions can occur *within* the chain coils to form a spiral structure called an **α-helix**, as shown in Fig. 22.20 and Fig. 22.21. This type of secondary structure gives the protein elasticity (springiness) and is found in the fibrous proteins in wool, hair, and tendons. Hydrogen bonding can also occur *between different* protein chains, joining them together in an arrangement called a **pleated sheet**, as shown in Fig. 22.22. Silk contains this arrangement of proteins, making its fibers flexible yet very strong and resistant to stretching. The pleated sheet is also found in muscle fibers. The hydrogen bonds in the **α-helical** protein are called *intrachain* (within a given protein chain), and those in the pleated sheet are said to be *interchain* (between protein chains).

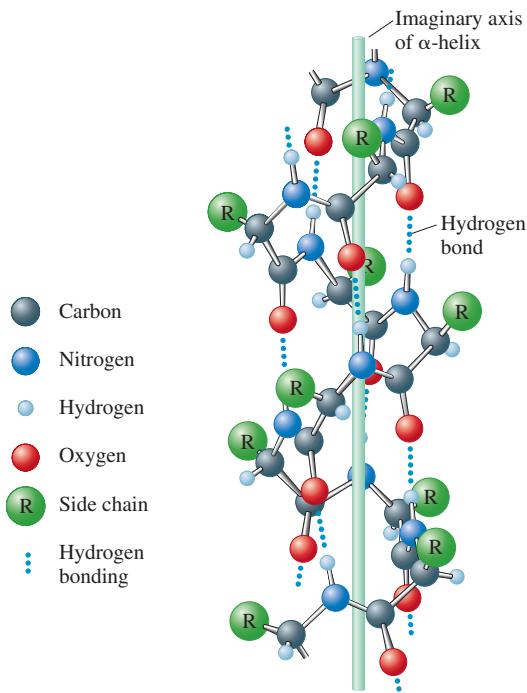
As you might imagine, a molecule as large as a protein has a great deal of flexibility and can assume a variety of overall shapes. The specific shape that a protein assumes depends on its function. For long, thin structures, such as hair, wool and silk fibers, and tendons, an elongated shape is required. This may involve an **α-helical** secondary structure, as found in the protein **α-keratin** in hair and wool or in the collagen found in tendons [Fig. 22.23(a)], or it may involve a pleated-sheet secondary structure, as found in

Carbon  
Nitrogen



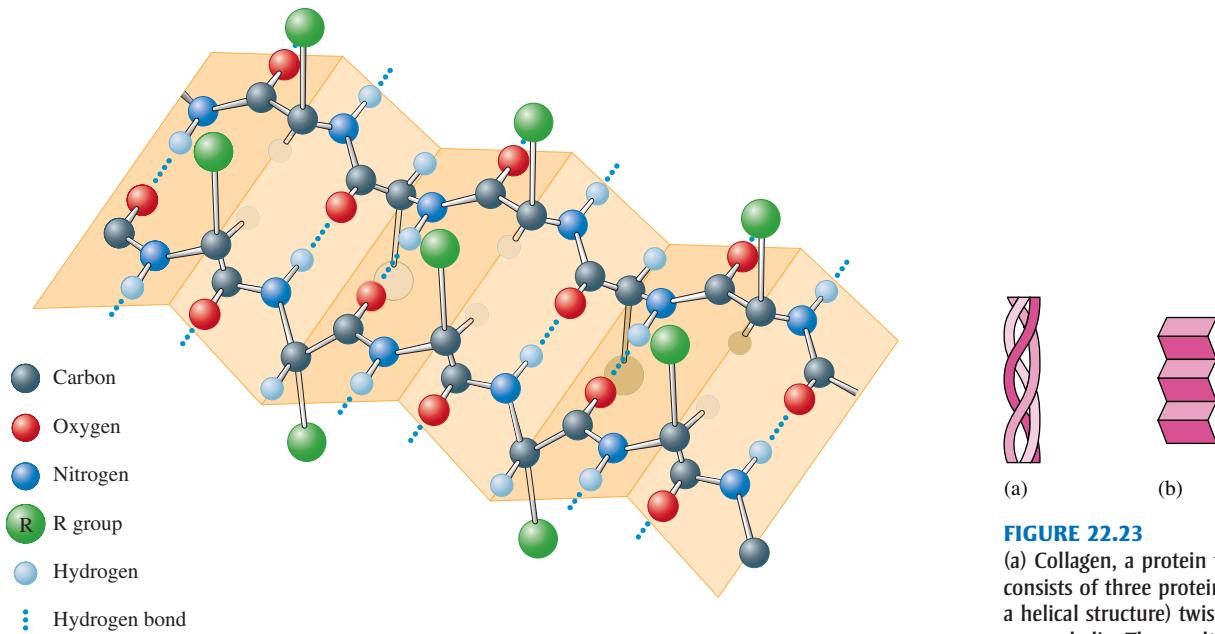
**FIGURE 22.20**

Hydrogen bonding within a protein chain causes it to form a stable helical structure called the **α-helix**. Only the main atoms in the helical backbone are shown here. The hydrogen bonds are not shown.

**FIGURE 22.21**

Ball-and-stick model of a portion of a protein chain in the  $\alpha$ -helical arrangement, showing the hydrogen-bonding interactions.

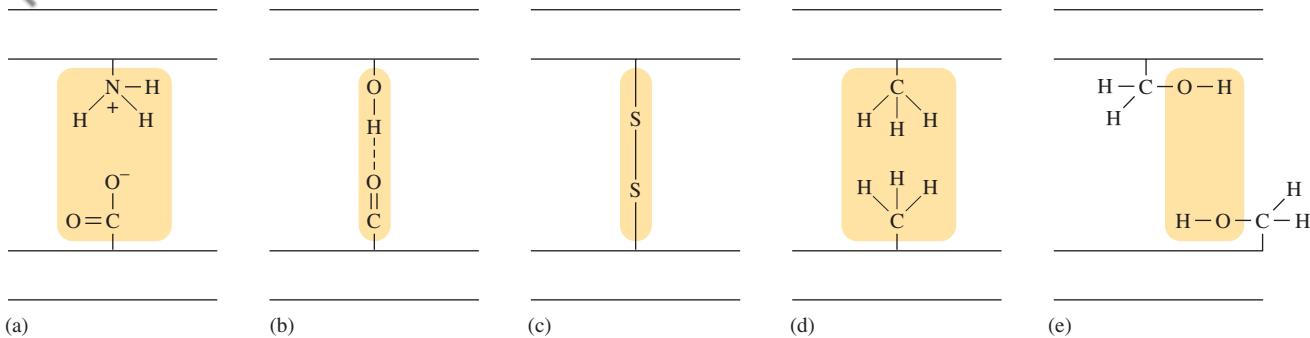
silk [Fig. 22.23(b)]. Many of the proteins in the body having nonstructural functions are globular, such as myoglobin (see Fig. 21.31). Note that the secondary structure of myoglobin is basically  $\alpha$ -helical. However, in the areas where the chain bends to give the protein its compact globular structure, the  $\alpha$ -helix breaks down to give a secondary configuration known as the **random-coil arrangement**.

**FIGURE 22.22**

When hydrogen bonding occurs between protein chains rather than within them, a stable structure (the pleated sheet) results. This structure contains many protein chains and is found in natural fibers, such as silk, and in muscles.

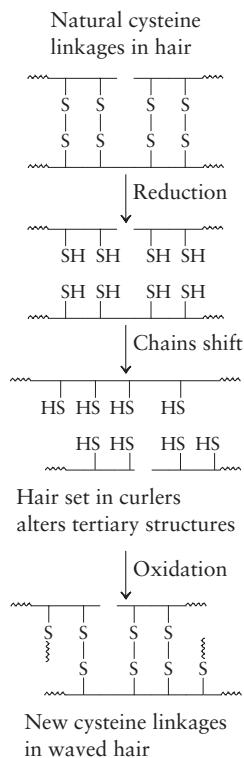
**FIGURE 22.23**

(a) Collagen, a protein found in tendons, consists of three protein chains (each with a helical structure) twisted together to form a superhelix. The result is a long, relatively narrow protein. (b) The pleated-sheet arrangement of many proteins bound together to form the elongated protein found in silk fibers.



## FIGURE 22.24

Summary of the various types of interactions that stabilize the tertiary structure of a protein: (a) ionic, (b) hydrogen bonding, (c) covalent, (d) London dispersion, and (e) dipole-dipole.

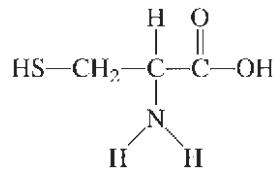


## **FIGURE 22.25**

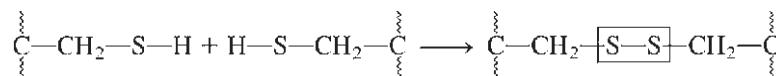
The permanent waving of hair.

The overall shape of the protein, long and narrow or globular, is called its **tertiary structure** and is maintained by several different types of interactions: hydrogen bonding, dipole–dipole interactions, ionic bonds, covalent bonds, and London dispersion forces between nonpolar groups. These bonds, which represent all the bonding types discussed in this text, are summarized in Fig. 22.24.

## The amino acid *cysteine*



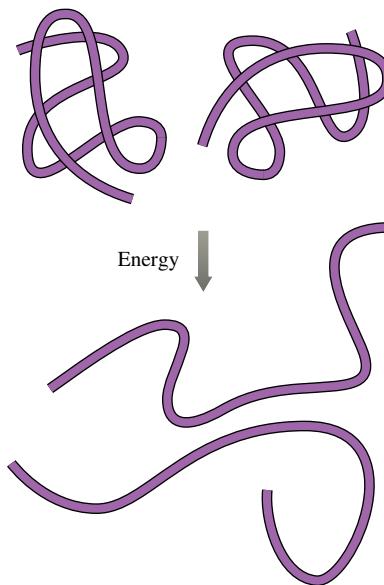
plays a special role in stabilizing the tertiary structure of many proteins because the —SH groups on two cysteines can react in the presence of an oxidizing agent to form a S—S bond called a **disulfide linkage**:



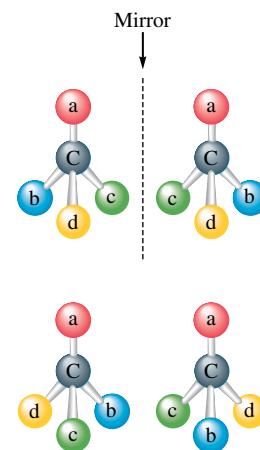
A practical application of the chemistry of disulfide bonds is permanent waving of hair, as summarized in Fig. 22.25. The S—S linkages in the protein of hair are broken by treatment with a reducing agent. The hair is then set in curlers to change the tertiary protein structure to the desired shape. Then treatment with an oxidizing agent causes new S—S bonds to form, which allow the hair protein to retain the new structure.

The three-dimensional structure of a protein is crucial to its function. The process of breaking down this structure is called **denaturation** (Fig. 22.26). For example, the denaturation of egg proteins occurs when an egg is cooked. Any source of energy can cause denaturation of proteins and is thus potentially dangerous to living organisms. For example, ultraviolet and X-ray radiation or nuclear radioactivity can disrupt protein structure, which may lead to cancer or genetic damage. Protein damage is also caused by chemicals like benzene, trichloroethane, and 1,2-dibromoethane. The metals lead and mercury, which have a very high affinity for sulfur, cause protein denaturation by disrupting disulfide bonds between protein chains.

The tremendous flexibility in the various levels of protein structure allows the tailoring of proteins for a wide range of specific functions. Proteins are the “workhorse” molecules of living organisms.



**FIGURE 22.26**  
A schematic representation of the thermal denaturation of a protein.

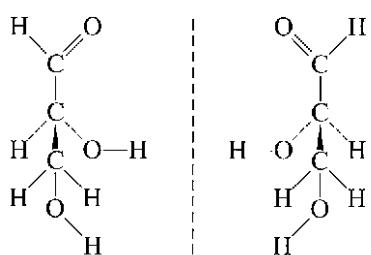
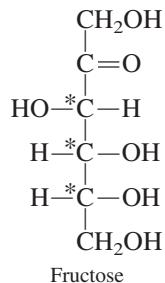


**FIGURE 22.27**  
When a tetrahedral carbon atom has four different substituents, there is no way that its mirror image can be superimposed. The lower two forms show other possible orientations of the molecule. Compare these with the mirror image and note that they cannot be superimposed.

## Carbohydrates

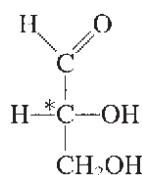
**Carbohydrates** form another class of biologically important molecules. They serve as a food source for most organisms and as a structural material for plants. Because many carbohydrates have the empirical formula  $\text{CH}_2\text{O}$ , it was originally believed that these substances were hydrates of carbon, thus accounting for the name.

Most important carbohydrates, such as starch and cellulose, are polymers composed of monomers called **monosaccharides**, or **simple sugars**. The monosaccharides are polyhydroxy ketones and aldehydes. The most important contain five carbon atoms (**pentoses**) or six carbon atoms (**hexoses**). One important hexose is *fructose*, a sugar found in honey and fruit. Its structure is



**FIGURE 22.28**  
The mirror image optical isomers of glyceraldehyde. Note that these mirror images cannot be superimposed.

where the asterisks indicate chiral carbon atoms. In Section 21.4 we saw that molecules with nonsuperimposable mirror images exhibit optical isomerism. A carbon atom with four *different* groups bonded to it in a tetrahedral arrangement *always* has a nonsuperimposable mirror image (see Fig. 22.27), which gives rise to a pair of optical isomers. For example, the simplest sugar, glyceraldehyde,



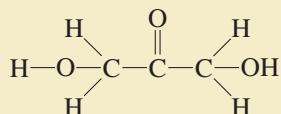
which has one chiral carbon, has two optical isomers, as shown in Fig. 22.28.



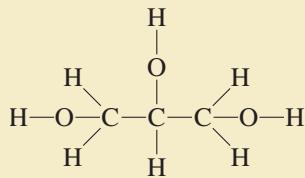
## CHEMICAL IMPACT

### Tanning in the Shade

**A**mong today's best-selling cosmetics are self-tanning lotions. Many light-skinned people want to look like they have just spent a vacation in the Caribbean, but they recognize the dangers of too much sun—it causes premature aging and may lead to skin cancer. Chemistry has come to the rescue in the form of lotions that produce an authentic-looking tan. All of these lotions have the same active ingredient: dihydroxyacetone (DHA). DHA, which has the structure



is a nontoxic, simple sugar that occurs as an intermediate in carbohydrate metabolism in higher-order plants and animals. The DHA used in self-tanners is prepared by bacterial fermentation of glycerine,



The tanning effects of DHA were discovered by accident in the 1950s at Children's Hospital at the University of Cincinnati, where DHA was being used to treat children with glycogen storage disease. When the DHA was accidentally spilled on the skin, it produced brown spots.

The mechanism of the browning process involves the Maillard reaction, which was discovered by Louis-Camille Maillard in 1912. In this process amino acids react with sugars to create brown or golden brown products. The same reaction is responsible for much of the browning that occurs during the manufacture and storage of foods. It is also the reason that beer is golden brown.

The browning of skin occurs in the stratum corneum—the outermost, dead layer—where the DHA reacts with free amino ( $-\text{NH}_2$ ) groups of the proteins found there.

DHA is present in most tanning lotions at concentrations between 2% and 5%, although some products designed to give a deeper tan are more concentrated. Because the lotions themselves turn brown above pH 7, the tanning lotions are buffered at pH 5.

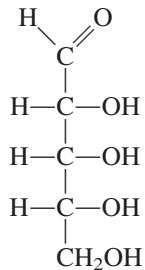
Thanks to these new products, tanning is now both safe and easy.

In fructose each of the three chiral carbon atoms satisfies the requirement of being surrounded by four different groups. This leads to a total of  $2^3$ , or 8, isomers that differ in their ability to rotate polarized light. The particular isomer whose structure is shown in Table 22.8 is called D-fructose. Generally, monosaccharides have one isomer that is more common in nature than the others. The most important pentoses and hexoses are shown in Table 22.8.

#### Sample Exercise 22.9

#### Chiral Carbons in Carbohydrates

Determine the number of chiral carbon atoms in the following pentose:



#### Solution

We must look for carbon atoms that have four different substituents. The top carbon has only three substituents and thus cannot be chiral. The three carbon atoms shown in blue



Self-tanning products and a close-up of a label showing the contents.

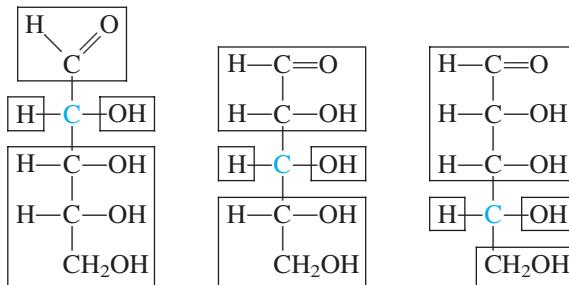


General Name of Sugar	Number of Carbon Atoms
Triose	3
Tetrose	4
Pentose	5
Hexose	6
Heptose	7
Octose	8
Nonose	9

TABLE 22.8 Some Important Monosaccharides

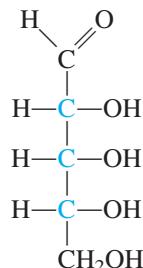
Pentoses			
D-Ribose	D-Arabinose	D-Ribulose	
$\begin{array}{c} \text{CHO} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CHO} \\   \\ \text{HO}-\text{C}-\text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{C}=\text{O} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$	
Hexoses			
D-Glucose	D-Mannose	D-Galactose	D-Fructose
$\begin{array}{c} \text{CHO} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{HO}-\text{C}-\text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CHO} \\   \\ \text{HO}-\text{C}-\text{H} \\   \\ \text{HO}-\text{C}-\text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{C}=\text{O} \\   \\ \text{HO}-\text{C}-\text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{C}=\text{O} \\   \\ \text{HO}-\text{C}-\text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$

each have four different groups attached to them:



Since the fifth carbon atom has only three types of substituents (it has two hydrogen atoms), it is not chiral.

Thus the three chiral carbon atoms in this pentose are those shown in blue:



Note that D-ribose and D-arabinose, shown in Table 22.8, are two of the eight isomers of this pentose.

*See Exercises 22.108 and 22.113 through 22.116.*

Although we have so far represented the monosaccharides as straight-chain molecules, they usually cyclize, or form a ring structure, in aqueous solution. Figure 22.29 shows this reaction for fructose. Note that a new bond is formed between the oxygen of the terminal hydroxyl group and the carbon of the ketone group. In the cyclic form fructose is a five-membered ring containing a C—O—C bond. The same type of reaction can occur between a hydroxyl group and an aldehyde group, as shown for D-glucose in Fig. 22.30. In this case a six-membered ring is formed.

More complex carbohydrates are formed by combining monosaccharides. For example, **sucrose**, common table sugar, is a **disaccharide** formed from glucose and fructose by elimination of water to form a C—O—C bond between the rings, which is called a **glycoside linkage** (Fig. 22.31). When sucrose is consumed in food, the above reaction is reversed. An enzyme in saliva catalyzes the breakdown of this disaccharide.

Large polymers consisting of many monosaccharide units, called polysaccharides, can form when each ring forms two glycoside linkages, as shown in Fig. 22.32. Three of the most important of these polymers are starch, cellulose, and glycogen. All these substances are polymers of glucose, differing from each other in the nature of the glycoside linkage, the amount of branching, and molecular weight (molar mass).

**Starch**, a polymer of  $\alpha$ -D-glucose, consists of two parts: *amylose*, a straight-chain polymer of  $\alpha$ -glucose [see Fig. 22.32(a)], and *amylopectin*, a highly branched polymer of  $\alpha$ -glucose with a molecular weight that is 10 to 20 times that of amylose. Branching occurs when a third glycoside linkage attaches a branch to the main polymer chain.

Starch, the carbohydrate reservoir in plants, is the form in which glucose is stored by the plant for later use as cellular fuel. Glucose is stored in this high-molecular-weight form because it results in less stress on the plant's internal structure by osmotic pressure. Recall

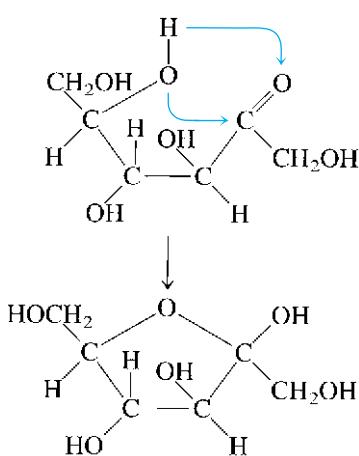
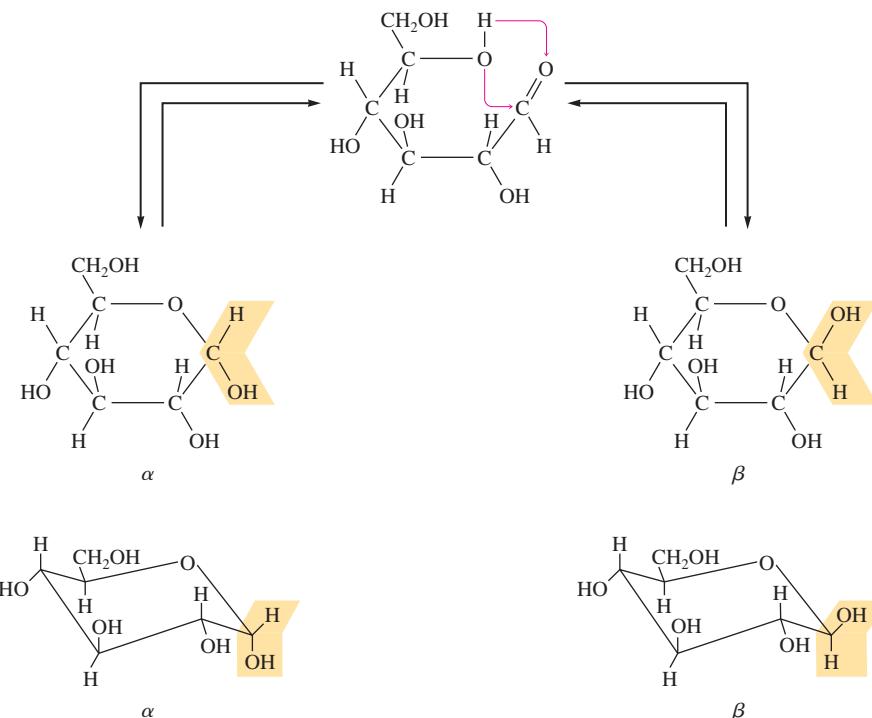


FIGURE 22.29

The cyclization of D-fructose.

**FIGURE 22.30**

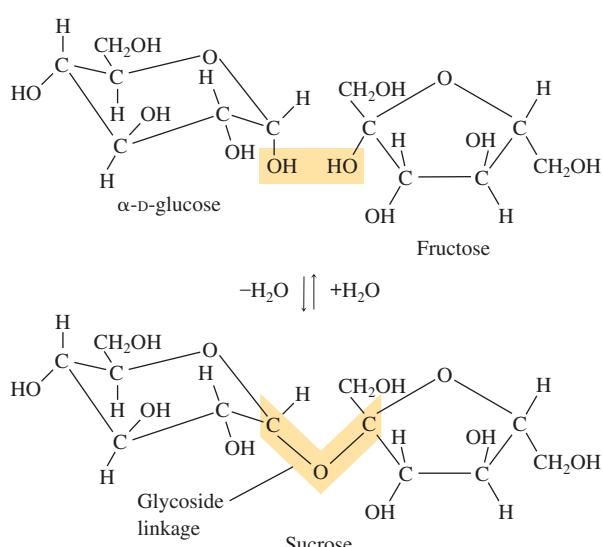
The cyclization of glucose. Two different rings are possible; they differ in the orientation of the hydroxy group and hydrogen on one carbon, as indicated. The two forms are designated  $\alpha$  and  $\beta$  and are shown here in two representations.



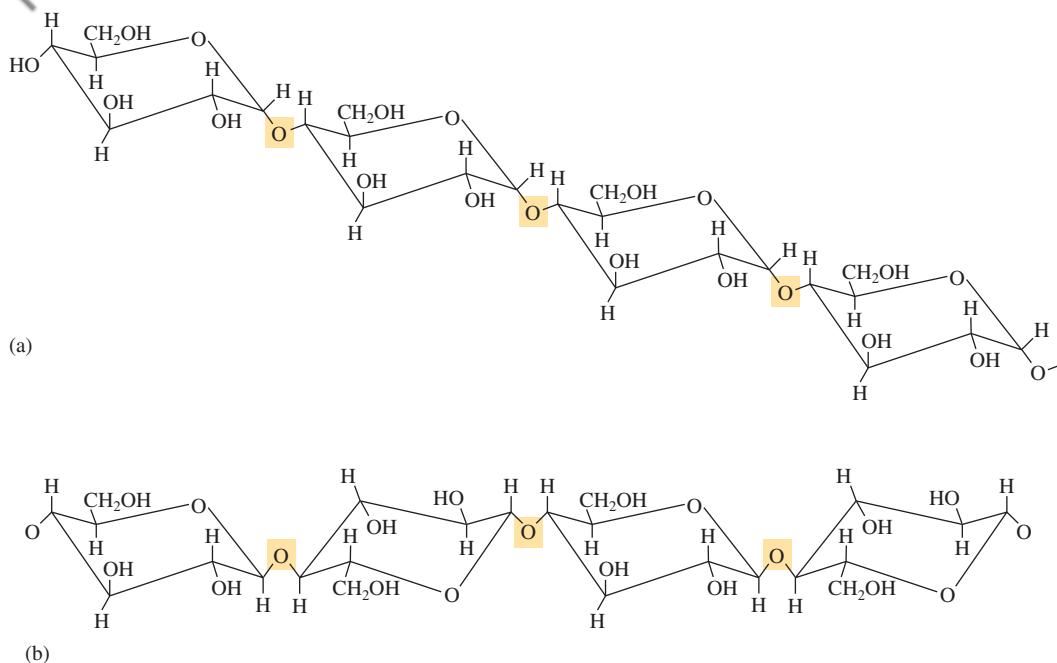
Bowl of sugar cubes.

from Section 11.6 that it is the concentration of solute molecules (or ions) that determines the osmotic pressure. Combining the individual glucose molecules into one large chain keeps the concentration of solute molecules relatively low, minimizing the osmotic pressure.

**Cellulose**, the major structural component of woody plants and natural fibers (such as cotton), is a polymer of  $\beta$ -D-glucose and has the structure shown in Fig. 22.32(b). Note that the  $\beta$ -glycoside linkages in cellulose give the glucose rings a different relative orientation than is found in starch. Although this difference may seem minor, it has very important consequences. The human digestive system contains  $\alpha$ -glycosidases, enzymes that can catalyze breakage of the  $\alpha$ -glycoside bonds in starch. These enzymes are not effective on the  $\beta$ -glycoside bonds of cellulose, presumably because the different structure

**FIGURE 22.31**

Sucrose is a disaccharide formed from  $\alpha$ -D-glucose and fructose.

**1036 Chapter Twenty-Two Organic and Biological Molecules**
**FIGURE 22.32**

(a) The polymer amylose is a major component of starch and is made up of  $\alpha$ -D-glucose monomers. (b) The polymer cellulose, which consists of  $\beta$ -D-glucose monomers.

results in a poor fit between the enzyme's active site and the carbohydrate. The enzymes necessary to cleave  $\beta$ -glycoside linkages, the  $\beta$ -glycosidases, are found in bacteria that exist in the digestive tracts of termites, cows, deer, and many other animals. Thus, unlike humans, these animals can derive nutrition from cellulose.

**Glycogen**, the main carbohydrate reservoir in animals, has a structure similar to that of amylopectin but with more branching. It is this branching that is thought to facilitate the rapid breakdown of glycogen into glucose when energy is required.

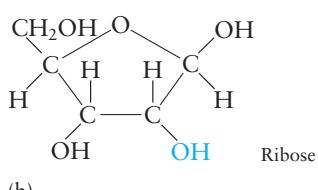
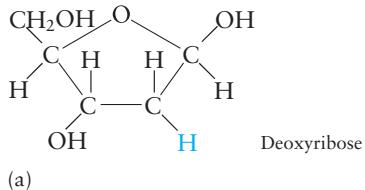
### Nucleic Acids

Life is possible only because each cell, when it divides, can transmit the vital information about how it works to the next generation. It has been known for a long time that this process involves the chromosomes in the nucleus of the cell. Only since 1953, however, have scientists understood the molecular basis of this intriguing cellular "talent."

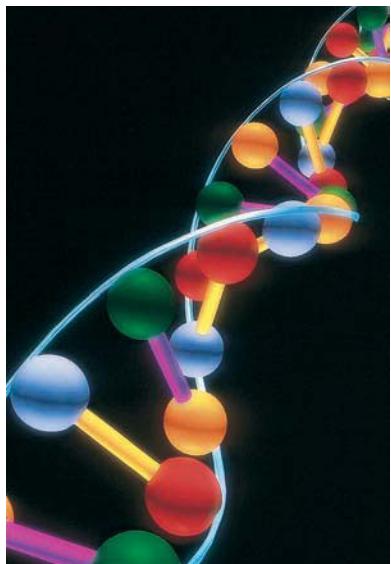
The substance that stores and transmits the genetic information is a polymer called **deoxyribonucleic acid (DNA)**, a huge molecule with a molecular weight as high as several billion grams per mole. Together with other similar nucleic acids called the **ribonucleic acids (RNA)**, DNA is also responsible for the synthesis of the various proteins needed by the cell to carry out its life functions. The RNA molecules, which are found in the cytoplasm outside the nucleus, are much smaller than DNA polymers, with molecular weights of only 20,000 to 40,000 grams per mole.

The monomers of the nucleic acids, called **nucleotides**, are composed of three distinct parts:

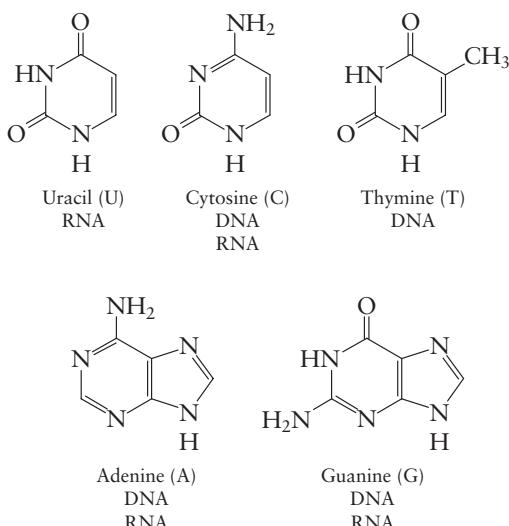
1. A five-carbon sugar, deoxyribose in DNA and ribose in RNA (Fig. 22.33)
2. A nitrogen-containing organic base of the type shown in Fig. 22.34
3. A phosphoric acid molecule ( $H_3PO_4$ )

**FIGURE 22.33**

The structure of the pentoses (a) deoxyribose and (b) ribose. Deoxyribose is the sugar molecule present in DNA; ribose is found in RNA.



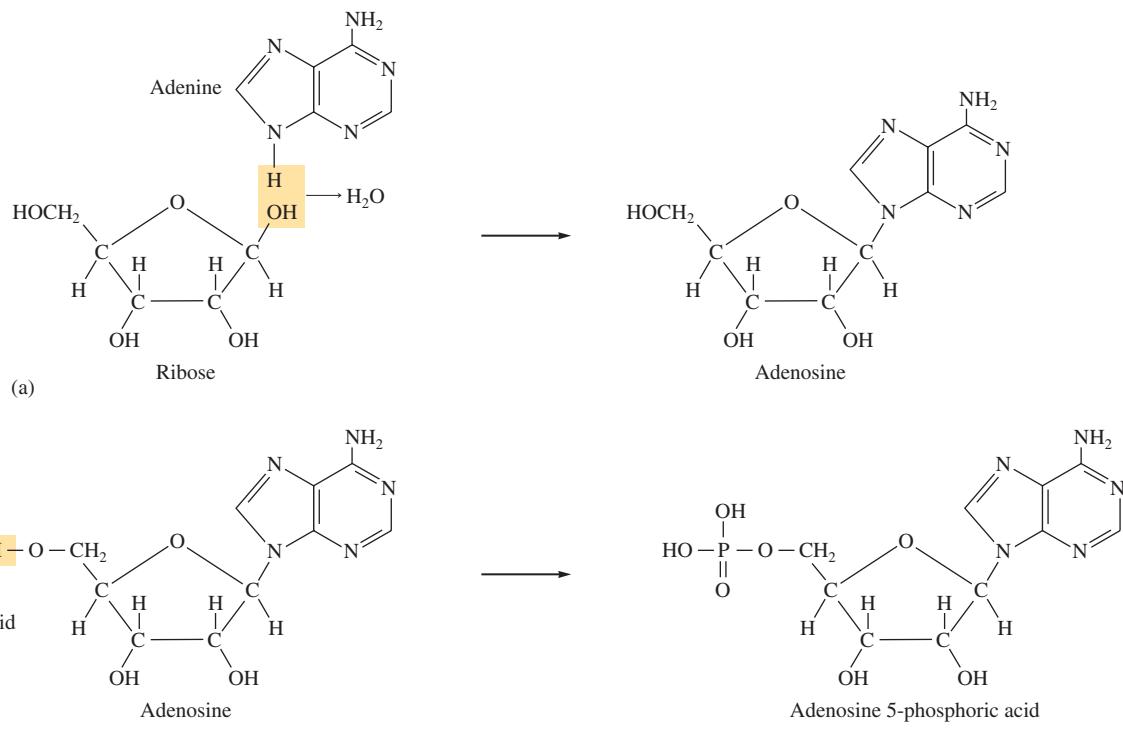
A computer image of the base pairs of DNA. The blue lines represent the sugar–phosphate backbone and the colored bars represent the hydrogen bonding between the base pairs.



**FIGURE 22.34**

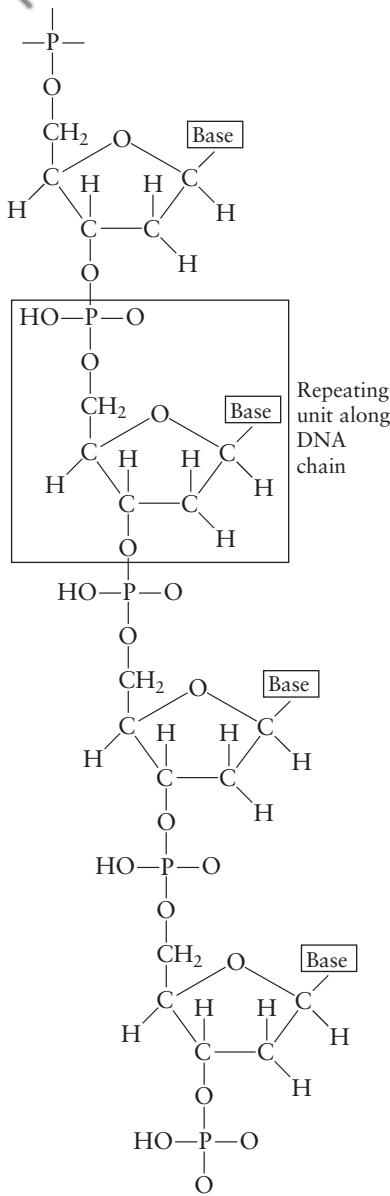
The organic bases found in DNA and RNA.

The base and the sugar combine as shown in Fig. 22.35(a) to form a unit that in turn reacts with phosphoric acid to create the nucleotide, which is an ester [see Fig. 22.35(b)]. The nucleotides become connected through condensation reactions that eliminate water to give a polymer of the type represented in Fig. 22.36; such a polymer can contain a billion units.



**FIGURE 22.35**

(a) Adenosine is formed by the reaction of adenine with ribose. (b) The reaction of phosphoric acid with adenosine to form the ester adenosine 5-phosphoric acid, a nucleotide. (At biological pH, the phosphoric acid would not be fully protonated as is shown here.)

**FIGURE 22.36**

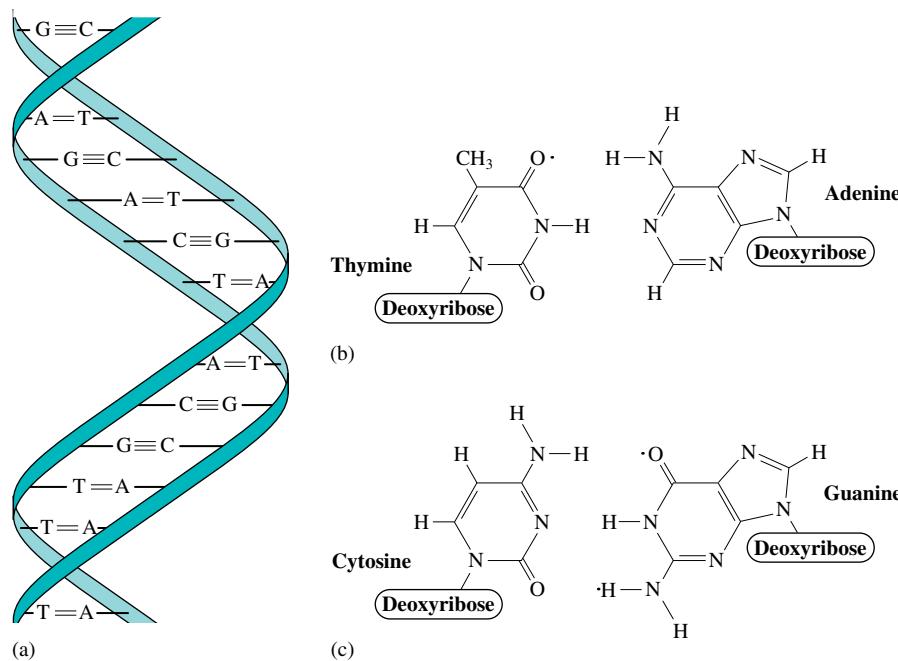
A portion of a typical nucleic acid chain. Note that the backbone consists of sugar-phosphate esters.

The key to DNA's functioning is its *double-helical structure with complementary bases on the two strands*. The bases form hydrogen bonds to each other, as shown in Fig. 22.37. Note that the structures of cytosine and guanine make them perfect partners for hydrogen bonding, and they are *always* found as pairs on the two strands of DNA. Thymine and adenine form similar hydrogen-bonding pairs.

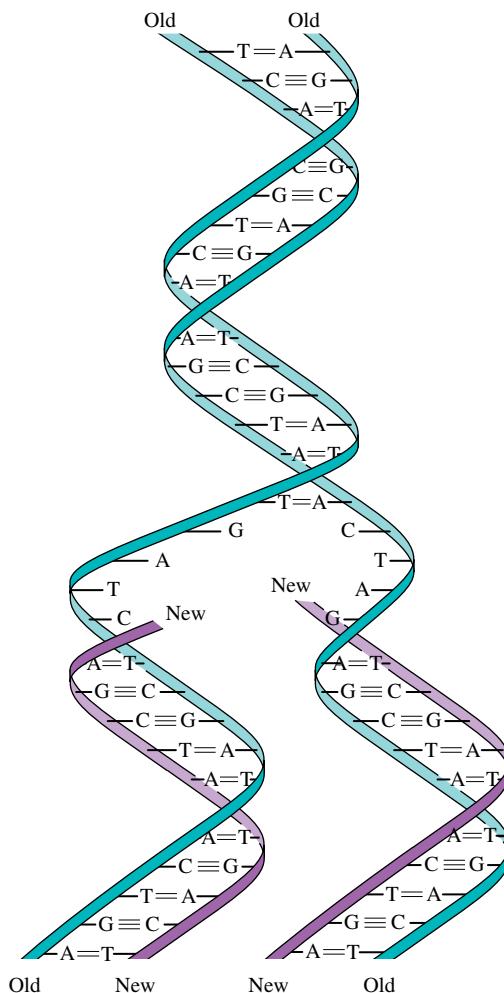
There is much evidence to suggest that the two strands of DNA unwind during cell division and that new complementary strands are constructed on the unraveled strands (Fig. 22.38). Because the bases on the strands always pair in the same way—cytosine with guanine and thymine with adenine—each unraveled strand serves as a template for attaching the complementary bases (along with the rest of the nucleotide). This process results in two double-helix DNA structures that are identical to the original one. Each new double strand contains one strand from the original DNA double helix and one newly synthesized strand. This replication of DNA allows for the transmission of genetic information as the cells divide.

The other major function of DNA is **protein synthesis**. A given segment of the DNA, called a **gene**, contains the code for a specific protein. These codes transmit the primary structure of the protein (the sequence of amino acids) to the construction “machinery” of the cell. There is a specific code for each amino acid in the protein, which ensures that the correct amino acid will be inserted as the protein chain grows. A code consists of a set of three bases called a **codon**.

DNA stores the genetic information, while RNA molecules are responsible for transmitting this information to the ribosomes, where protein synthesis actually occurs. This complex process involves, first, the construction of a special RNA molecule called **messenger RNA (mRNA)**. The mRNA is built in the cell nucleus on the appropriate section of DNA (the gene); the double helix is “unzipped,” and the complementarity of the bases

**FIGURE 22.37**

(a) The DNA double helix contains two sugar-phosphate backbones, with the bases from the two strands hydrogen-bonded to each other. The complementarity of the (b) thymine-adenine and (c) cytosine-guanine pairs.

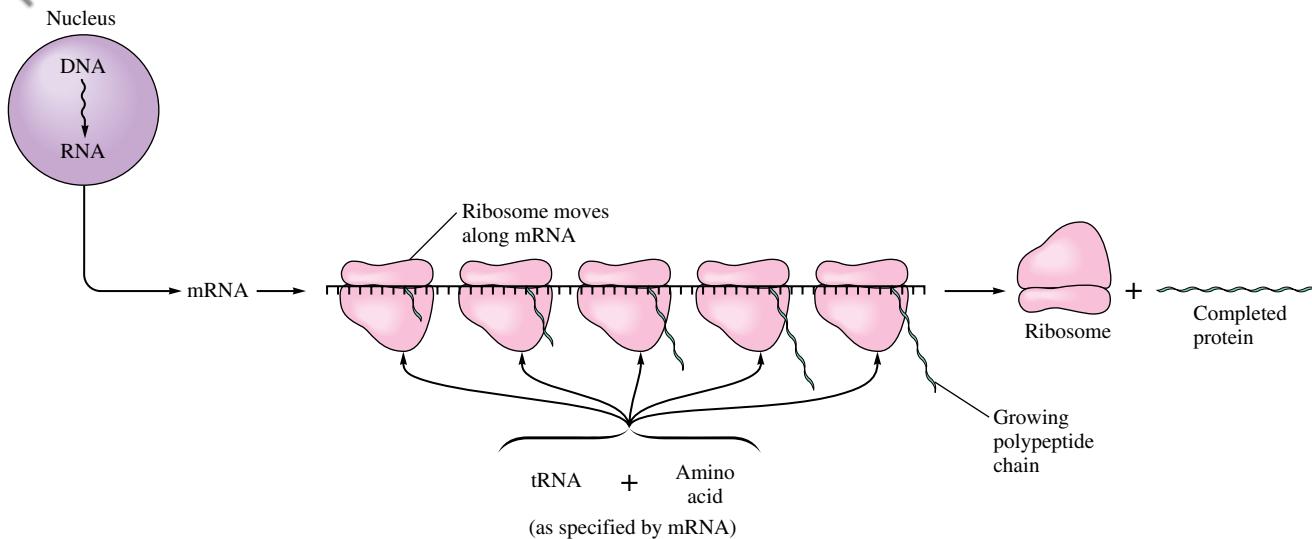
**FIGURE 22.38**

During cell division the original DNA double helix unwinds and new complementary strands are constructed on each original strand.

is used in a process similar to that used in DNA replication. The mRNA then migrates into the cytoplasm of the cell where, with the assistance of the ribosomes, the protein is synthesized.

Small RNA fragments, called **transfer RNA (tRNA)**, are tailored to find specific amino acids and then to attach them to the growing protein chain as dictated by the codons in the mRNA. Transfer RNA has a lower molecular weight than messenger RNA. It consists of a chain of 75 to 80 nucleotides, including the bases adenine, cytosine, guanine, and uracil, among others. The chain folds back onto itself in various places as the complementary bases along the chain form hydrogen bonds. The tRNA decodes the genetic message from the mRNA, using a complementary triplet of bases called an **anticodon**. The nature of the anticodon governs which amino acid will be brought to the protein under construction.

The protein is built in several steps. First, a tRNA molecule brings an amino acid to the mRNA [the anticodon of the tRNA must complement the codon of the mRNA (see Fig. 22.39)]. Once this amino acid is in place, another tRNA moves to the second codon site of the mRNA with its specific amino acid. The two amino acids link via a peptide bond, and the tRNA on the first codon breaks away. The process is repeated down the chain, always matching the tRNA anticodon with the mRNA codon.

**FIGURE 22.39**

The mRNA molecule, constructed from a specific gene on the DNA, is used as the pattern to construct a given protein with the assistance of ribosomes. The tRNA molecules attach to specific amino acids and put them in place as called for by the codons on the mRNA.

## Key Terms

biomolecule  
organic chemistry

### Section 22.1

hydrocarbons  
saturated  
unsaturated  
alkanes  
normal (straight-chain or unbranched)  
hydrocarbons  
structural isomerism  
combustion reaction  
substitution reaction  
dehydrogenation reaction  
cyclic alkanes

### Section 22.2

alkenes  
*cis-trans* isomerism  
alkynes  
addition reaction  
hydrogenation reaction  
halogenation  
polymerization

### Section 22.3

aromatic hydrocarbons  
phenyl group

### Section 22.4

hydrocarbon derivatives  
functional group  
alcohols  
phenol  
carbonyl group

## For Review

### Hydrocarbons

- Compounds composed of mostly carbon and hydrogen atoms that typically contain chains or rings of carbon atoms
- Alkanes
  - Contain compounds with only C—C single bonds
  - Can be represented by the formula  $C_nH_{2n+2}$
  - Are said to be saturated because each carbon present is bonded to the maximum number of atoms (4)
  - The carbon atoms are described as being  $sp^3$  hybridized
  - Their structural isomerism involves the formation of branched chains
  - React with  $O_2$  to form  $CO_2$  and  $H_2O$  (called a combustion reaction)
  - Undergo substitution reactions
- Alkenes
  - Contain one or more C=C double bonds
  - Simplest alkene is  $C_2H_4$  (ethylene) which is described as containing  $sp^2$  hybridized carbon atoms
  - Restricted rotation about the C=C bonds in alkenes can lead to *cis-trans* isomerism
  - Undergo addition reactions
- Alkynes
  - Contain one or more C≡C triple bonds
  - Simplest example is  $C_2H_2$  (acetylene), described as containing  $sp$ -hybridized carbon atoms
  - Undergo addition reactions
- Aromatic hydrocarbons
  - Contain rings of carbon atoms with delocalized  $\pi$  electrons
  - Undergo substitution reactions rather than addition reactions

ketones  
aldehydes  
carboxylic acids  
carboxyl group  
ester  
amines

### Section 22.5

polymers  
thermoset polymer  
thermoplastic polymer  
crosslinking  
vulcanization  
addition polymerization  
free radical  
condensation polymerization  
copolymer  
homopolymer  
dimer  
polyester  
isotactic chain  
syndiotactic chain  
atactic chain  
polystyrene  
polyvinyl chloride (PVC)

### Section 22.6

proteins  
fibrous proteins  
globular proteins  
 $\alpha$ -amino acids  
side chains  
dipeptide  
peptide linkage  
polypeptide  
primary structure  
secondary structure  
 $\alpha$ -helix  
pleated sheet  
random-coil arrangement  
tertiary structure  
disulfide linkage  
denaturation  
carbohydrates  
monosaccharides (simple sugars)  
pentoses  
hexoses  
sucrose  
disaccharide  
glycoside linkage  
starch  
cellulose  
glycogen  
deoxyribonucleic acid (DNA)  
ribonucleic acid (RNA)  
nucleotides  
protein synthesis  
gene  
codon

### Hydrocarbon derivatives

- Contain one or more functional groups
- Alcohols: contain the  $-\text{OH}$  group
- Aldehydes: contain a  $\begin{array}{c} \diagup \\ \text{C}=\text{O} \\ \diagdown \end{array}$  group
- Ketones: contain the  $\begin{array}{c} \diagup \\ \text{C}=\text{O} \\ \diagdown \end{array}$  group
- Carboxylic acids: contain the  $\begin{array}{c} \diagup \\ \text{C}=\text{O} \\ \diagdown \\ \text{OH} \end{array}$  group

### Polymers

- Large molecules formed from many small molecules (called monomers)
  - Addition polymerization: monomers add together by a free radical mechanism
  - Condensation polymerization: monomers connect by splitting out a small molecule, such as water

### Proteins

- A class of natural polymers with molar masses ranging from 600 to 1,000,000
- Fibrous proteins form the structural basis of muscle, hair, and cartilage
- Globular proteins perform many biologic functions, including transport and storage of oxygen, catalysis of biologic reactions, and regulation of biologic systems
- Building blocks of proteins (monomers) are  $\alpha$ -amino acids, which connect by a condensation reaction to form a peptide linkage
- Protein structure
  - Primary: the order of amino acids in the chain
  - Secondary: the arrangement of the protein chain
    - $\alpha$ -helix
    - pleated sheet
  - Tertiary structure: the overall shape of the protein

### Carbohydrates

- Contain carbon, hydrogen, and oxygen
- Serve as food sources for most organisms
- Monosaccharides are most commonly five-carbon and six-carbon polyhydroxy ketones and aldehydes
  - Monosaccharides combine to form more complex carbohydrates, such as sucrose, starch, and cellulose

### Genetic processes

- When a cell divides, the genetic information is transmitted via deoxyribonucleic acid (DNA), which has a double helical structure
  - During cell division, the double helix unravels and a new polymer forms along each strand of the original DNA
  - The genetic code is carried by organic bases that hydrogen-bond to each other in specific pairs in the interior of the DNA double helix

### REVIEW QUESTIONS

- What is a hydrocarbon? What is the difference between a saturated hydrocarbon and an unsaturated hydrocarbon? Distinguish between normal and branched hydrocarbons. What is an alkane? What is a cyclic alkane? What are the two general formulas for alkanes? What is the hybridization of carbon atoms in alkanes? What are the bond angles in alkanes? Why are cyclopropane and cyclobutane so reactive?

messenger RNA (mRNA)  
transfer RNA (tRNA)  
anticodon

The normal (unbranched) hydrocarbons are often referred to as *straight-chain hydrocarbons*. What does this name refer to? Does it mean that the carbon atoms in a straight-chain hydrocarbon really have a linear arrangement? Explain. In the shorthand notation for cyclic alkanes, the hydrogens are usually omitted. How do you determine the number of hydrogens bonded to each carbon in a ring structure?

2. What is an alkene? What is an alkyne? What are the general formulas for alkenes and alkynes, assuming one multiple bond in each? What are the bond angles in alkenes and alkynes? Describe the bonding in alkenes and alkynes using  $C_2H_4$  and  $C_2H_2$  as your examples. Why is there restricted rotation in alkenes and alkynes? Is the general formula for a cyclic alkene  $C_nH_{2n}$ ? If not, what is the general formula, assuming one multiple bond?
3. What are aromatic hydrocarbons? Benzene exhibits resonance. Explain. What are the bond angles in benzene? Give a detailed description of the bonding in benzene. The  $\pi$  electrons in benzene are delocalized, while the  $\pi$  electrons in alkenes and alkynes are localized. Explain the difference.
4. Summarize the nomenclature rules for alkanes, alkenes, alkynes, and aromatic compounds. Correct the following false statements regarding nomenclature of hydrocarbons.
  - a. The root name for a hydrocarbon is based on the shortest continuous chain of carbon atoms.
  - b. The suffix used to name all hydrocarbons is *-ane*.
  - c. Substituent groups are numbered so as to give the largest numbers possible.
  - d. No number is required to indicate the positions of double or triple bonds in alkenes and alkynes.
  - e. Substituent groups get the lowest number possible in alkenes and alkynes.
  - f. The *ortho*- term in aromatic hydrocarbons indicates the presence of two substituent groups bonded to carbon-1 and carbon-3 in benzene.
5. What functional group distinguishes each of the following hydrocarbon derivatives?
  - a. halohydrocarbons
  - b. alcohols
  - c. ethers
  - d. aldehydes
  - e. ketones
  - f. carboxylic acids
  - g. esters
  - h. amines

Give examples of each functional group. What prefix or suffix is used to name each functional group? What are the bond angles in each? Describe the bonding in each functional group. What is the difference between a primary, secondary, and tertiary alcohol? For the functional groups in a–h, when is a number required to indicate the position of the functional group? Carboxylic acids are often written as  $RCOOH$ . What does  $-COOH$  indicate and what does R indicate? Aldehydes are sometimes written as  $RCHO$ . What does  $-CHO$  indicate?

6. Distinguish between isomerism and resonance. Distinguish between structural and geometric isomerism. When writing the various structural isomers, the most difficult task is identifying which are different isomers and which are identical to a previously written structure—that is, which are compounds that differ only by the rotation of a carbon single bond. How do you distinguish between structural isomers and those that are identical?

Alkenes and cycloalkanes are structural isomers of each other. Give an example of each using  $C_4H_{10}$ . Another common feature of alkenes and cycloalkanes

is that both have restricted rotation about one or more bonds in the compound, so both can exhibit *cis-trans* isomerism. What is required for an alkene or cycloalkane to exhibit *cis-trans* isomerism? Explain the difference between *cis* and *trans* isomers.

Alcohols and ethers are structural isomers of each other, as are aldehydes and ketones. Give an example of each to illustrate. Which functional group in Table 22.4 can be structural isomers of carboxylic acids?

What is optical isomerism? What do you look for to determine whether an organic compound exhibits optical isomerism? 1-Bromo-1-chloroethane is optically active whereas 1-bromo-2-chloroethane is not optically active. Explain.

7. What type of intermolecular forces do hydrocarbons exhibit? Explain why the boiling point of *n*-heptane is greater than that of *n*-butane. A general rule for a group of hydrocarbon isomers is that as the amount of branching increases, the boiling point decreases. Explain why this would be true.

The functional groups listed in Table 22.4 all exhibit London dispersion forces, but they also usually exhibit additional dipole–dipole forces. Explain why this is the case for each functional group. Although alcohols and ethers are structural isomers of each other, alcohols always boil at significantly higher temperatures than similar-size ethers. Explain. What would you expect when comparing the boiling points of similar-size carboxylic acids to esters? CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>OH, CH<sub>3</sub>CHO, and HCOOH all have about the same molar mass, but they boil at very different temperatures. Why? Place these compounds in order by increasing boiling point.

8. Distinguish between substitution and addition reactions. Give an example of each type of reaction. Alkanes and aromatics are fairly stable compounds. To make them react, a special catalyst must be present. What catalyst must be present when reacting Cl<sub>2</sub> with an alkane or with benzene? Adding Cl<sub>2</sub> to an alkene or alkyne does not require a special catalyst. Why are alkenes and alkynes more reactive than alkanes and aromatic compounds? All organic compounds can be combusted. What is the other reactant in a combustion reaction, and what are the products, assuming the organic compound contains only C, H, and perhaps O?

The following are some other organic reactions covered in Section 22.4. Give an example to illustrate each type of reaction.

- a. Adding H<sub>2</sub>O to an alkene (in the presence of H<sup>+</sup>) yields an alcohol.
- b. Primary alcohols are oxidized to aldehydes, which can be further oxidized to carboxylic acids.
- c. Secondary alcohols are oxidized to ketones.
- d. Reacting an alcohol with a carboxylic acid (in the presence of H<sup>+</sup>) produces an ester.
9. Define and give an example of each of the following.
  - a. addition polymer
  - b. condensation polymer
  - c. copolymer
  - d. homopolymer
  - e. polyester
  - f. polyamide

Distinguish between a thermoset polymer and a thermoplastic polymer. How do the physical properties of polymers depend on chain length and extent of chain branching? Explain how crosslinking agents are used to change the physical properties of polymers. Isotactic polypropylene makes stronger fibers than atactic polypropylene. Explain. In which polymer, polyethylene or polyvinyl chloride, would you expect to find the stronger intermolecular forces (assuming the average chain lengths are equal)?

10. Give the general formula for an amino acid. Some amino acids are labeled hydrophilic and some are labeled hydrophobic. What do these terms refer to? Aqueous solutions of amino acids are buffered solutions. Explain. Most of the amino acids in Fig. 22.18 are optically active. Explain. What is a peptide bond? Show how glycine, serine, and alanine react to form a tripeptide. What is a protein, and what are the monomers in proteins? Distinguish between the primary, secondary, and tertiary structures of a protein. Give examples of the types of forces that maintain each type of structure. Describe how denaturation affects the function of a protein.

What are carbohydrates, and what are the monomers in carbohydrates? The monosaccharides in Table 22.8 are all optically active. Explain. What is a *disaccharide*? Which monosaccharide units make up the disaccharide sucrose? What do you call the bond that forms between the monosaccharide units? What forces are responsible for the solubility of starch in water? What is the difference between starch, cellulose, and glycogen?

Describe the structural differences between DNA and RNA. The monomers in nucleic acids are called nucleotides. What are the three parts of a nucleotide? The compounds adenine, guanine, cytosine, and thymine are called the nucleic acid bases. What structural features in these compounds make them bases? DNA exhibits a double-helical structure. Explain. Describe how the complementary base pairing between the two individual strands of DNA forms the overall double-helical structure. How is complementary base pairing involved in the replication of DNA molecule during cell division? Describe how protein synthesis occurs. What is a codon, and what is a gene? The deletion of a single base from a DNA molecule can constitute a fatal mutation, whereas substitution of one base for another is often not as serious a mutation. Explain.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

## Questions

1. A confused student was doing an isomer problem and listed the following six names as different structural isomers of  $C_7H_{16}$ .

- a. 1-sec-butylpropane
- b. 4-methylhexane
- c. 2-ethylpentane
- d. 1-ethyl-1-methylbutane
- e. 3-methylhexane
- f. 4-ethylpentane

How many different structural isomers are actually present in these six names?

2. For the following formulas, what types of isomerism could be exhibited? For each formula, give an example that illustrates the specific type of isomerism. The types of isomerism are structural, geometric, and optical.

- a.  $C_6H_{12}$
- b.  $C_5H_{12}O$
- c.  $C_6H_4Br_2$

3. What is wrong with the following names? Give the correct name for each compound.

- a. 2-ethylpropane
- b. 5-iodo-5, 6-dimethylhexane

- c. *cis*-4-methyl-3-pentene
- d. 2-bromo-3-butanol

4. The following organic compounds cannot exist. Why?

- a. 2-chloro-2-butyne
- b. 2-methyl-2-propanone
- c. 1,1-dimethylbenzene
- d. 2-pentanal
- e. 3-hexanoic acid
- f. 5,5-dibromo-1-cyclobutanol

5. If you had a group of hydrocarbons, what structural features would you look at to rank the hydrocarbons in order of increasing boiling point?

6. Which of the functional groups in Table 22.4 can exhibit hydrogen bonding intermolecular forces? Can  $CH_2CF_2$  exhibit hydrogen bonding? Explain.

7. A polypeptide is also called a polyamide. What is a polyamide? Consider a polyhydrocarbon, a polyester, and a polyamide. Assuming average chain lengths are equal, which polymer would you expect to make the strongest fibers and which polymer would you expect to make the weakest fibers? Explain.

8. Give an example reaction that would yield the following products. Name the organic reactant and product in each reaction.

- a. alkane
- b. monohalogenated alkane

- c. dihalogenated alkane  
d. tetrahalogenated alkane  
e. monohalogenated benzene  
f. alkene
9. Give an example reaction that would yield the following products as major organic products. See Exercises 22.62 and 22.65 for some hints. For oxidation reactions, just write oxidation over the arrow and don't worry about the actual reagent.  
a. primary alcohol  
b. secondary alcohol  
c. tertiary alcohol  
d. aldehyde  
e. ketone  
f. carboxylic acid  
g. ester
10. What is polystyrene? The following processes result in a stronger polystyrene polymer. Explain why in each case.  
a. addition of catalyst to form syndiotactic polystyrene  
b. addition of 1,3-butadiene and sulfur  
c. producing long chains of polystyrene  
d. addition of a catalyst to make linear polystyrene
11. Answer the following questions regarding the formation of polymers.  
a. What structural features must be present in a monomer in order to form a homopolymer polyester?  
b. What structural features must be present in the monomers in order to form a copolymer polyamide?  
c. What structural features must be present in a monomer that can form both an addition polymer and a condensation polymer?
12. In Section 22.6, three important classes of biologically important natural polymers are discussed. What are the three classes, what are the monomers used to form the polymers, and why are they biologically important?

## Exercises

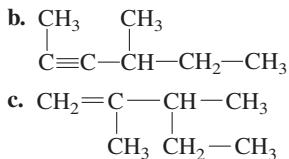
In this section similar exercises are paired.

### Hydrocarbons

13. Draw the five structural isomers of hexane ( $C_6H_{14}$ ).  
14. Name the structural isomers in Exercise 13.
15. Draw all the structural isomers for  $C_8H_{18}$  that have the following root name (longest carbon chain). Name the structural isomers.  
a. heptane    b. butane
16. Draw all the structural isomers for  $C_8H_{18}$  that have the following root name (longest carbon chain). Name the structural isomers.  
a. hexane    b. pentane
17. Draw a structural formula for each of the following compounds.  
a. 2-methylpropane  
b. 2-methylbutane  
c. 2-methylpentane  
d. 2-methylhexane
18. Draw a structural formula for each of the following compounds.  
a. 2,2-dimethylheptane    c. 3,3-dimethylheptane  
b. 2,3-dimethylheptane    d. 2,4-dimethylheptane

19. Draw the structural formula for each of the following.  
a. 3-isobutylhexane  
b. 2,2,4-trimethylpentane, also called *isooctane*. This substance is the reference (100 level) for octane ratings.  
c. 2-*tert*-butylpentane  
d. The names given in parts a and c are incorrect. Give the correct names for these hydrocarbons.
20. Draw the structure for 4-ethyl-2,3-diisopropylpentane. This name is incorrect. Give the correct systematic name.
21. Name each of the following:  
a.  $\begin{array}{ccccccc} & & CH_3 & & & & \\ & & | & & & & \\ CH_3 & - & C & - & CH_2 & - & CH & - CH_2 & - CH_3 \\ & & | & & & & | & & \\ & & CH_3 & & & & CH_3 & & \end{array}$   
b.  $\begin{array}{ccccccccc} & & CH_2 & & & & & & \\ & & | & & & & & & \\ & & CH_3 & - & CH_2 & - & CH_2 & - & CH & - CH_2 & - CH_2 & - CH_2 & - CH_2 & - CH_3 \\ & & | & & & & & & | & & & & & | & & \\ & & CH_3 & & & & & & CH_3 & & & & & CH_3 & & \end{array}$   
c.  $\begin{array}{ccccc} & CH_3 & & CH_3 & \\ & | & & | & \\ CH_3 & - & C & - & CH_2 & - & C & - & CH_3 \\ & | & & | & & & | & & \\ & CH_3 & & CH_3 & & & CH_3 & & \end{array}$   
d.  $\begin{array}{ccccccc} & & CH_2 & - & CH_3 & & \\ & & | & & & & \\ & & CH_3 & - & C & - & CH_2 & - & CH_2 & - & CH_2 & - & CH_2 & - & CH_3 \\ & & | & & & & | & & & & & & & & | & & \\ & & CH_2 & - & CH_3 & & & & & & & & & & & CH_3 & & \end{array}$
22. Name each of the following cyclic alkanes, and indicate the formula of the compound.  
a.  $\begin{array}{c} \square \\ | \\ CHCH_3 \\ | \\ CH_3 \end{array}$   
b.  $\begin{array}{c} CH_3 \\ | \\ \square \\ | \\ CCH_3 \\ | \\ CH_3 \\ | \\ CH_3 \end{array}$   
c.  $\begin{array}{c} CH_3 \\ | \\ \square \\ | \\ CH_2CH_2CH_3 \\ | \\ CH_3 \end{array}$
23. Give two examples of saturated hydrocarbons. How many other atoms are bonded to each carbon in a saturated hydrocarbon?  
24. Draw the structures for two examples of *unsaturated* hydrocarbons. What structural feature makes a hydrocarbon unsaturated?  
25. Name each of the following alkenes.  
a.  $CH_2=CH-CH_2-CH_3$   
b.  $\begin{array}{c} CH_2CH_3 \\ | \\ CH_3-CH=CH-CHCH_3 \end{array}$   
c.  $\begin{array}{c} CH_3 \\ | \\ CH_3CH_2CH-CH=CH-CHCH_3 \\ | \\ CH_3 \end{array}$   
26. Name each of the following alkenes or alkynes.  
a.  $\begin{array}{c} CH_3CH_3 \\ | \\ CH_3-C=C-CH_3 \end{array}$

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27. Give the structure for each of the following.

- a. 3-hexene    b. 2,4-heptadiene    c. 2-methyl-3-octene

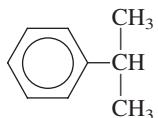
28. Give the structure for each of the following.

- a. 4-methyl-1-pentyne  
b. 2,3,3-trimethyl-1-hexene  
c. 3-ethyl-4-decene

29. Give the structure of each of the following aromatic hydrocarbons.

- a. *o*-ethyltoluene  
b. *p*-di-*tert*-butylbenzene  
c. *m*-diethylbenzene  
d. 1-phenyl-2-butene

30. Cumene is the starting material for the industrial production of acetone and phenol. The structure of cumene is



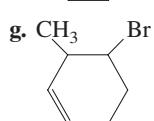
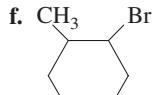
Give the systematic name for cumene.

31. Name each of the following.

- a.  $\text{Cl}-\text{CH}_2-\text{CH}_2-\overset{\text{CH}-\text{CH}_3}{\underset{\text{Cl}}{|}}\text{CH}_2-\text{CH}_3$   
b.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CCl}_3$   
c.  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{CCl}-\text{CH}-\text{CH}-\text{CH}_3 \\ | \quad | \\ \text{CH}_3 \quad \text{Cl} \quad \text{CH}_2-\text{CH}_3 \end{array}$   
d.  $\text{CH}_2\text{FCH}_2\text{F}$

32. Name each of the following compounds.

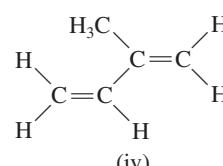
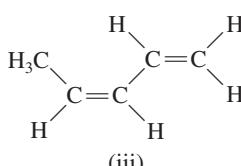
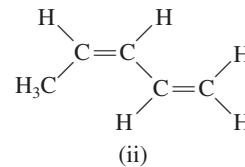
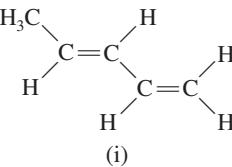
- a.  $\begin{array}{c} \text{CH}_3\text{CHCH}=\text{CH}_2 \\ | \\ \text{Cl} \end{array}$   
b.  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2=\text{CH}-\text{CH}_2\text{CH}_3 \end{array}$   
c.  $\begin{array}{c} \text{Cl} \\ | \\ \text{CH}_2=\text{CH}-\text{CH}_2\text{CH}_3 \end{array}$   
d.  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2=\text{CH}-\text{CH}_2\text{CH}_3 \end{array}$   
e.  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2=\text{CH}-\text{CH}_2\text{Br} \end{array}$



### Isomerism

33. There is only one compound that is named 1,2-dichloroethane, but there are two distinct compounds that can be named 1,2-dichloroethene. Why?

34. Consider the following four structures:



- a. Which of these compounds would have the same physical properties (melting point, boiling point, density, and so on)?  
b. Which of these compounds is (are) *trans* isomers?  
c. Which of these compounds do not exhibit *cis-trans* isomerism?

35. Which of the compounds in Exercises 25 and 27 exhibit *cis-trans* isomerism?

36. Which of the compounds in Exercises 26 and 28 exhibit *cis-trans* isomerism?

37. Draw all the structural isomers of  $\text{C}_5\text{H}_{10}$ . Ignore any cyclic isomers.

38. Which of the structural isomers in Exercise 37 exhibit *cis-trans* isomerism?

39. Draw all the structural and geometrical (*cis-trans*) isomers of  $\text{C}_3\text{H}_5\text{Cl}$ .

40. Draw all the structural and geometrical (*cis-trans*) isomers of bromochloropropene.

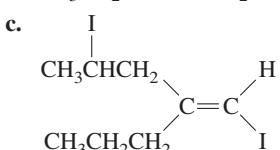
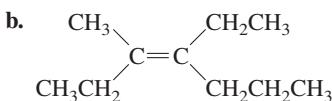
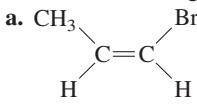
41. Draw all structural and geometrical (*cis-trans*) isomers of  $\text{C}_4\text{H}_7\text{F}$ . Ignore any cyclic isomers.

42. *Cis-trans* isomerism is also possible in molecules with rings. Draw the *cis* and *trans* isomers of 1,2-dimethylcyclohexane. In Exercise 41, you drew all of the noncyclic structural and geometric isomers of  $\text{C}_4\text{H}_7\text{F}$ . Now draw the cyclic structural and geometric isomers of  $\text{C}_4\text{H}_7\text{F}$ .

43. Draw the following.

- a. *cis*-2-hexene  
b. *trans*-2-butene  
c. *cis*-2,3-dichloro-2-pentene

**44.** Name the following compounds.



**45.** If one hydrogen in a hydrocarbon is replaced by a halogen atom, the number of isomers that exist for the substituted compound depends on the number of types of hydrogen in the original hydrocarbon. Thus there is only one form of chloroethane (all hydrogens in ethane are equivalent), but there are two isomers of propane that arise from the substitution of a methyl hydrogen or a methylene hydrogen. How many isomers can be obtained when one hydrogen in each of the compounds named below is replaced by a chlorine atom?

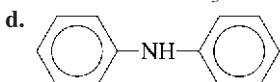
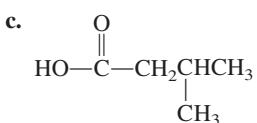
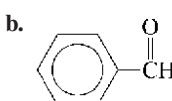
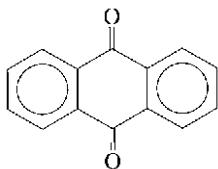
- a. *n*-pentane      c. 2,4-dimethylpentane  
 b. 2-methylbutane    d. methylcyclobutane

**46.** There are three isomers of dichlorobenzene, one of which has now replaced naphthalene as the main constituent of mothballs.  
 a. Identify the *ortho*, the *meta*, and the *para* isomers of dichlorobenzene.  
 b. Predict the number of isomers for trichlorobenzene.  
 c. It turns out that the presence of one chlorine atom on a benzene ring will cause the next substituent to add *ortho* or *para* to the first chlorine atom on the benzene ring. What does this tell you about the synthesis of *m*-dichlorobenzene?  
 d. Which of the isomers of trichlorobenzene will be the hardest to prepare?

## Functional Groups

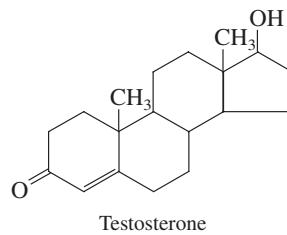
**47.** Identify each of the following compounds as a carboxylic acid, ester, ketone, aldehyde, or amine.

- a. Anthraquinone, an important starting material in the manufacture of dyes:

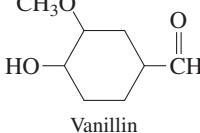


**48.** Identify the functional groups present in the following compounds.

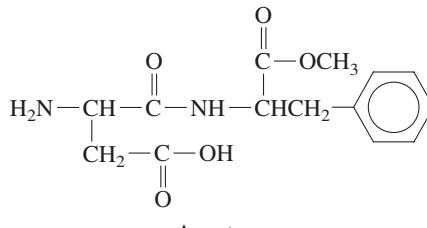
a.



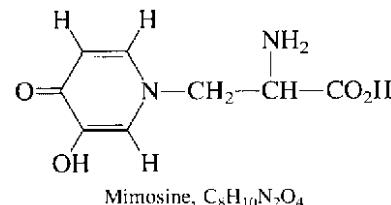
b.



c.



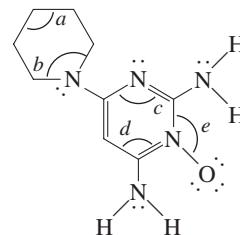
**49.** Mimosine is a natural product found in large quantities in the seeds and foliage of some legume plants and has been shown to cause inhibition of hair growth and hair loss in mice.



Mimosine,  $C_8H_{10}N_2O_4$

- a. What functional groups are present in mimosine?  
 b. Give the hybridization of the eight carbon atoms in mimosine.  
 c. How many  $\sigma$  and  $\pi$  bonds are found in mimosine?

**50.** Minoxidil ( $C_9H_{15}N_5O$ ) is a compound produced by Pharmacia Company that has been approved as a treatment of some types of male pattern baldness.

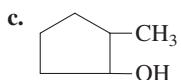
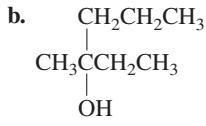
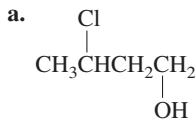


- a. Would minoxidil be more soluble in acidic or basic aqueous solution? Explain.  
 b. Give the hybridization of the five nitrogen atoms in minoxidil.  
 c. Give the hybridization of each of the nine carbon atoms in minoxidil.  
 d. Give approximate values of the bond angles marked *a*, *b*, *c*, *d*, and *e*.

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- e. Including all the hydrogen atoms, how many  $\sigma$  bonds exist in minoxidil?  
 f. How many  $\pi$  bonds exist in minoxidil?

- 51.** For each of the following alcohols, give the systematic name and specify whether the alcohol is primary, secondary, or tertiary.



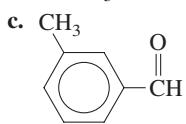
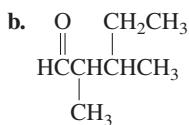
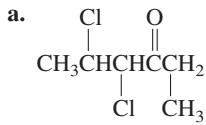
- 52.** Draw structural formulas for each of the following alcohols. Indicate whether the alcohol is primary, secondary, or tertiary.

- a. 1-butanol      c. 2-methyl-1-butanol  
 b. 2-butanol      d. 2-methyl-2-butanol

- 53.** Name all the alcohols that have the formula  $\text{C}_5\text{H}_{12}\text{O}$ . How many ethers have the formula  $\text{C}_5\text{H}_{12}\text{O}$ ?

- 54.** Name all the aldehydes and ketones that have the formula  $\text{C}_5\text{H}_{10}\text{O}$ .

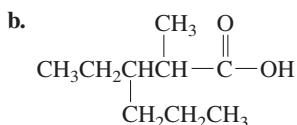
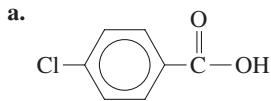
- 55.** Name the following compounds.



- 56.** Draw the structural formula for each of the following.

- a. formaldehyde (methanal)  
 b. 4-heptanone  
 c. 3-chlorobutanal  
 d. 5,5-dimethyl-2-hexanone

- 57.** Name the following compounds.



- 58.** Draw a structural formula for each of the following.

- a. 3-methylpentanoic acid  
 b. ethyl methanoate  
 c. methyl benzoate  
 d. 3-chloro-2,4-dimethylhexanoic acid

- 59.** Which of the following statements is (are) false? Explain why the statement(s) is (are) false.

- a.  $\begin{array}{c} \text{O} \\ || \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_3 \end{array}$  is a structural isomer of pentanoic acid.  
 b.  $\begin{array}{c} \text{O} \quad \text{CH}_3 \\ || \quad | \\ \text{HCCH}_2\text{CH}_2\text{CHCH}_3 \end{array}$  is a structural isomer of 2-methyl-3-pentanone.  
 c.  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3$  is a structural isomer of 2-pentanol.  
 d.  $\begin{array}{c} \text{CH}_2=\text{CHCHCH}_3 \\ | \\ \text{OH} \end{array}$  is a structural isomer of 2-butenal.

- e. Trimethylamine is a structural isomer of  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ .

- 60.** Draw the isomer(s) specified. There may be more than one possible isomer for each part.

- a. a cyclic compound that is an isomer of *trans*-2-butene  
 b. an ester that is an isomer of propanoic acid  
 c. a ketone that is an isomer of butanal  
 d. a secondary amine that is an isomer of butylamine  
 e. a tertiary amine that is an isomer of butylamine  
 f. an ether that is an isomer of 2-methyl-2-propanol  
 g. a secondary alcohol that is an isomer of 2-methyl-2-propanol

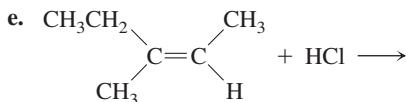
### Reactions of Organic Compounds

- 61.** Complete the following reactions.

- a.  $\text{CH}_3\text{CH}=\text{CHCH}_3 + \text{H}_2 \xrightarrow{\text{Pt}}$   
 b.  $\begin{array}{c} \text{O} \quad \text{CH}_2=\text{CHCHCH}=\text{CH} \\ || \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array} + 2\text{Cl}_2 \longrightarrow$   
 c.  $\begin{array}{c} \text{C}_6\text{H}_6 \\ || \\ \text{C}_6\text{H}_5 \end{array} + \text{Cl}_2 \xrightarrow{\text{FeCl}_3}$   
 d.  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{C}=\text{CH}_2 \end{array} + \text{O}_2 \xrightarrow{\text{Spark}}$

- 62.** Reagents such as  $\text{HCl}$ ,  $\text{HBr}$ , and  $\text{HOH} (\text{H}_2\text{O})$  can add across carbon–carbon double and triple bonds, with H forming a bond to one of the carbon atoms in the multiple bond and Cl, Br, or OH forming a bond to the other carbon atom in the multiple bond. In some cases, two products are possible. For the major organic product, the addition occurs so that the hydrogen atom in the reagent attaches to the carbon atom in the multiple bond that already has the greater number of hydrogen atoms bonded to it. With this rule in mind, draw the structure of the major product in each of the following reactions.

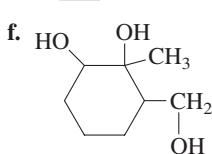
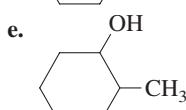
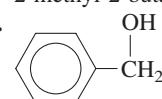
- a.  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{H}_2\text{O} \longrightarrow$   
 b.  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{HBr} \longrightarrow$   
 c.  $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH} + 2\text{HBr} \longrightarrow$   
 d.  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{C}_5\text{H}_8 \end{array} + \text{H}_2\text{O} \longrightarrow$



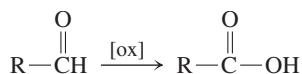
63. When toluene ( $\text{C}_6\text{H}_5\text{CH}_3$ ) reacts with chlorine gas in the presence of iron(III) catalyst, the product is a mixture of the *ortho* and *para* isomers of  $\text{C}_6\text{H}_4\text{ClCH}_3$ . However, when the reaction is light-catalyzed with no  $\text{Fe}^{3+}$  catalyst present, the product is  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ . Explain.
64. Why is it preferable to produce chloroethane by the reaction of  $\text{HCl}(g)$  with ethene than by the reaction of  $\text{Cl}_2(g)$  with ethane? (See Exercise 62.)

65. Using appropriate reactants, alcohols can be oxidized into aldehydes, ketones, and/or carboxylic acids. Primary alcohols can be oxidized into aldehydes, which can then be oxidized into carboxylic acids. Secondary alcohols can be oxidized into ketones, while tertiary alcohols do not undergo this type of oxidation. Give the structure of the product(s) resulting from the oxidation of each of the following alcohols.

- a. 3-methyl-1-butanol  
b. 3-methyl-2-butanol  
c. 2-methyl-2-butanol  
d.



66. Oxidation of an aldehyde yields a carboxylic acid:



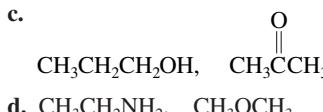
Draw the structures for the products of the following oxidation reactions.

- a. propanal  $\xrightarrow{[\text{ox}]}$   
b. 2,3-dimethylpentanal  $\xrightarrow{[\text{ox}]}$   
c. 3-ethylbenzaldehyde  $\xrightarrow{[\text{ox}]}$

67. How would you synthesize each of the following?
- a. 1,2-dibromopropane from propene  
b. acetone (2-propanone) from an alcohol  
c. *tert*-butyl alcohol (2-methyl-2-propanol) from an alkene (See Exercise 62.)  
d. propanoic acid from an alcohol

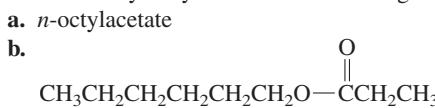
68. What tests could you perform to distinguish between the following pairs of compounds?

- a.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ ,  $\text{CH}_2=\text{CHCH}_2\text{CH}_3$   
b.

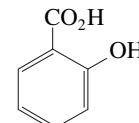


- d.  $\text{CH}_3\text{CH}_2\text{NH}_2$ ,  $\text{CH}_3\text{OCH}_3$

69. How would you synthesize the following esters?



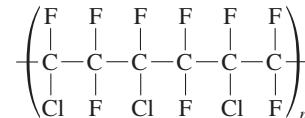
70. Salicylic acid has the following structure:



Since salicylic acid has both an alcohol functional group and a carboxylic acid functional group, it can undergo two different esterification reactions depending on which functional group reacts. For example, when treated with ethanoic acid (acetic acid), salicylic acid behaves as an alcohol and the ester produced is acetylsalicylic acid (aspirin). On the other hand, when reacted with methanol, salicylic acid behaves as an acid and the ester methyl salicylate (oil of wintergreen) is produced. Methyl salicylate is also an analgesic and part of the formulation of many liniments for sore muscles. What are the structures of acetylsalicylic acid and methyl salicylate?

## Polymers

71. Kel-F is a polymer with the structure



What is the monomer for Kel-F?

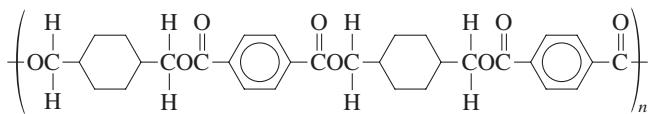
72. What monomer(s) must be used to produce the following polymers?

- a.
- $$\left( \begin{array}{ccccc} \text{CH} & -\text{CH}_2 & -\text{CH} & -\text{CH}_2 & -\text{CH}-\text{CH}_2 \\ | & & | & & | \\ \text{F} & & \text{F} & & \text{F} \end{array} \right)_n$$
- b.
- $$\left( \begin{array}{ccccc} \text{O} & -\text{CH}_2 & -\text{CH}_2 & \overset{\text{O}}{\underset{||}{\text{C}}} & \text{O} \\ | & & & | & | \\ \text{O} & -\text{CH}_2 & -\text{CH}_2 & -\text{C} & -\text{O}-\text{CH}_2-\text{CH}_2 & \overset{\text{O}}{\underset{||}{\text{C}}} \\ & & & | & | & | \\ & & & \text{O} & \text{O} & \text{O} \end{array} \right)_n$$
- c.
- $$\left( \begin{array}{ccccc} \text{H} & & \text{H} & & \text{O} \\ | & & | & & || \\ \text{N} & -\text{CH}_2 & -\text{CH}_2 & \text{N} & -\text{C}-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\underset{||}{\text{C}}} \\ & & & & | \\ & & & & \text{O} \end{array} \right)_n$$
- d.
- $$\left( \begin{array}{ccccc} \text{CH}_3 & & \text{CH}_3 & & \text{CH}_3 \\ | & & | & & | \\ \text{C} & -\text{CH}_2 & -\text{C} & -\text{CH}_2 & -\text{C} \\ | & & | & & | \\ \text{C}_6\text{H}_5 & & \text{C}_6\text{H}_5 & & \text{C}_6\text{H}_5 \end{array} \right)_n$$
- e.
- $$\left( \begin{array}{ccccc} \text{CH} & & \text{CH} & & \text{CH} \\ | & & | & & | \\ \text{C}_6\text{H}_5 & & \text{CH}_3 & & \text{C}_6\text{H}_5 \\ & & & & \text{CH}_3 \end{array} \right)_n$$

## 1050 Chapter Twenty-Two Organic and Biological Molecules



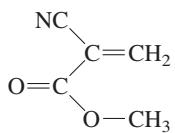
g.



(This polymer is Kodel, used to make fibers of stain-resistant carpeting.)

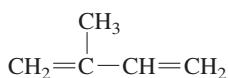
Classify these polymers as condensation or addition polymers. Which are copolymers?

73. "Super glue" contains methyl cyanoacrylate,



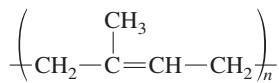
which readily polymerizes upon exposure to traces of water or alcohols on the surfaces to be bonded together. The polymer provides a strong bond between the two surfaces. Draw the structure of the polymer formed by methyl cyanoacrylate.

74. Isoprene is the repeating unit in natural rubber. The structure of isoprene is



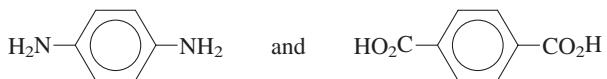
a. Give a systematic name for isoprene.

b. When isoprene is polymerized, two polymers of the form



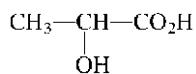
are possible. In natural rubber, the *cis* configuration is found. The polymer with the *trans* configuration about the double bond is called gutta percha and was once used in the manufacture of golf balls. Draw the structure of natural rubber and gutta percha showing three repeating units and the configuration about the carbon–carbon double bonds.

75. Kevlar, used in bulletproof vests, is made by the condensation copolymerization of the monomers



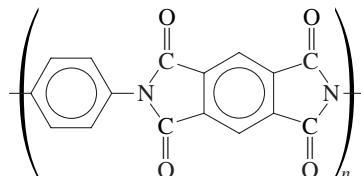
Draw the structure of a portion of the Kevlar chain.

76. The polyester formed from lactic acid,

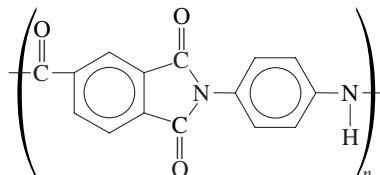


is used for tissue implants and surgical sutures that will dissolve in the body. Draw the structure of a portion of this polymer.

77. Polyimides are polymers that are tough and stable at temperatures of up to  $400^\circ\text{C}$ . They are used as a protective coating on the quartz fibers used in fiber optics. What monomers were used to make the following polyimide?

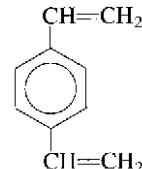


78. The Amoco Chemical Company has successfully raced a car with a plastic engine. Many of the engine parts, including piston skirts, connecting rods, and valve-train components, were made of a polymer called *Torlon*:



What monomers are used to make this polymer?

79. Polystyrene can be made more rigid by copolymerizing styrene with divinylbenzene:



How does the divinylbenzene make the copolymer more rigid?

80. Polyesters containing double bonds are often crosslinked by reacting the polymer with styrene.

a. Draw the structure of the copolymer of



b. Draw the structure of the crosslinked polymer (after the polyester has been reacted with styrene).

81. Which of the following polymers would be stronger or more rigid? Explain your choices.

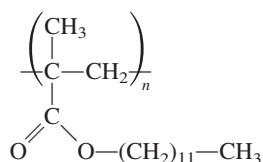
a. The copolymer of ethylene glycol and terephthalic acid or the copolymer of 1,2-diaminoethane and terephthalic acid (1,2-diaminoethane =  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ )

b. The polymer of  $\text{HO--(CH}_2\text{)}_6\text{--CO}_2\text{H}$  or that of



c. Polyacetylene or polyethylene (The monomer in polyacetylene is ethyne.)

82. Poly(lauryl methacrylate) is used as an additive in motor oils to counter the loss of viscosity at high temperature. The structure is



The long hydrocarbon chain of poly(lauryl methacrylate) makes the polymer soluble in oil (a mixture of hydrocarbons with mostly 12 or more carbon atoms). At low temperatures the polymer is coiled into balls. At higher temperatures the balls uncoil and the polymer exists as long chains. Explain how this helps control the viscosity of oil.

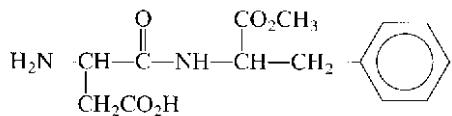
### Natural Polymers

83. Which of the amino acids in Fig. 22.18 contain the following functional groups in their R group?

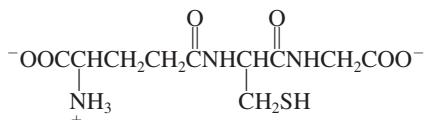
- a. alcohol
- c. amine
- b. carboxylic acid
- d. amide

84. When pure crystalline amino acids are heated, decomposition generally occurs before the solid melts. Account for this observation. (*Hint:* Crystalline amino acids exist as  $\text{H}_3\text{N}^+ \text{CRHC}\text{OO}^-$ , called zwitterions.)

85. Aspartame, the artificial sweetener marketed under the name Nutra-Sweet, is a methyl ester of a dipeptide:



- a. What two amino acids are used to prepare aspartame?
  - b. There is concern that methanol may be produced by the decomposition of aspartame. From what portion of the molecule can methanol be produced? Write an equation for this reaction.
86. Glutathione, a tripeptide found in virtually all cells, functions as a reducing agent. The structure of glutathione is



What amino acids make up glutathione?

87. Draw the structures of the two dipeptides that can be formed from serine and alanine.

88. Draw the structures of the tripeptides gly–ala–ser and ser–ala–gly. How many other tripeptides are possible using these three amino acids?

89. Write the sequence of all possible tetrapeptides composed of the following amino acids.

- a. two phenylalanines and two glycines
- b. two phenylalanines, glycine, and alanine

90. How many different pentapeptides can be formed using five different amino acids?

91. Give an example of amino acids that could give rise to the interactions pictured in Fig. 22.24 that maintain the tertiary structures of proteins.

92. What types of interactions can occur between the side chains of the following amino acids that would help maintain the tertiary structure of a protein?

- a. cysteine and cysteine
- c. glutamic acid and lysine
- b. glutamine and serine
- d. proline and leucine

93. Oxygen is carried from the lungs to tissues by the protein hemoglobin in red blood cells. Sickle cell anemia is a disease resulting from abnormal hemoglobin molecules in which a valine is substituted for a single glutamic acid in normal hemoglobin. How might this substitution affect the structure of hemoglobin?

94. Over 100 different kinds of mutant hemoglobin molecules have been detected in humans. Unlike sickle cell anemia (see Exercise 93), not all of these mutations are as serious. In one nonlethal mutation, glutamine substitutes for a single glutamic acid in normal hemoglobin. Rationalize why this substitution is nonlethal.

95. Draw cyclic structures for D-ribose and D-mannose.

96. Indicate the chiral carbon atoms found in the monosaccharides D-ribose and D-mannose.

97. In addition to using *numerical* prefixes in the general names of sugars to indicate how many carbon atoms are present, we often use the prefixes *keto-* and *aldo-* to indicate whether the sugar is a ketone or an aldehyde. For example, the monosaccharide fructose is frequently called a *ketohexose* to emphasize that it contains six carbons as well as the ketone functional group. For each of the monosaccharides shown in Table 22.8 classify the sugars as aldohexoses, aldopentoses, ketohexoses, or ketopentoses.

98. Glucose can occur in three forms: two cyclic forms and one open-chain structure. In aqueous solution, only a tiny fraction of the glucose is in the open-chain form. Yet tests for the presence of glucose depend on reaction with the aldehyde group, which is found only in the open-chain form. Explain why these tests work.

99. What are the structural differences between  $\alpha$ - and  $\beta$ -glucose? These two cyclic forms of glucose are the building blocks to form two different polymers. Explain.

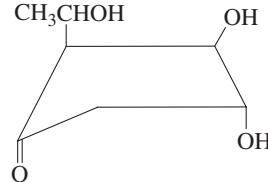
100. Cows can digest cellulose, but humans can't. Why not?

101. Which of the amino acids in Fig. 22.18 contain more than one chiral carbon atom? Draw the structures of these amino acids and indicate all chiral carbon atoms.

102. Why is glycine not optically active?

103. Which of the noncyclic isomers of bromochloropropene are optically active?

104. How many chiral carbon atoms does the following structure have?



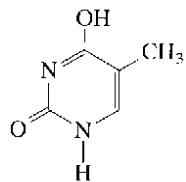
## Chapter Twenty-Two Organic and Biological Molecules

**105.** Part of a certain DNA sequence is G–G–T–C–T–A–T–A–C. What is the complementary sequence?

**106.** The codons (words) in DNA (that specify which amino acid should be at a particular point in a protein) are three bases long. How many such three-letter words can be made from the four bases adenine, cytosine, guanine, and thymine?

**107.** Which base will hydrogen-bond with uracil within an RNA molecule? Draw the structure of this base pair.

**108.** Tautomers are molecules that differ in the position of a hydrogen atom. A tautomeric form of thymine has the structure



If the tautomer above, rather than the stable form of thymine were present in a strand of DNA during replication, what would be the result?

**109.** The base sequences in mRNA that code for certain amino acids are

Glu:	GAA, GAG
Val:	GUU, GUC, GUA, GUG
Met:	AUG
Trp:	UGG
Phe:	UUU, UUC
Asp:	GAU, GAC

These sequences are complementary to the sequences in DNA.

- Give the corresponding sequences in DNA for the amino acids listed above.
- Give a DNA sequence that would code for the peptide trp–glu–phe–met.
- How many different DNA sequences can code for the butapeptide in part b?
- What is the peptide that is produced from the DNA sequence T–A–C–C–T–G–A–A–G?
- What other DNA sequences would yield the same tripeptide as in part d?

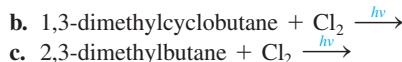
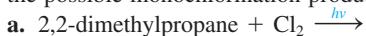
**110.** The change of a single base in the DNA sequence for normal hemoglobin can encode for the abnormal hemoglobin giving rise to sickle cell anemia. Which base in the codon for glu in DNA is replaced to give the codon(s) for val? (See Exercises 93 and 109.)

### Additional Exercises

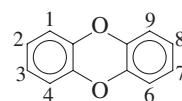
**111.** Draw the following incorrectly named compounds and name them correctly.

- 2-ethyl-3-methyl-5-isopropylhexane
- 2-ethyl-4-*tert*-butylpentane
- 3-methyl-4-isopropylpentane
- 2-ethyl-3-butyne

**112.** In the presence of light, chlorine can substitute for one (or more) of the hydrogens in an alkane. For the following reactions, draw the possible monochlorination products.



**113.** Polychlorinated dibenzo-*p*-dioxins (PCDDs) are highly toxic substances that are present in trace amounts as by-products of some chemical manufacturing processes. They have been implicated in a number of environmental incidents—for example, the chemical contamination at Love Canal and the herbicide spraying in Vietnam. The structure of dibenzo-*p*-dioxin, along with the customary numbering convention, is



The most toxic PCDD is 2,3,7,8-tetrachloro-dibenzo-*p*-dioxin. Draw the structure of this compound. Also draw the structures of two other isomers containing four chlorine atoms.

**114.** Consider the following five compounds.

- CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>
- CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH
- CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>
- CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>C=O
- CH<sub>3</sub>|  
|  
CH<sub>3</sub>C(CH<sub>3</sub>)<sub>2</sub>  
|  
CH<sub>3</sub>

The boiling points of these five compounds are 9.5°C, 36°C, 69°C, 76°C, and 117°C. Which compound boils at 36°C? Explain.

**115.** The two isomers having the formula C<sub>2</sub>H<sub>6</sub>O boil at -23°C and 78.5°C. Draw the structure of the isomer that boils at -23°C and of the isomer that boils at 78.5°C.

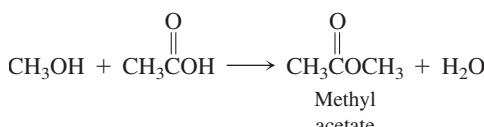
**116.** Ignoring ring compounds, which isomer of C<sub>2</sub>H<sub>4</sub>O<sub>2</sub> should boil at the lowest temperature?

**117.** Explain why methyl alcohol is soluble in water in all proportions, while stearyl alcohol [CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>OH] is a waxy solid that is not soluble in water.

**118.** Is octanoic acid more soluble in 1 M HCl, 1 M NaOH, or pure water? Explain. Drugs such as morphine (C<sub>17</sub>H<sub>19</sub>NO<sub>3</sub>) are often treated with strong acids. The most commonly used form of morphine is morphine hydrochloride (C<sub>17</sub>H<sub>20</sub>ClNO<sub>3</sub>). Why is morphine treated in this way? (*Hint:* Morphine is an amine.)

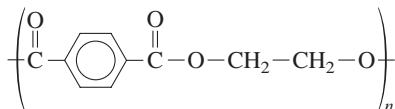
**119.** Consider the compounds butanoic acid, pentanal, *n*-hexane, and 1-pentanol. The boiling points of these compounds (in no specific order) are 69°C, 103°C, 137°C, and 164°C. Match the boiling points to the correct compound.

**120.** Consider the reaction to produce the ester methyl acetate:



When this reaction is carried out with  $\text{CH}_3\text{OH}$  containing radioactive oxygen-18, the water produced does not contain oxygen-18. Explain the results of this radioisotope tracer experiment.

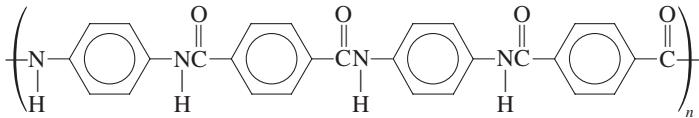
- 121.** A compound containing only carbon and hydrogen is 85.63% C by mass. Reaction of this compound with  $\text{H}_2\text{O}$  produces a secondary alcohol as the major product and a primary alcohol as the minor product (see Exercise 62). If the molar mass of the hydrocarbon is between 50 and 60 g/mol, name the compound.
- 122.** Diborane,  $\text{B}_2\text{H}_6$ , is a highly unstable compound that reacts explosively with oxygen. Ethane,  $\text{C}_2\text{H}_6$ , combines with oxygen only at elevated temperatures. Explain the differences in these two compounds.
- 123.** Three different organic compounds have the formula  $\text{C}_3\text{H}_8\text{O}$ . Only two of these isomers react with  $\text{KMnO}_4$  (a strong oxidizing agent). What are the names of the products when these isomers react with excess  $\text{KMnO}_4$ ?
- 124.** Consider the following polymer:



Is this polymer a homopolymer or a copolymer, and is it formed by addition polymerization or condensation polymerization? What is (are) the monomer(s) for this polymer?

- 125.** Nylon is named according to the number of C atoms between the N atoms in the chain. Nylon-46 has 4 C atoms then 6 C atoms, and this pattern repeats. Nylon-6 always has 6 atoms in a row. Speculate as to why nylon-46 is stronger than nylon-6. (*Hint:* Consider the strengths of interchain forces.)
- 126.** The polymer nitrile is a copolymer made from acrylonitrile and butadiene; it is used to make automotive hoses and gaskets. Draw the structure of nitrile. (*Hint:* See Table 22.7.)
- 127.** *Polyaramid* is a term applied to polyamides containing aromatic groups. These polymers were originally made for use as tire cords but have since found many other uses.

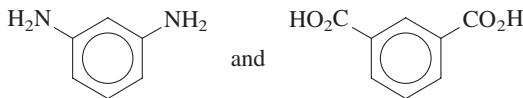
- a. Kevlar is used in bulletproof vests and many high-strength



composites. The structure of Kevlar is

Which monomers are used to make Kevlar?

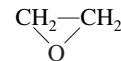
- b. Nomex is a polyaramid used in fire-resistant clothing. It is a copolymer of



Draw the structure of the Nomex polymer. How do Kevlar and Nomex differ in their structures?

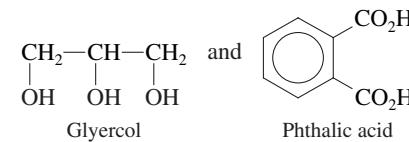
- 128.** When acrylic polymers are burned, toxic fumes are produced. For example, in many airplane fires, more passenger deaths have been caused by breathing toxic fumes than by the fire itself. Using polyacrylonitrile as an example, what would you expect to be one of the most toxic, gaseous combustion products created in the reaction?

- 129.** Ethylene oxide,



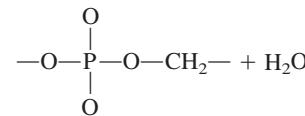
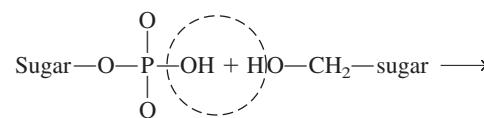
is an important industrial chemical. Although most ethers are unreactive, ethylene oxide is quite reactive. It resembles  $\text{C}_2\text{H}_4$  in its reactions in that addition reactions occur across the C—O bond in ethylene oxide.

- a. Why is ethylene oxide so reactive? (*Hint:* Consider the bond angles in ethylene oxide as compared with those predicted by the VSEPR model.)
- b. Ethylene oxide undergoes addition polymerization, forming a polymer used in many applications requiring a nonionic surfactant. Draw the structure of this polymer.
- 130.** Another way of producing highly crosslinked polyesters is to use glycerol. Alkyd resins are a polymer of this type. The polymer forms very tough coatings when baked onto a surface and is used in paints for automobiles and large appliances. Draw the structure of the polymer formed from the condensation of



Explain how crosslinking occurs in this polymer.

- 131.** Monosodium glutamate (MSG) is commonly used as a flavoring in foods. Draw the structure of MSG.
- 132.** a. Use bond energies (Table 8.4) to estimate  $\Delta H$  for the reaction of two molecules of glycine to form a peptide linkage.
- b. Would you predict  $\Delta S$  to favor the formation of peptide linkages between two molecules of glycine?
- c. Would you predict the formation of proteins to be a spontaneous process?
- 133.** The reaction to form a phosphate ester linkage between two nucleotides can be approximated as follows:



Would you predict the formation of a dinucleotide from two nucleotides to be a spontaneous process?

- 134.** Considering your answers to Exercises 132 and 133, how can you justify the existence of proteins and nucleic acids in light of the second law of thermodynamics?
- 135.** All amino acids have at least two functional groups with acidic or basic properties. In alanine, the carboxylic acid group has  $K_a = 4.5 \times 10^{-3}$  and the amino group has  $K_b = 7.4 \times 10^{-5}$ . Three ions of alanine are possible when alanine is dissolved in

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water. Which of these ions would predominate in a solution with  $[H^+] = 1.0\text{ M}$ ? In a solution with  $[OH^-] = 1.0\text{ M}$ ?

136. The average molar mass of one base pair of nucleotides in DNA is approximately 600 g/mol. The spacing between successive base pairs is about 0.34 nm, and a complete turn in the helical structure of DNA occurs about every 3.4 nm. If a DNA molecule has a molar mass of  $4.5 \times 10^9\text{ g/mol}$ , approximately how many complete turns exist in the DNA  $\alpha$ -helix structure?
137. When heat is added to proteins, the hydrogen bonding in the secondary structure is disrupted. What are the algebraic signs of  $\Delta H$  and  $\Delta S$  for the denaturation process?
138. In glycine, the carboxylic acid group has  $K_a = 4.3 \times 10^{-3}$  and the amino group has  $K_b = 6.0 \times 10^{-5}$ . Use these equilibrium constant values to calculate the equilibrium constants for the following.
- ${}^+H_3NCH_2CO_2^- + H_2O \rightleftharpoons H_2NCH_2CO_2^- + {}^+H_3O^+$
  - $H_2NCH_2CO_2^- + H_2O \rightleftharpoons H_2NCH_2CO_2H + OH^-$
  - ${}^+H_3NCH_2CO_2H \rightleftharpoons 2H^+ + H_2NCH_2CO_2^-$

## Challenge Problems

139. The isoelectric point of an amino acid is the pH at which the molecule has no net charge. For glycine, that point would be the pH at which virtually all glycine molecules are in the form  ${}^+H_3NCH_2CO_2^-$ . This form of glycine is amphoteric since it can act as both an acid and a base. If we assume that the principal equilibrium at the isoelectric point has the best acid reacting with the best base present, then the reaction is

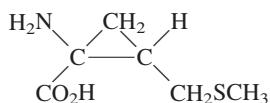


Assuming this reaction is the principal equilibrium, then the following relationship must hold true:

$$[H_2NCH_2CO_2^-] = [{}^+H_3NCH_2CO_2H] \quad (\text{ii})$$

Use this result and your answer to part c of Exercise 138 to calculate the pH at which equation (ii) is true. It will be the isoelectric point of glycine.

140. In 1994 chemists at Texas A & M University reported the synthesis of a non-naturally occurring amino acid (*C & E News*, April 18, 1994, pp. 26–27):

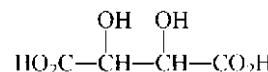


- To which naturally occurring amino acid is this compound most similar?
- A tetrapeptide, phe–met–arg–phe—NH<sub>2</sub>, is synthesized in the brains of rats addicted to morphine and heroin. (The

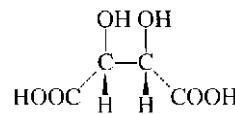
—NH<sub>2</sub> indicates that the peptide ends in —C=O—NH<sub>2</sub> instead of —CO<sub>2</sub>H.) The TAMU scientists synthesized a similar tetrapeptide, with the synthetic amino acid above replacing one of the original amino acids. Draw a structure for the tetrapeptide containing the synthetic amino acid.

- Indicate the chiral carbon atoms in the synthetic amino acid.

141. The structure of tartaric acid is



- Is the form of tartaric acid pictured below optically active? Explain.



Note: The dashed lines show groups behind the plane of the page. The wedges show groups in front of the plane.

- Draw the optically active forms of tartaric acid.

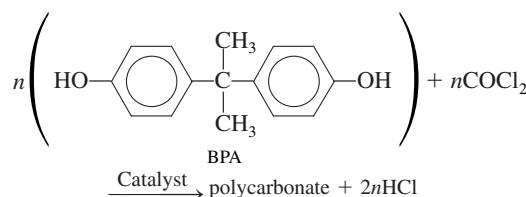
142. Using one of the Lewis structures for benzene (C<sub>6</sub>H<sub>6</sub>), estimate  $\Delta H_f^\circ$  for C<sub>6</sub>H<sub>6</sub>(g) using bond energies and given the standard enthalpy of formation of C(g) is 717 kJ/mol. The experimental  $\Delta H_f^\circ$  value for C<sub>6</sub>H<sub>6</sub>(g) is 83 kJ/mol. Explain the discrepancy between the experimental value and the calculated  $\Delta H_f^\circ$  value for C<sub>6</sub>H<sub>6</sub>(g).
143. Mycomycin, a naturally occurring antibiotic produced by the fungus *Nocardia acidophilus*, has the molecular formula C<sub>13</sub>H<sub>10</sub>O<sub>2</sub> and the systematic name 3,5,7,8-tridecatetraene-10,12-diyenoic acid. Draw the structure of mycomycin.

144. Sorbic acid is used to prevent mold and fungus growth in some food products, especially cheeses. The systematic name for sorbic acid is 2,4-hexadienoic acid. Draw structures for the four geometrical isomers of sorbic acid.

145. Consider the following reactions. For parts b–d, see Exercise 62.

- When C<sub>5</sub>H<sub>12</sub> is reacted with Cl<sub>2</sub>(g) in the presence of ultraviolet light, four different monochlorination products form. What is the structure of C<sub>5</sub>H<sub>12</sub> in this reaction?
- When C<sub>4</sub>H<sub>8</sub> is reacted with H<sub>2</sub>O, a tertiary alcohol is produced as the major product. What is the structure of C<sub>4</sub>H<sub>8</sub> in this reaction?
- When C<sub>7</sub>H<sub>12</sub> is reacted with HCl, 1-chloro-1-methylcyclohexane is produced as the major product. What are the two possible structures for C<sub>7</sub>H<sub>12</sub> in this reaction?
- When a hydrocarbon is reacted with H<sub>2</sub>O and the major product of this reaction is then oxidized, acetone (2-propanone) is produced. What is the structure of the hydrocarbon in this reaction?
- When C<sub>5</sub>H<sub>12</sub>O is oxidized, a carboxylic acid is produced. What are the possible structures for C<sub>5</sub>H<sub>12</sub>O in this reaction?

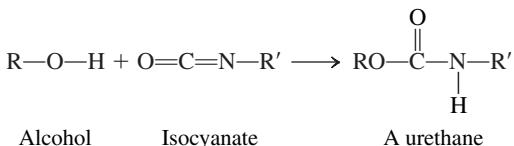
146. Polycarbonates are a class of thermoplastic polymers that are used in the plastic lenses of eyeglasses and in the shells of bicycle helmets. A polycarbonate is made from the reaction of bisphenol A (BPA) with phosgene (COCl<sub>2</sub>):



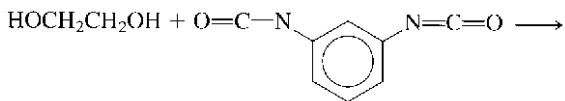
Phenol ( $C_6H_5OH$ ) is used to terminate the polymer (stop its growth).

- Draw the structure of the polycarbonate chain formed from the above reaction.
- Is this reaction a condensation or addition polymerization?

- 147.** A urethane linkage occurs when an alcohol adds across the carbon–nitrogen double bond in an isocyanate:



Polyurethanes (formed from the copolymerization of a diol with a diisocyanate) are used in foamed insulation and a variety of other construction materials. What is the structure of the polyurethane formed by the following reaction?



- 148.** ABS plastic is a tough, hard plastic used in applications requiring shock resistance. The polymer consists of three monomer units: acrylonitrile ( $C_3H_3N$ ), butadiene ( $C_4H_6$ ), and styrene ( $C_8H_8$ ).

- Draw two repeating units of ABS plastic assuming that the three monomer units react in a 1:1:1 mole ratio and react in the same order as the monomers listed above.
- A sample of ABS plastic contains 8.80% N by mass. It took 0.605 g of  $Br_2$  to react completely with a 1.20-g sample of ABS plastic. What is the percent by mass of acrylonitrile, butadiene, and styrene in this polymer sample?
- ABS plastic does not react in a 1:1:1 mole ratio among the three monomer units. Using the results from part b, determine the relative numbers of the monomer units in this sample of ABS plastic.

- 149.** Stretch a rubber band while holding it gently to your lips. Then slowly let it relax while still in contact with your lips.

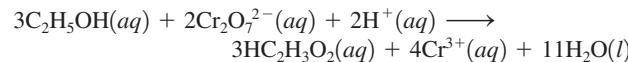
- What happens to the temperature of the rubber band on stretching?
- Is the stretching an exothermic or endothermic process?
- Explain the above result in terms of intermolecular forces.
- What is the sign of  $\Delta S$  and  $\Delta G$  for stretching the rubber band?
- Give the molecular explanation for the sign of  $\Delta S$  for stretching.

- 150.** Alcohols are very useful starting materials for the production of many different compounds. The following conversions, starting with 1-butanol, can be carried out in two or more steps. Show the steps (reactants/catalysts) you would follow to carry out the conversions, drawing the formula for the organic product in each step. For each step, a major product must be produced.

See Exercise 62. Hint: in the presence of  $H^+$ , an alcohol is converted into an alkene and water. This is the exact reverse of the reaction of adding water to an alkene to form an alcohol.

- 1-butanol  $\longrightarrow$  butane
- 1-butanol  $\longrightarrow$  2-butanone

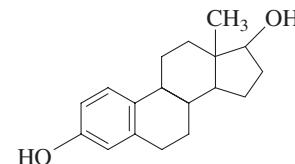
- 151.** A chemical “breathalyzer” test works because ethyl alcohol in the breath is oxidized by the dichromate ion (orange) to form acetic acid and chromium(III) ion (green). The balanced reaction is



You analyze a breathalyzer test in which 4.2 mg of  $K_2Cr_2O_7$  was reduced. Assuming the volume of the breath was 0.500 L at 30.°C and 750. mm Hg, what was the mole percent alcohol of the breath?

- 152.** Consider a sample of a hydrocarbon at 0.959 atm and 298 K. Upon combusting the entire sample in oxygen, you collect a mixture of gaseous carbon dioxide and water vapor at 1.51 atm and 375 K. This mixture has a density of 1.391 g/L and occupies a volume four times as large as that of the pure hydrocarbon. Determine the molecular formula of the hydrocarbon and name it.

- 153.** Estradiol is a female hormone with the following structure:



How many chiral carbon atoms are in estradiol?

## Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

- 154.** Helicenes are extended fused polyaromatic hydrocarbons that have a helical or screw-shaped structure.

- A 0.1450-g sample of solid helicene is combusted in air to give 0.5063 g of  $CO_2$ . What is the empirical formula of this helicene?
- If a 0.0938-g sample of this helicene is dissolved in 12.5 g of solvent to give a  $0.0175\text{ }m$  solution, what is the molecular formula of this helicene?
- What is the balanced reaction for the combustion of this helicene?

- 155.** An organometallic compound is one containing at least one metal–carbon bond. An example of an organometallic species is  $(CH_3CH_2)MBr$ , which contains a metal–ethyl bond.

- If  $M^{2+}$  has the electron configuration  $[Ar]3d^{10}$ , what is the percent by mass of M in  $(CH_3CH_2)MBr$ ?
- One of the reactions in which  $(CH_3CH_2)MBr$  becomes involved is the conversion of a ketone to an alcohol as illustrated here:



How does the hybridization of the starred carbon atom change, if at all, in going from reactants to products?

- c. What is the systematic name of the product?

*Hint:* In this shorthand notation, all the C—H bonds have been eliminated and the lines represent C—C bonds, unless shown differently. As is typical of most organic compounds, each carbon atom has four bonds to it and the oxygen atoms have only two bonds.

## Marathon Problems

These problems are designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

156. For each of the following, fill in the blank with the correct response. All of these fill-in-the-blank problems pertain to material covered in the sections on alkanes, alkenes and alkynes, aromatic hydrocarbons, and hydrocarbon derivatives.
- The first “organic” compound to be synthesized in the laboratory, rather than being isolated from nature, was \_\_\_\_\_, which was prepared from \_\_\_\_\_.
  - An organic compound whose carbon–carbon bonds are all single bonds is said to be \_\_\_\_\_.
  - The general orientation of the four pairs of electrons around the carbon atoms in alkanes is \_\_\_\_\_.
  - Alkanes in which the carbon atoms form a single unbranched chain are said to be \_\_\_\_\_ alkanes.
  - Structural isomerism occurs when two molecules have the same number of each type of atom but exhibit different arrangements of the \_\_\_\_\_ between those atoms.
  - The systematic names of all saturated hydrocarbons have the ending \_\_\_\_\_ added to a root name that indicates the number of carbon atoms in the molecule.
  - For a branched hydrocarbon, the root name for the hydrocarbon comes from the number of carbon atoms in the \_\_\_\_\_ continuous chain in the molecule.
  - The positions of substituents along the hydrocarbon framework of a molecule are indicated by the \_\_\_\_\_ of the carbon atom to which the substituents are attached.
  - The major use of alkanes has been in \_\_\_\_\_ reactions, as a source of heat and light.
  - With very reactive agents, such as, the halogen elements, alkanes undergo \_\_\_\_\_ reactions, whereby a new atom replaces one or more hydrogen atoms of the alkane.
  - Alkenes and alkynes are characterized by their ability to undergo rapid, complete \_\_\_\_\_ reactions, by which other atoms attach themselves to the carbon atoms of the double or triple bond.
  - Unsaturated fats may be converted to saturated fats by the process of \_\_\_\_\_.
  - Benzene is the parent member of the group of hydrocarbons called \_\_\_\_\_ hydrocarbons.
  - An atom or group of atoms that imparts new and characteristic properties to an organic molecule is called a \_\_\_\_\_ group.
  - A \_\_\_\_\_ alcohol is one in which there is only one hydrocarbon group attached to the carbon atom holding the hydroxyl group.
  - The simplest alcohol, methanol, is prepared industrially by the hydrogenation of \_\_\_\_\_.
  - Ethanol is commonly prepared by the \_\_\_\_\_ of certain sugars by yeast.
  - Both aldehydes and ketones contain the \_\_\_\_\_ group, but they differ in where this group occurs along the hydrocarbon chain.
  - Aldehydes and ketones can be prepared by \_\_\_\_\_ of the corresponding alcohol.
  - Organic acids, which contain the \_\_\_\_\_ group, are typically weak acids.

- The typically sweet-smelling compounds called \_\_\_\_\_ result from the condensation reaction of an organic acid with an \_\_\_\_\_.

157. Choose one of the following terms to match the description given in statements (1)–(17). All of the following pertain to proteins or carbohydrates.

- |                      |                      |                      |
|----------------------|----------------------|----------------------|
| a. aldohexose        | g. disaccharides     | m. ketohexoses       |
| b. saliva            | h. disulfide         | n. oxytocin          |
| c. cellulose         | i. globular          | o. pleated sheet     |
| d. CH <sub>2</sub> O | j. glycogen          | p. polypeptide       |
| e. cysteine          | k. glycoside linkage | q. primary structure |
| f. denaturation      | l. hydrophobic       |                      |

- (1) polymer consisting of many amino acids
- (2) linkage that forms between two cysteine species
- (3) peptide hormone that triggers milk secretion
- (4) proteins with roughly spherical shape
- (5) sequence of amino acids in a protein
- (6) silk protein secondary structure
- (7) water-repelling amino acid side chain
- (8) amino acid responsible for permanent wave in hair
- (9) breakdown of a protein’s tertiary and/or secondary structure
- (10) animal polymer of glucose
- (11) —C—O—C— bond between rings in disaccharide sugars
- (12) empirical formula leading to the name carbohydrate
- (13) where enzymes catalyzing the breakdown of glycoside linkages are found
- (14) six-carbon ketone sugars
- (15) structural component of plants, polymer of glucose
- (16) sugars consisting of two monomer units
- (17) six-carbon aldehyde sugars

158. For each of the following, fill in the blank with the correct response(s). All of the following pertain to nucleic acids.

- The substance in the nucleus of the cell that stores and transmits genetic information is DNA, which stands for \_\_\_\_\_.
- The basic repeating monomer units of DNA and RNA are called \_\_\_\_\_.
- The pentose deoxyribose is found in DNA, whereas \_\_\_\_\_ is found in RNA.
- The basic linkage in DNA or RNA between the sugar molecule and phosphoric acid is a phosphate \_\_\_\_\_ linkage.
- The bases on opposite strands of DNA are said to be \_\_\_\_\_ to each other, which means the bases fit together specifically by hydrogen bonding to one another.
- In a strand of normal DNA, the base \_\_\_\_\_ is always found paired with the base adenine, whereas \_\_\_\_\_ is always found paired with cytosine.
- A given segment of the DNA molecule, which contains the molecular coding for a specific protein to be synthesized, is referred to as a \_\_\_\_\_.
- During protein synthesis, \_\_\_\_\_ RNA molecules attach to and transport specific amino acids to the appropriate position on the pattern provided by \_\_\_\_\_ RNA molecules.
- The codes specified by \_\_\_\_\_ are responsible for assembling the correct primary structure of proteins.



Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at [college.hmco.com/PIC/zumdahl7e](http://college.hmco.com/PIC/zumdahl7e).

# Appendices

## Appendix One Mathematical Procedures

### A1.1 Exponential Notation

The numbers characteristic of scientific measurements are often very large or very small; thus it is convenient to express them using powers of 10. For example, the number 1,300,000 can be expressed as  $1.3 \times 10^6$ , which means multiply 1.3 by 10 six times, or

$$1.3 \times 10^6 = 1.3 \times \underbrace{10 \times 10 \times 10 \times 10 \times 10 \times 10}_{10^6} = 1 \text{ million}$$

Note that each multiplication by 10 moves the decimal point one place to the right:

$$\begin{aligned} 1.3 \times 10 &= 13. \\ 13 \times 10 &= 130. \\ 130 \times 10 &= 1300. \\ &\vdots \end{aligned}$$

Thus the easiest way to interpret the notation  $1.3 \times 10^6$  is that it means move the decimal point in 1.3 to the right six times:

$$1.3 \times 10^6 = \underbrace{1 \ 3 \ 0 \ 0 \ 0 \ 0 \ 0}_{\substack{\text{1 2 3 4 5 6}}} = 1,300,000$$

Using this notation, the number 1985 can be expressed as  $1.985 \times 10^3$ . Note that the usual convention is to write the number that appears before the power of 10 as a number between 1 and 10. To end up with the number 1.985, which is between 1 and 10, we had to move the decimal point three places to the left. To compensate for that, we must multiply by  $10^3$ , which says that to get the intended number we start with 1.985 and move the decimal point three places to the right; that is:

$$1.985 \times 10^3 = \underbrace{1 \ 9 \ 8 \ 5}_{\substack{\text{1 2 3}}}$$

Some other examples are given below.

Number	Exponential Notation
5.6	$5.6 \times 10^0$ or $5.6 \times 1$
39	$3.9 \times 10^1$
943	$9.43 \times 10^2$
1126	$1.126 \times 10^3$

So far we have considered numbers greater than 1. How do we represent a number such as 0.0034 in exponential notation? We start with a number between 1 and 10 and *divide* by the appropriate power of 10:

$$0.0034 = \frac{3.4}{10 \times 10 \times 10} = \frac{3.4}{10^3} = 3.4 \times 10^{-3}$$

Division by 10 moves the decimal point one place to the *left*. Thus the number

$$\begin{array}{r} 0.0000014 \\ \hline 7654321 \end{array}$$

can be written as  $1.4 \times 10^{-7}$ .

To summarize, we can write any number in the form

$$N \times 10^{\pm n}$$

where  $N$  is between 1 and 10 and the exponent  $n$  is an integer. If the sign preceding  $n$  is positive, it means the decimal point in  $N$  should be moved  $n$  places to the right. If a negative sign precedes  $n$ , the decimal point in  $N$  should be moved  $n$  places to the left.

## Multiplication and Division

When two numbers expressed in exponential notation are multiplied, the initial numbers are multiplied and the exponents of 10 are added:

$$(M \times 10^m)(N \times 10^n) = (MN) \times 10^{m+n}$$

For example (to two significant figures, as required),

$$(3.2 \times 10^4)(2.8 \times 10^3) = 9.0 \times 10^7$$

When the numbers are multiplied, if a result greater than 10 is obtained for the initial number, the decimal point is moved one place to the left and the exponent of 10 is increased by 1:

$$\begin{aligned} (5.8 \times 10^2)(4.3 \times 10^8) &= 24.9 \times 10^{10} \\ &= 2.49 \times 10^{11} \\ &= 2.5 \times 10^{11} \quad (\text{two significant figures}) \end{aligned}$$

Division of two numbers expressed in exponential notation involves normal division of the initial numbers and *subtraction* of the exponent of the divisor from that of the dividend. For example,

$$\frac{4.8 \times 10^8}{\underbrace{2.1 \times 10^3}_{\text{Divisor}}} = \frac{4.8}{2.1} \times 10^{(8-3)} = 2.3 \times 10^5$$

If the initial number resulting from the division is less than 1, the decimal point is moved one place to the right and the exponent of 10 is decreased by 1. For example,

$$\begin{aligned} \frac{6.4 \times 10^3}{8.3 \times 10^5} &= \frac{6.4}{8.3} \times 10^{(3-5)} = 0.77 \times 10^{-2} \\ &= 7.7 \times 10^{-3} \end{aligned}$$

## Addition and Subtraction

To add or subtract numbers expressed in exponential notation, *the exponents of the numbers must be the same*. For example, to add  $1.31 \times 10^5$  and  $4.2 \times 10^4$ , we must rewrite one number so that the exponents of both are the same. The number  $1.31 \times 10^5$  can be written  $13.1 \times 10^4$ , since moving the decimal point one place to the right can be compensated for by decreasing the exponent by 1. Now we can add the numbers:

$$\begin{array}{r} 13.1 \times 10^4 \\ + 4.2 \times 10^4 \\ \hline 17.3 \times 10^4 \end{array}$$

In correct exponential notation the result is expressed as  $1.73 \times 10^5$ .

To perform addition or subtraction with numbers expressed in exponential notation, only the initial numbers are added or subtracted. The exponent of the result is the same as those of the numbers being added or subtracted. To subtract  $1.8 \times 10^2$  from  $8.99 \times 10^3$ , we write

$$\begin{array}{r} 8.99 \times 10^3 \\ - 0.18 \times 10^3 \\ \hline 8.81 \times 10^3 \end{array}$$

## Powers and Roots

When a number expressed in exponential notation is taken to some power, the initial number is taken to the appropriate power and the exponent of 10 is multiplied by that power:

$$(N \times 10^n)^m = N^m \times 10^{m \cdot n}$$

For example,\*

$$\begin{aligned} (7.5 \times 10^2)^3 &= 7.5^3 \times 10^{3 \cdot 2} \\ &= 422 \times 10^6 \\ &= 4.22 \times 10^8 \\ &= 4.2 \times 10^8 \quad (\text{two significant figures}) \end{aligned}$$

When a root is taken of a number expressed in exponential notation, the root of the initial number is taken and the exponent of 10 is divided by the number representing the root:

$$\sqrt{N \times 10^n} = (n \times 10^n)^{1/2} = \sqrt{N} \times 10^{n/2}$$

For example,

$$\begin{aligned} (2.9 \times 10^6)^{1/2} &= \sqrt{2.9} \times 10^{6/2} \\ &= 1.7 \times 10^3 \end{aligned}$$

Because the exponent of the result must be an integer, we may sometimes have to change the form of the number so that the power divided by the root equals an integer. For example,

$$\begin{aligned} \sqrt{1.9 \times 10^3} &= (1.9 \times 10^3)^{1/2} = (0.19 \times 10^4)^{1/2} \\ &= \sqrt{0.19} \times 10^2 \\ &= 0.44 \times 10^2 \\ &= 4.4 \times 10^1 \end{aligned}$$

In this case, we moved the decimal point one place to the left and increased the exponent from 3 to 4 to make  $n/2$  an integer.

The same procedure is followed for roots other than square roots. For example,

$$\begin{aligned} \sqrt[3]{6.9 \times 10^5} &= (6.9 \times 10^5)^{1/3} = (0.69 \times 10^6)^{1/3} \\ &= \sqrt[3]{0.69} \times 10^2 \\ &= 0.88 \times 10^2 \\ &= 8.8 \times 10^1 \end{aligned}$$

and

$$\begin{aligned} \sqrt[3]{4.6 \times 10^{10}} &= (4.6 \times 10^{10})^{1/3} = (46 \times 10^9)^{1/3} \\ &= \sqrt[3]{46} \times 10^3 \\ &= 3.6 \times 10^3 \end{aligned}$$

---

\*Refer to the instruction booklet for your calculator for directions concerning how to take roots and powers of numbers.

## A1.2 Logarithms

A logarithm is an exponent. Any number  $N$  can be expressed as follows:

$$N = 10^x$$

For example,

$$1000 = 10^3$$

$$100 = 10^2$$

$$10 = 10^1$$

$$1 = 10^0$$

The common, or base 10, logarithm of a number is the power to which 10 must be taken to yield the number. Thus, since  $1000 = 10^3$ ,

$$\log 1000 = 3$$

Similarly,

$$\log 100 = 2$$

$$\log 10 = 1$$

$$\log 1 = 0$$

For a number between 10 and 100, the required exponent of 10 will be between 1 and 2. For example,  $65 = 10^{1.8129}$ , that is,  $\log 65 = 1.8129$ . For a number between 100 and 1000, the exponent of 10 will be between 2 and 3. For example,  $650 = 10^{2.8129}$  and  $\log 650 = 2.8129$ .

A number  $N$  greater than 0 and less than 1 can be expressed as follows:

$$N = 10^{-x} = \frac{1}{10^x}$$

For example,

$$0.001 = \frac{1}{1000} = \frac{1}{10^3} = 10^{-3}$$

$$0.01 = \frac{1}{100} = \frac{1}{10^2} = 10^{-2}$$

$$0.1 = \frac{1}{10} = \frac{1}{10^1} = 10^{-1}$$

Thus

$$\log 0.001 = -3$$

$$\log 0.01 = -2$$

$$\log 0.1 = -1$$

Although common logs are often tabulated, the most convenient method for obtaining such logs is to use an electronic calculator. On most calculators the number is first entered and then the log key is punched. The log of the number then appears in the display.\* Some examples are given below. You should reproduce these results on your calculator to be sure that you can find common logs correctly.

Number	Common Log
36	1.56
1849	3.2669
0.156	-0.807
$1.68 \times 10^{-5}$	-4.775

\*Refer to the instruction booklet for your calculator for the exact sequence to obtain logarithms.

Note that the number of digits after the decimal point in a common log is equal to the number of significant figures in the original number.

Since logs are simply exponents, they are manipulated according to the rules for exponents. For example, if  $A = 10^x$  and  $B = 10^y$ , then their product is

$$A \cdot B = 10^x \cdot 10^y = 10^{x+y}$$

and

$$\log AB = x + y = \log A + \log B$$

For division, we have

$$\frac{A}{B} = \frac{10^x}{10^y} = 10^{x-y}$$

and

$$\log \frac{A}{B} = x - y = \log A - \log B$$

For a number raised to a power, we have

$$A^n = (10^x)^n = 10^{nx}$$

and

$$\log A^n = nx = n \log A$$

It follows that

$$\log \frac{1}{A^n} = \log A^{-n} = -n \log A$$

or, for  $n = 1$ ,

$$\log \frac{1}{A} = -\log A$$

When a common log is given, to find the number it represents, we must carry out the process of exponentiation. For example, if the log is 2.673, then  $N = 10^{2.673}$ . The process of exponentiation is also called taking the antilog, or the inverse logarithm. This operation is usually carried out on calculators in one of two ways. The majority of calculators require that the log be entered first and then the keys [INV] and [LOG] pressed in succession. For example, to find  $N = 10^{2.673}$  we enter 2.673 and then press [INV] and [LOG]. The number 471 will be displayed; that is,  $N = 471$ . Some calculators have a [ $10^x$ ] key. In that case, the log is entered first and then the [ $10^x$ ] key is pressed. Again, the number 471 will be displayed.

Natural logarithms, another type of logarithm, are based on the number 2.7183, which is referred to as  $e$ . In this case, a number is represented as  $N = e^x = 2.7183^x$ . For example,

$$N = 7.15 = e^x$$

$$\ln 7.15 = x = 1.967$$

To find the natural log of a number using a calculator, the number is entered and then the [ $\ln$ ] key is pressed. Use the following examples to check your technique for finding natural logs with your calculator:

Number ( $e^x$ )	Natural Log(x)
784	6.664
$1.61 \times 10^3$	7.384
$1.00 \times 10^{-7}$	-16.118
1.00	0

If a natural logarithm is given, to find the number it represents, exponentiation to the base  $e$  (2.7183) must be carried out. With many calculators this is done using a key marked  $[e^x]$  (the natural log is entered, with the correct sign, and then the  $[e^x]$  key is pressed). The other common method for exponentiation to base  $e$  is to enter the natural log and then press the  $[INV]$  and  $[ln]$  keys in succession. The following examples will help you check your technique:

$\ln N(x)$	$N(e^x)$
3.256	25.9
-5.169	$5.69 \times 10^{-3}$
13.112	$4.95 \times 10^5$

Since natural logarithms are simply exponents, they are also manipulated according to the mathematical rules for exponents given earlier for common logs.

## A1.3 Graphing Functions

In interpreting the results of a scientific experiment, it is often useful to make a graph. If possible, the function to be graphed should be in a form that gives a straight line. The equation for a straight line (a *linear equation*) can be represented by the general form

$$y = mx + b$$

where  $y$  is the *dependent variable*,  $x$  is the *independent variable*,  $m$  is the *slope*, and  $b$  is the *intercept* with the  $y$  axis.

To illustrate the characteristics of a linear equation, the function  $y = 3x + 4$  is plotted in Fig. A.1. For this equation  $m = 3$  and  $b = 4$ . Note that the  $y$  intercept occurs when  $x = 0$ . In this case the intercept is 4, as can be seen from the equation ( $b = 4$ ).

The slope of a straight line is defined as the ratio of the rate of change in  $y$  to that in  $x$ :

$$m = \text{slope} = \frac{\Delta y}{\Delta x}$$

For the equation  $y = 3x + 4$ ,  $y$  changes three times as fast as  $x$  (since  $x$  has a coefficient of 3). Thus the slope in this case is 3. This can be verified from the graph. For the triangle shown in Fig. A.1,

$$\Delta y = 34 - 10 = 24 \quad \text{and} \quad \Delta x = 10 - 2 = 8$$

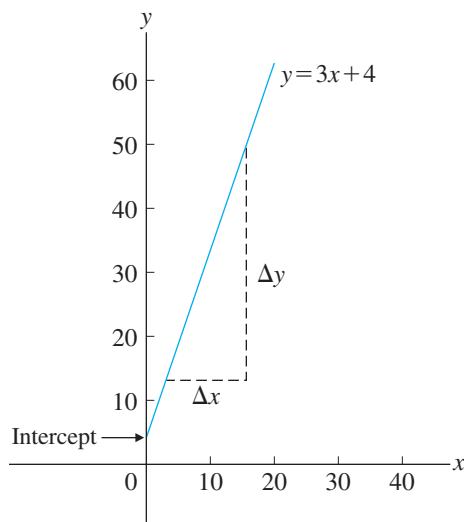
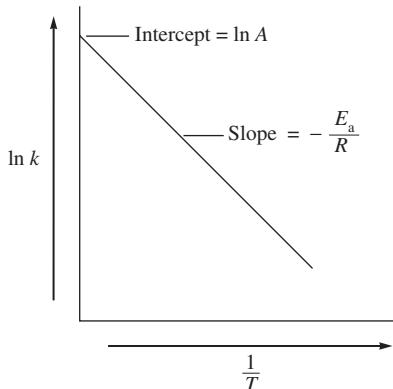


FIGURE A.1

Graph of the linear equation  $y = 3x + 4$ .



**FIGURE A.2**  
Graph of  $\ln k$  versus  $1/T$ .

**TABLE A.1 Some Useful Linear Equations in Standard Form**

Equation ( $y = mx + b$ )	What Is Plotted ( $y$ vs. $x$ )	Slope ( $m$ )	Intercept ( $b$ )	Section in Text
$[A] = -kt + [A]_0$	$[A]$ vs. $t$	$-k$	$[A]_0$	12.4
$\ln[A] = -kt + \ln[A]_0$	$\ln[A]$ vs. $t$	$-k$	$\ln[A]_0$	12.4
$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$	$\frac{1}{[A]}$ vs. $t$	$k$	$\frac{1}{[A]_0}$	12.4
$\ln P_{\text{vap}} = -\frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T} \right) + C$	$\ln P_{\text{vap}}$ vs. $\frac{1}{T}$	$-\frac{\Delta H_{\text{vap}}}{R}$	$C$	10.8

Thus

$$\text{Slope} = \frac{\Delta y}{\Delta x} = \frac{24}{8} = 3$$

The preceding example illustrates a general method for obtaining the slope of a line from the graph of that line. Simply draw a triangle with one side parallel to the  $y$  axis and the other parallel to the  $x$  axis as shown in Fig. A.1. Then determine the lengths of the sides to give  $\Delta y$  and  $\Delta x$ , respectively, and compute the ratio  $\Delta y/\Delta x$ .

Sometimes an equation that is not in standard form can be changed to the form  $y = mx + b$  by rearrangement or mathematical manipulation. An example is the equation  $k = Ae^{-E_a/RT}$  described in Section 12.7, where  $A$ ,  $E_a$ , and  $R$  are constants;  $k$  is the dependent variable; and  $1/T$  is the independent variable. This equation can be changed to standard form by taking the natural logarithm of both sides,

$$\ln k = \ln A e^{-E_a/RT} = \ln A + \ln e^{-E_a/RT} = \ln A - \frac{E_a}{RT}$$

noting that the log of a product is equal to the sum of the logs of the individual terms and that the natural log of  $e^{-E_a/RT}$  is simply the exponent  $-E_a/RT$ . Thus, in standard form, the equation  $k = Ae^{-E_a/RT}$  is written

$$\ln k = -\frac{E_a}{R} \left( \frac{1}{T} \right) + \ln A$$

$\begin{matrix} \uparrow & \uparrow & \uparrow \\ y & m & x \\ \uparrow & \uparrow & \uparrow \\ b \end{matrix}$

A plot of  $\ln k$  versus  $1/T$  (see Fig. A.2) gives a straight line with slope  $-E_a/R$  and intercept  $\ln A$ .

Other linear equations that are useful in the study of chemistry are listed in standard form in Table A.1.

## A1.4 Solving Quadratic Equations

A *quadratic equation*, a polynomial in which the highest power of  $x$  is 2, can be written as

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

One method for finding the two values of  $x$  that satisfy a quadratic equation is to use the *quadratic formula*:

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

where  $a$ ,  $b$ , and  $c$  are the coefficients of  $x^2$  and  $x$  and the constant, respectively. For example, in determining  $[H^+]$  in a solution of  $1.0 \times 10^{-4} M$  acetic acid the following expression arises:

$$1.8 \times 10^{-5} = \frac{x^2}{1.0 \times 10^{-4} - x}$$

which yields

$$x^2 + (1.8 \times 10^{-5})x - 1.8 \times 10^{-9} = 0$$

where  $a = 1$ ,  $b = 1.8 \times 10^{-5}$ , and  $c = -1.8 \times 10^{-9}$ . Using the quadratic formula, we have

$$\begin{aligned} x &= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\ &= \frac{-1.8 \times 10^{-5} \pm \sqrt{3.24 \times 10^{-10} - (4)(1)(-1.8 \times 10^{-9})}}{2(1)} \\ &= \frac{-1.8 \times 10^{-5} \pm \sqrt{3.24 \times 10^{-10} + 7.2 \times 10^{-9}}}{2} \\ &= \frac{-1.8 \times 10^{-5} \pm \sqrt{7.5 \times 10^{-9}}}{2} \\ &= \frac{-1.8 \times 10^{-5} \pm 8.7 \times 10^{-5}}{2} \end{aligned}$$

Thus

$$x = \frac{6.9 \times 10^{-5}}{2} = 3.5 \times 10^{-5}$$

and

$$x = \frac{-10.5 \times 10^{-5}}{2} = -5.2 \times 10^{-5}$$

Note that there are two roots, as there always will be, for a polynomial in  $x^2$ . In this case  $x$  represents a concentration of  $H^+$  (see Section 14.3). Thus the positive root is the one that solves the problem, since a concentration cannot be a negative number.

A second method for solving quadratic equations is by *successive approximations*, a systematic method of trial and error. A value of  $x$  is guessed and substituted into the equation everywhere  $x$  (or  $x^2$ ) appears, except for one place. For example, for the equation

$$x^2 + (1.8 \times 10^{-5})x - 1.8 \times 10^{-9} = 0$$

we might guess  $x = 2 \times 10^{-5}$ . Substituting that value into the equation gives

$$x^2 + (1.8 \times 10^{-5})(2 \times 10^{-5}) - 1.8 \times 10^{-9} = 0$$

or

$$x^2 = 1.8 \times 10^{-9} - 3.6 \times 10^{-10} = 1.4 \times 10^{-9}$$

Thus

$$x = 3.7 \times 10^{-5}$$

Note that the guessed value of  $x(2 \times 10^{-5})$  is not the same as the value of  $x$  that is calculated ( $3.7 \times 10^{-5}$ ) after inserting the estimated value. This means that  $x = 2 \times 10^{-5}$  is not the correct solution, and we must try another guess. We take the calculated value ( $3.7 \times 10^{-5}$ ) as our next guess:

$$\begin{aligned} x^2 + (1.8 \times 10^{-5})(3.7 \times 10^{-5}) - 1.8 \times 10^{-9} &= 0 \\ x^2 = 1.8 \times 10^{-9} - 6.7 \times 10^{-10} &= 1.1 \times 10^{-9} \end{aligned}$$

Thus

$$x = 3.3 \times 10^{-5}$$

Now we compare the two values of  $x$  again:

$$\text{Guessed: } x = 3.7 \times 10^{-5}$$

$$\text{Calculated: } x = 3.3 \times 10^{-5}$$

These values are closer but not close enough. Next we try  $3.3 \times 10^{-5}$  as our guess:

$$x^2 + (1.8 \times 10^{-5})(3.3 \times 10^{-5}) - 1.8 \times 10^{-9} = 0$$

$$x^2 = 1.8 \times 10^{-9} - 5.9 \times 10^{-10} = 1.2 \times 10^{-9}$$

Thus

$$x = 3.5 \times 10^{-5}$$

Again we compare:

$$\text{Guessed: } x = 3.3 \times 10^{-5}$$

$$\text{Calculated: } x = 3.5 \times 10^{-5}$$

Next we guess  $x = 3.5 \times 10^{-5}$  to give

$$x^2 + (1.8 \times 10^{-5})(3.5 \times 10^{-5}) - 1.8 \times 10^{-9} = 0$$

$$x^2 = 1.8 \times 10^{-9} - 6.3 \times 10^{-10} = 1.2 \times 10^{-9}$$

Thus

$$x = 3.5 \times 10^{-5}$$

Now the guessed value and the calculated value are the same; we have found the correct solution. Note that this agrees with one of the roots found with the quadratic formula in the first method.

To further illustrate the method of successive approximations, we will solve Sample Exercise 14.17 using this procedure. In solving for  $[\text{H}^+]$  for  $0.010\text{ M H}_2\text{SO}_4$ , we obtain the following expression:

$$1.2 \times 10^{-2} = \frac{x(0.010 + x)}{0.010 - x}$$

which can be rearranged to give

$$x = (1.2 \times 10^{-2}) \left( \frac{0.010 - x}{0.010 + x} \right)$$

We will guess a value for  $x$ , substitute it into the right side of the equation, and then calculate a value for  $x$ . In guessing a value for  $x$ , we know it must be less than 0.010, since a larger value will make the calculated value for  $x$  negative and the guessed and calculated values will never match. We start by guessing  $x = 0.005$ .

The results of the successive approximations are shown in the following table:

Trial	Guessed Value for $x$	Calculated Value for $x$
1	0.0050	0.0040
2	0.0040	0.0051
3	0.00450	0.00455
4	0.00452	0.00453

Note that the first guess was close to the actual value and that there was oscillation between 0.004 and 0.005 for the guessed and calculated values. For trial 3, an average of

these values was used as the guess, and this led rapidly to the correct value (0.0045 to the correct number of significant figures). Also, note that it is useful to carry extra digits until the correct value is obtained. That value can then be rounded off to the correct number of significant figures.

The method of successive approximations is especially useful for solving polynomials containing  $x$  to a power of 3 or higher. The procedure is the same as for quadratic equations: Substitute a guessed value for  $x$  into the equation for every  $x$  term but one, and then solve for  $x$ . Continue this process until the guessed and calculated values agree.

## A1.5 Uncertainties in Measurements

Like all the physical sciences, chemistry is based on the results of measurements. Every measurement has an inherent uncertainty, so if we are to use the results of measurements to reach conclusions, we must be able to estimate the sizes of these uncertainties.

For example, the specification for a commercial 500-mg acetaminophen (the active painkiller in Tylenol) tablet is that each batch of tablets must contain 450 to 550 mg of acetaminophen per tablet. Suppose that chemical analysis gave the following results for a batch of acetaminophen tablets: 428 mg, 479 mg, 442 mg, and 435 mg. How can we use these results to decide if the batch of tablets meets the specification? Although the details of how to draw such conclusions from measured data are beyond the scope of this text, we will consider some aspects of how this is done. We will focus here on the types of experimental uncertainty, the expression of experimental results, and a simplified method for estimating experimental uncertainty when several types of measurement contribute to the final result.

### Types of Experimental Error

There are two types of experimental uncertainty (error). A variety of names are applied to these types of errors:

$$\begin{array}{lll} \text{Precision} \longleftrightarrow \text{random error} & \equiv & \text{indeterminate error} \\ \text{Accuracy} \longleftrightarrow \text{systematic error} & \equiv & \text{determinate error} \end{array}$$

The difference between the two types of error is well illustrated by the attempts to hit a target shown in Fig. 1.7 in Chapter 1.

Random error is associated with every measurement. To obtain the last significant figure for any measurement, we must always make an estimate. For example, we interpolate between the marks on a meter stick, a buret, or a balance. The precision of replicate measurements (repeated measurements of the same type) reflects the size of the random errors. Precision refers to the reproducibility of replicate measurements.

The accuracy of a measurement refers to how close it is to the true value. An inaccurate result occurs as a result of some flaw (systematic error) in the measurement: the presence of an interfering substance, incorrect calibration of an instrument, operator error, and so on. The goal of chemical analysis is to eliminate systematic error, but random errors can only be minimized. In practice, an experiment is almost always done to find an unknown value (the true value is not known—someone is trying to obtain that value by doing the experiment). In this case the precision of several replicate determinations is used to assess the accuracy of the result. The results of the replicate experiments are expressed as an average (which we assume is close to the true value) with an error limit that gives some indication of how close the average value may be to the true value. The error limit represents the uncertainty of the experimental result.

### Expression of Experimental Results

If we perform several measurements, such as for the analysis for acetaminophen in painkiller tablets, the results should express two things: the average of the measurements and the size of the uncertainty.

There are two common ways of expressing an average: the mean and the median. The mean ( $\bar{x}$ ) is the arithmetic average of the results, or

$$\text{Mean} = \bar{x} = \frac{\sum_{i=1}^n x_i}{n} = \frac{x_1 + x_2 + \cdots + x_n}{n}$$

where  $\Sigma$  means take the sum of the values. The mean is equal to the sum of all the measurements divided by the number of measurements. For the acetaminophen results given previously, the mean is

$$\bar{x} = \frac{428 + 479 + 442 + 435}{4} = 446 \text{ mg}$$

The median is the value that lies in the middle among the results. Half the measurements are above the median and half are below the median. For results of 465 mg, 485 mg, and 492 mg, the median is 485 mg. When there is an even number of results, the median is the average of the two middle results. For the acetaminophen results, the median is

$$\frac{442 + 435}{2} = 438 \text{ mg}$$

There are several advantages to using the median. If a small number of measurements is made, one value can greatly affect the mean. Consider the results for the analysis of acetaminophen: 428 mg, 479 mg, 442 mg, and 435 mg. The mean is 446 mg, which is larger than three of the four weights. The median is 438 mg, which lies near the three values that are relatively close to one another.

In addition to expressing an average value for a series of results, we must express the uncertainty. This usually means expressing either the precision of the measurements or the observed range of the measurements. The range of a series of measurements is defined by the smallest value and the largest value. For the analytical results on the acetaminophen tablets, the range is from 428 mg to 479 mg. Using this range, we can express the results by saying that the true value lies between 428 mg and 479 mg. That is, we can express the amount of acetaminophen in a typical tablet as  $446 \pm 33$  mg, where the error limit is chosen to give the observed range (approximately).

The most common way to specify precision is by the standard deviation,  $s$ , which for a small number of measurements is given by the formula

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

where  $x_i$  is an individual result,  $\bar{x}$  is the average (either mean or median), and  $n$  is the total number of measurements. For the acetaminophen example, we have

$$s = \sqrt{\frac{(428 - 446)^2 + (479 - 446)^2 + (442 - 446)^2 + (435 - 446)^2}{4-1}} = 23$$

Thus we can say the amount of acetaminophen in the typical tablet in the batch of tablets is 446 mg with a sample standard deviation of 23 mg. Statistically this means that any additional measurement has a 68% probability (68 chances out of 100) of being between 423 mg ( $446 - 23$ ) and 469 mg ( $446 + 23$ ). Thus the standard deviation is a measure of the precision of a given type of determination.

The standard deviation gives us a means of describing the precision of a given type of determination using a series of replicate results. However, it is also useful to be able to estimate the precision of a procedure that involves several measurements by combining the precisions of the individual steps. That is, we want to answer the following question:

How do the uncertainties propagate when we combine the results of several different types of measurements? There are many ways to deal with the propagation of uncertainty. We will discuss only one simple method here.

### A Simplified Method for Estimating Experimental Uncertainty

To illustrate this method, we will consider the determination of the density of an irregularly shaped solid. In this determination we make three measurements. First, we measure the mass of the object on a balance. Next, we must obtain the volume of the solid. The easiest method for doing this is to partially fill a graduated cylinder with a liquid and record the volume. Then we add the solid and record the volume again. The difference in the measured volumes is the volume of the solid. We can then calculate the density of the solid from the equation

$$D = \frac{M}{V_2 - V_1}$$

where  $M$  is the mass of the solid,  $V_1$  is the initial volume of liquid in the graduated cylinder, and  $V_2$  is the volume of liquid plus solid. Suppose we get the following results:

$$M = 23.06 \text{ g}$$

$$V_1 = 10.4 \text{ mL}$$

$$V_2 = 13.5 \text{ mL}$$

The calculated density is

$$\frac{23.06 \text{ g}}{13.5 \text{ mL} - 10.4 \text{ mL}} = 7.44 \text{ g/mL}$$

Now suppose that the precision of the balance used is  $\pm 0.02 \text{ g}$  and that the volume measurements are precise to  $\pm 0.05 \text{ mL}$ . How do we estimate the uncertainty of the density? We can do this by assuming a worst case. That is, we assume the largest uncertainties in all measurements, and see what combinations of measurements will give the largest and smallest possible results (the greatest range). Since the density is the mass divided by the volume, the largest value of the density will be that obtained using the largest possible mass and the smallest possible volume:

$$D_{\max} = \frac{23.08}{13.45 - 10.45} = 7.69 \text{ g/mL}$$

Largest possible mass = 23.06 + .02  
 ↙  
 Smallest possible  $V_2$   
 ↘  
 Largest possible  $V_1$

The smallest value of the density is

$$D_{\min} = \frac{23.04}{13.35 - 10.35} = 7.20 \text{ g/mL}$$

Smallest possible mass  
 ↙  
 Largest possible  $V_2$   
 ↘  
 Smallest possible  $V_1$

Thus the calculated range is from 7.20 to 7.69 and the average of these values is 7.44. The error limit is the number that gives the high and low range values when added and subtracted from the average. Therefore, we can express the density as  $7.44 \pm 0.25 \text{ g/mL}$ , which is the average value plus or minus the quantity that gives the range calculated by assuming the largest uncertainties.

Analysis of the propagation of uncertainties is useful in drawing qualitative conclusions from the analysis of measurements. For example, suppose that we obtained the preceding results for the density of an unknown alloy and we want to know if it is one of the following alloys:

$$\text{Alloy A: } D = 7.58 \text{ g/mL}$$

$$\text{Alloy B: } D = 7.42 \text{ g/mL}$$

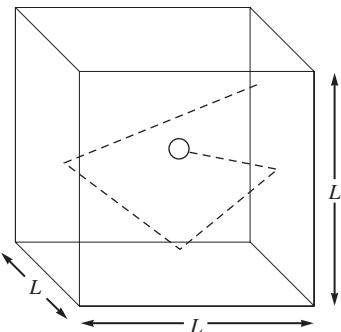
$$\text{Alloy C: } D = 8.56 \text{ g/mL}$$

We can safely conclude that the alloy is not C. But the values of the densities for alloys A and B are both within the inherent uncertainty of our method. To distinguish between A and B, we need to improve the precision of our determination: The obvious choice is to improve the precision of the volume measurement.

The worst-case method is very useful in estimating uncertainties when the results of several measurements are combined to calculate a result. We assume the maximum uncertainty in each measurement and calculate the minimum and maximum possible result. These extreme values describe the range and thus the error limit.

## Appendix Two

## The Quantitative Kinetic Molecular Model



**FIGURE A.3**

An ideal gas particle in a cube whose sides are of length  $L$ . The particle collides elastically with the walls in a random, straight-line motion.

We have seen that the kinetic molecular model successfully accounts for the properties of an ideal gas. This appendix will show in some detail how the postulates of the kinetic molecular model lead to an equation corresponding to the experimentally obtained ideal gas equation.

Recall that the particles of an ideal gas are assumed to be volumeless, to have no attraction for each other, and to produce pressure on their container by colliding with the container walls.

Suppose there are  $n$  moles of an ideal gas in a cubical container with sides each of length  $L$ . Assume each gas particle has a mass  $m$  and that it is in rapid, random, straight-line motion colliding with the walls, as shown in Fig. A.3. The collisions will be assumed to be *elastic*—no loss of kinetic energy occurs. We want to compute the force on the walls from the colliding gas particles and then, since pressure is force per unit area, to obtain an expression for the pressure of the gas.

Before we can derive the expression for the pressure of a gas, we must first discuss some characteristics of velocity. Each particle in the gas has a particular velocity  $u$  that can be divided into components  $u_x$ ,  $u_y$ , and  $u_z$ , as shown in Fig. A.4. First, using  $u_x$  and  $u_y$  and the Pythagorean theorem, we can obtain  $u_{xy}$  as shown in Fig. A.4(c):

$$u_{xy}^2 = u_x^2 + u_y^2$$

Hypotenuse of right triangle      Sides of right triangle

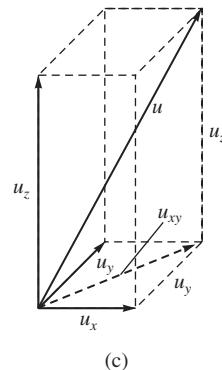
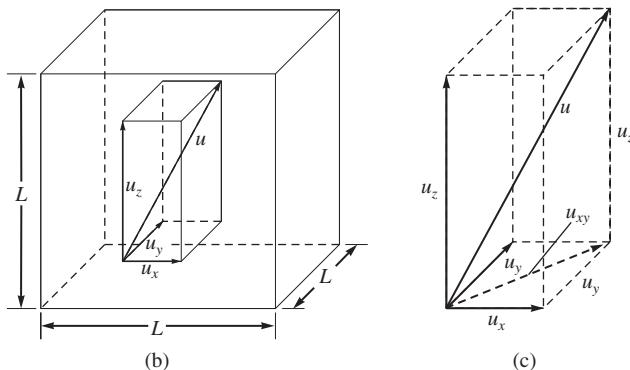
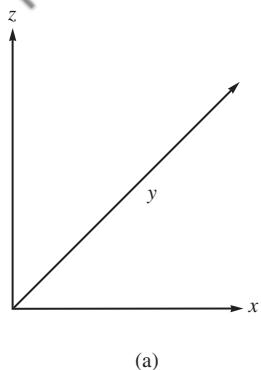
Then, constructing another triangle as shown in Fig. A.4(c), we find

$$u^2 = u_{xy}^2 + u_z^2$$

or

$$u^2 = u_x^2 + u_y^2 + u_z^2$$

Now let's consider how an “average” gas particle moves. For example, how often does this particle strike the two walls of the box that are perpendicular to the  $x$  axis? It is important to realize that only the  $x$  component of the velocity affects the particle’s impacts on these two walls, as shown in Fig. A.5(a). The larger the  $x$  component of the velocity, the faster the particle travels between these two walls, and the more impacts per unit of time it will make on these walls. Remember, the pressure of the gas is due to these collisions with the walls.

**FIGURE A.4**

(a) The Cartesian coordinate axes.

(b) The velocity  $u$  of any gas particle can be broken down into three mutually perpendicular components,  $u_x$ ,  $u_y$ , and  $u_z$ . This can be represented as a rectangular solid with sides  $u_x$ ,  $u_y$ , and  $u_z$  and body diagonal  $u$ .(c) In the  $xy$  plane,

$$u_x^2 + u_y^2 = u_{xy}^2$$

by the Pythagorean theorem. Since  $u_{xy}$  and  $u_x$  are also perpendicular,

$$u^2 = u_{xy}^2 + u_z^2 = u_x^2 + u_y^2 + u_z^2$$

The collision frequency (collisions per unit of time) with the two walls that are perpendicular to the  $x$  axis is given by

$$\begin{aligned} \text{(Collision frequency)}_x &= \frac{\text{velocity in the } x \text{ direction}}{\text{distance between the walls}} \\ &= \frac{u_x}{L} \end{aligned}$$

Next, what is the force of a collision? Force is defined as mass times acceleration (change in velocity per unit of time):

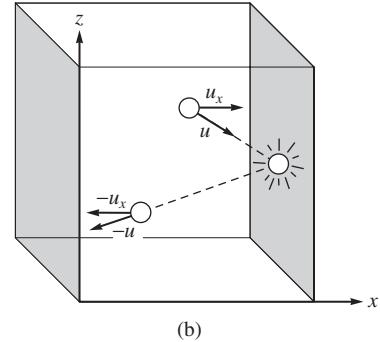
$$F = ma = m\left(\frac{\Delta u}{\Delta t}\right)$$

where  $F$  represents force,  $a$  represents acceleration,  $\Delta u$  represents a change in velocity, and  $\Delta t$  represents a given length of time.

Since we assume that the particle has constant mass, we can write

$$F = \frac{m\Delta u}{\Delta t} = \frac{\Delta(mu)}{\Delta t}$$

The quantity  $mu$  is the momentum of the particle (momentum is the product of mass and velocity), and the expression  $F = \Delta(mu)/\Delta t$  implies that force is the change in momentum per unit of time. When a particle hits a wall perpendicular to the  $x$  axis, as shown in Fig. A.5(b), an elastic collision results in an *exact reversal* of the  $x$  component of velocity. That is, the sign, or direction, of  $u_x$  reverses when the particle collides with one of the walls perpendicular to the  $x$  axis. Thus the final momentum is the *negative*, or opposite, of the initial momentum. Remember that an elastic collision means that there is no change in the *magnitude* of the velocity. The change in momentum in the  $x$  direction is then



(a) Only the  $x$  component of the gas particle's velocity affects the frequency of impacts on the shaded walls, the walls that are perpendicular to the  $x$  axis.  
 (b) For an elastic collision, there is an exact reversal of the  $x$  component of the velocity and of the total velocity. The change in momentum (final – initial) is then

$$-mu_x - mu_x = -2mu_x$$

$$\text{Change in momentum} = \Delta(mu_x) = \text{final momentum} - \text{initial momentum}$$

$$\begin{aligned} &= -mu_x - mu_x \\ &\quad \text{Final momentum in } x \text{ direction} \quad \text{Initial momentum in } x \text{ direction} \end{aligned}$$

$$= -2mu_x$$

But we are interested in the force the gas particle exerts on the walls of the box. Since we know that every action produces an equal but opposite reaction, the change in momentum with respect to the wall on impact is  $-(-2mu_x)$ , or  $2mu_x$ .

Recall that since force is the change in momentum per unit of time,

$$\text{Force}_x = \frac{\Delta(mu_x)}{\Delta t}$$

for the walls perpendicular to the  $x$  axis.

This expression can be obtained by multiplying the change in momentum per impact by the number of impacts per unit of time:

$$\text{Force}_x = (2mu_x) \left( \frac{u_x}{L} \right) = \text{change in momentum per unit of time} \cdot \text{Impacts per unit of time}$$

↑                      ↑  
Change in momentum per impact    Impacts per unit of time

That is,

$$\text{Force}_x = \frac{2mu_x^2}{L}$$

So far we have considered only the two walls of the box perpendicular to the  $x$  axis. We can assume that the force on the two walls perpendicular to the  $y$  axis is given by

$$\text{Force}_y = \frac{2mu_y^2}{L}$$

and that on the two walls perpendicular to the  $z$  axis by

$$\text{Force}_z = \frac{2mu_z^2}{L}$$

Since we have shown that

$$u^2 = u_x^2 + u_y^2 + u_z^2$$

the total force on the box is

$$\begin{aligned}\text{Force}_{\text{TOTAL}} &= \text{force}_x + \text{force}_y + \text{force}_z \\ &= \frac{2mu_x^2}{L} + \frac{2mu_y^2}{L} + \frac{2mu_z^2}{L} \\ &= \frac{2m}{L}(u_x^2 + u_y^2 + u_z^2) = \frac{2m}{L}(u^2)\end{aligned}$$

Now since we want the average force, we use the average of the square of the velocity ( $\bar{u}^2$ ) to obtain

$$\overline{\text{Force}}_{\text{TOTAL}} = \frac{2m}{L}(\bar{u}^2)$$

Next, we need to compute the pressure (force per unit of area)

$$\begin{aligned}\text{Pressure due to "average" particle} &= \frac{\overline{\text{force}}_{\text{TOTAL}}}{\overline{\text{area}}_{\text{TOTAL}}} \\ &= \frac{\frac{2m}{L}(\bar{u}^2)}{\frac{6L^2}{6L^2}} = \frac{m\bar{u}^2}{3L^3} \\ &\quad \uparrow \quad \uparrow \\ &\quad \text{The 6 sides} \quad \text{Area of each side} \quad \text{of the cube} \quad \text{each side}\end{aligned}$$

Since the volume  $V$  of the cube is equal to  $L^3$ , we can write

$$\text{Pressure} = P = \frac{mu^2}{3V}$$

So far we have considered the pressure on the walls due to a single, “average” particle. Of course, we want the pressure due to the entire gas sample. The number of particles in a given gas sample can be expressed as follows:

$$\text{Number of gas particles} = nN_A$$

where  $n$  is the number of moles and  $N_A$  is Avogadro’s number.

The total pressure on the box due to  $n$  moles of a gas is therefore

$$P = nN_A \frac{mu^2}{3V}$$

Next we want to express the pressure in terms of the kinetic energy of the gas molecules. Kinetic energy (the energy due to motion) is given by  $\frac{1}{2}mu^2$ , where  $m$  is the mass and  $u$  is the velocity. Since we are using the average of the velocity squared ( $\bar{u^2}$ ), and since  $mu^2 = 2(\frac{1}{2}mu^2)$ , we have

$$P = \left(\frac{2}{3}\right) \frac{nN_A(\frac{1}{2}mu^2)}{V}$$

or

$$\frac{PV}{n} = \left(\frac{2}{3}\right) N_A(\frac{1}{2}mu^2)$$

Thus, based on the postulates of the kinetic molecular model, we have been able to derive an equation that has the same form as the ideal gas equation,

$$\frac{PV}{n} = RT$$

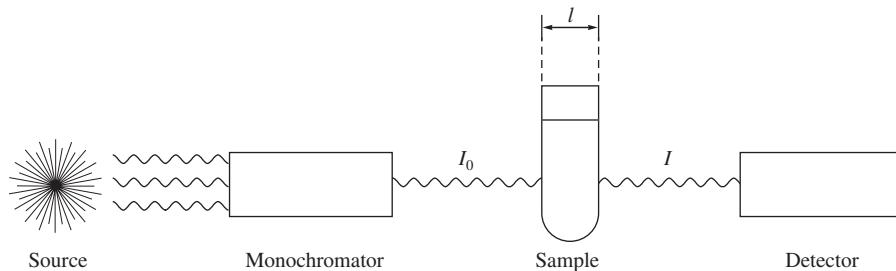
This agreement between experiment and theory supports the validity of the assumptions made in the kinetic molecular model about the behavior of gas particles, at least for the limiting case of an ideal gas.

## Appendix Three Spectral Analysis

Although volumetric and gravimetric analyses are still very commonly used, spectroscopy is the technique most often used for modern chemical analysis. *Spectroscopy* is the study of electromagnetic radiation emitted or absorbed by a given chemical species. Since the quantity of radiation absorbed or emitted can be related to the quantity of the absorbing or emitting species present, this technique can be used for quantitative analysis. There are many spectroscopic techniques, as electromagnetic radiation spans a wide range of energies to include X rays, ultraviolet, infrared, and visible light, and microwaves, to name a few of its familiar forms. We will consider here only one procedure, which is based on the absorption of visible light.

If a liquid is colored, it is because some component of the liquid absorbs visible light. In a solution the greater the concentration of the light-absorbing substance, the more light absorbed, and the more intense the color of the solution.

The quantity of light absorbed by a substance can be measured by a *spectrophotometer*, shown schematically in Fig. A.6. This instrument consists of a source that emits all wavelengths of light in the visible region (wavelengths of  $\sim 400$  to  $700$  nm); a monochromator, which selects a given wavelength of light; a sample holder for the solution

**FIGURE A.6**

A schematic diagram of a simple spectrophotometer. The source emits all wavelengths of visible light, which are dispersed using a prism or grating and then focused, one wavelength at a time, onto the sample. The detector compares the intensity of the incident light ( $I_0$ ) to the intensity of the light after it has passed through the sample ( $I$ ).

being measured; and a detector, which compares the intensity of incident light  $I_0$  to the intensity of light after it has passed through the sample  $I$ . The ratio  $I/I_0$ , called the *transmittance*, is a measure of the fraction of light that passes through the sample. The amount of light absorbed is given by the *absorbance*  $A$ , where

$$A = -\log \frac{I}{I_0}$$

The absorbance can be expressed by the *Beer–Lambert law*:

$$A = \epsilon lc$$

where  $\epsilon$  is the molar absorptivity or the molar extinction coefficient (in L/mol · cm),  $l$  is the distance the light travels through the solution (in cm), and  $c$  is the concentration of the absorbing species (in mol/L). The Beer–Lambert law is the basis for using spectroscopy in quantitative analysis. If  $\epsilon$  and  $l$  are known, measuring  $A$  for a solution allows us to calculate the concentration of the absorbing species in the solution.

Suppose we have a pink solution containing an unknown concentration of  $\text{Co}^{2+}(aq)$  ions. A sample of this solution is placed in a spectrophotometer, and the absorbance is measured at a wavelength where  $\epsilon$  for  $\text{Co}^{2+}(aq)$  is known to be 12 L/mol · cm. The absorbance  $A$  is found to be 0.60. The width of the sample tube is 1.0 cm. We want to determine the concentration of  $\text{Co}^{2+}(aq)$  in the solution. This problem can be solved by a straightforward application of the Beer–Lambert law,

$$A = \epsilon lc$$

where

$$A = 0.60$$

$$\epsilon = \frac{12 \text{ L}}{\text{mol} \cdot \text{cm}}$$

$$l = \text{light path} = 1.0 \text{ cm}$$

Solving for the concentration gives

$$c = \frac{A}{\epsilon l} = \frac{0.60}{\left(12 \frac{\text{L}}{\text{mol} \cdot \text{cm}}\right)(1.0 \text{ cm})} = 5.0 \times 10^{-2} \text{ mol/L}$$

To obtain the unknown concentration of an absorbing species from the measured absorbance, we must know the product  $\epsilon l$ , since

$$c = \frac{A}{\epsilon l}$$

We can obtain the product  $\epsilon l$  by measuring the absorbance of a solution of *known* concentration, since

$$\epsilon l = \frac{A}{c}$$

Measured using a  
spectrophotometer

Known from making up  
the solution

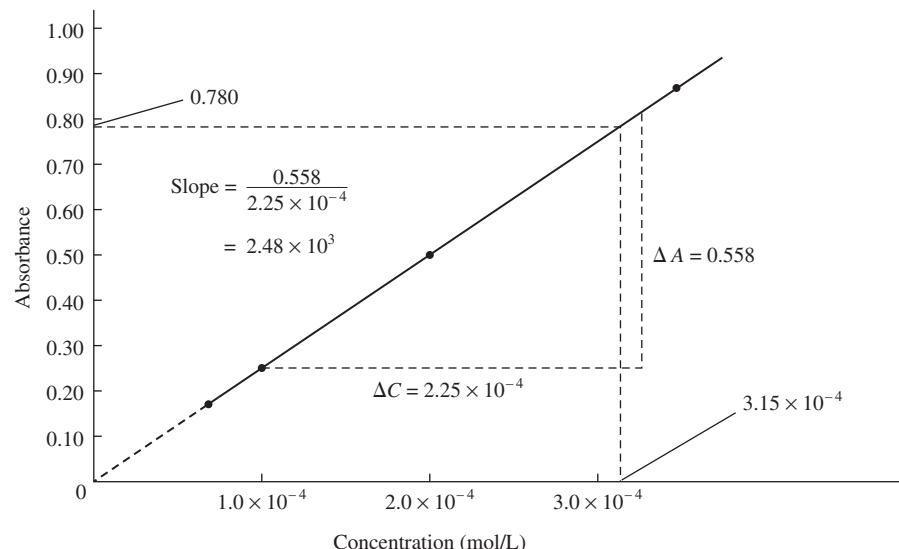
However, a more accurate value of the product  $\epsilon l$  can be obtained by plotting  $A$  versus  $c$  for a series of solutions. Note that the equation  $A = \epsilon lc$  gives a straight line with slope  $\epsilon l$  when  $A$  is plotted against  $c$ .

For example, consider the following typical spectroscopic analysis. A sample of steel from a bicycle frame is to be analyzed to determine its manganese content. The procedure involves weighing out a sample of the steel, dissolving it in strong acid, treating the resulting solution with a very strong oxidizing agent to convert all the manganese to permanganate ion ( $MnO_4^-$ ), and then using spectroscopy to determine the concentration of the intensely purple  $MnO_4^-$  ions in the solution. To do this, however, the value of  $\epsilon l$  for  $MnO_4^-$  must be determined at an appropriate wavelength. The absorbance values for four solutions with known  $MnO_4^-$  concentrations were measured to give the following data:

Solution	Concentration of $MnO_4^-$ (mol/L)	Absorbance
1	$7.00 \times 10^{-5}$	0.175
2	$1.00 \times 10^{-4}$	0.250
3	$2.00 \times 10^{-4}$	0.500
4	$3.50 \times 10^{-4}$	0.875

A plot of absorbance versus concentration for the solutions of known concentration is shown in Fig. A.7. The slope of this line (change in  $A$ /change in  $c$ ) is  $2.48 \times 10^3$  L/mol. This quantity represents the product  $\epsilon l$ .

A sample of the steel weighing 0.1523 g was dissolved and the unknown amount of manganese was converted to  $MnO_4^-$  ions. Water was then added to give a solution with a final volume of 100.0 mL. A portion of this solution was placed in a spectrophotometer,



**FIGURE A.7**

A plot of absorbance versus concentration of  $MnO_4^-$  in a series of solutions of known concentration.

and its absorbance was found to be 0.780. Using these data, we want to calculate the percent manganese in the steel. The  $\text{MnO}_4^-$  ions from the manganese in the dissolved steel sample show an absorbance of 0.780. Using the Beer–Lambert law, we calculate the concentration of  $\text{MnO}_4^-$  in this solution:

$$c = \frac{A}{\epsilon l} = \frac{0.780}{2.48 \times 10^3 \text{ L/mol}} \times 3.15 \times 10^{-4} \text{ mol/L}$$

There is a more direct way for finding  $c$ . Using a graph such as that in Fig. A.7 (often called a *Beer's law plot*), we can read the concentration that corresponds to  $A = 0.780$ . This interpolation is shown by dashed lines on the graph. By this method,  $c = 3.15 \times 10^{-4} \text{ mol/L}$ , which agrees with the value obtained above.

Recall that the original 0.1523-g steel sample was dissolved, the manganese was converted to permanganate, and the volume was adjusted to 100.0 mL. We now know that  $[\text{MnO}_4^-]$  in that solution is  $3.15 \times 10^{-4} M$ . Using this concentration, we can calculate the total number of moles of  $\text{MnO}_4^-$  in that solution:

$$\begin{aligned} \text{mol of } \text{MnO}_4^- &= 100.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times 3.15 \times 10^{-4} \frac{\text{mol}}{\text{L}} \\ &= 3.15 \times 10^{-5} \text{ mol} \end{aligned}$$

Since each mole of manganese in the original steel sample yields a mole of  $\text{MnO}_4^-$ , that is,



the original steel sample must have contained  $3.15 \times 10^{-5}$  mol of manganese. The mass of manganese present in the sample is

$$3.15 \times 10^{-5} \text{ mol of Mn} \times \frac{54.938 \text{ g of Mn}}{1 \text{ mol of Mn}} = 1.73 \times 10^{-3} \text{ g of Mn}$$

Since the steel sample weighed 0.1523 g, the present manganese in the steel is

$$\frac{1.73 \times 10^{-3} \text{ g of Mn}}{1.523 \times 10^{-1} \text{ g of sample}} \times 100 = 1.14\%$$

This example illustrates a typical use of spectroscopy in quantitative analysis. The steps commonly involved are as follows:

1. Preparation of a calibration plot (a Beer's law plot) by measuring the absorbance values of a series of solutions with known concentrations.
2. Measurement of the absorbance of the solution of unknown concentration.
3. Use of the calibration plot to determine the unknown concentration.

## Appendix Four Selected Thermodynamic Data

Note: All values are assumed precise to at least  $\pm 1$ .

Substance and State	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)	$S^\circ$ (J/K · mol)
Aluminum			
Al(s)	0	0	28
Al <sub>2</sub> O <sub>3</sub> (s)	-1676	-1582	51
Al(OH) <sub>3</sub> (s)	-1277		
AlCl <sub>3</sub> (s)	-704	-629	111

Substance and State	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)	$S^\circ$ (J/K · mol)
Barium			
Ba(s)	0	0	67
BaCO <sub>3</sub> (s)	-1219	-1139	112
BaO(s)	-582	-552	70
Ba(OH) <sub>2</sub> (s)	-946		

(continued)

**A20** Appendices

**Appendix Four (continued)**

<b>Substance and State</b>	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)	$S^\circ$ (J/K · mol)
<i>Baesium, continued</i>			
BaSO <sub>4</sub> (s)	-1465	-1353	132
<i>Beryllium</i>			
Be(s)	0	0	10
BeO(s)	-599	-569	14
Be(OH) <sub>2</sub> (s)	-904	-815	47
<i>Bromine</i>			
Br <sub>2</sub> (l)	0	0	152
Br <sub>2</sub> (g)	31	3	245
Br <sub>2</sub> (aq)	-3	4	130
Br <sup>-</sup> (aq)	-121	-104	82
HBr(g)	-36	-53	199
<i>Cadmium</i>			
Cd(s)	0	0	52
CdO(s)	-258	-228	55
Cd(OH) <sub>2</sub> (s)	-561	-474	96
CdS(s)	-162	-156	65
CdSO <sub>4</sub> (s)	-935	-823	123
<i>Calcium</i>			
Ca(s)	0	0	41
CaC <sub>2</sub> (s)	-63	-68	70
CaCO <sub>3</sub> (s)	-1207	-1129	93
CaO(s)	-635	-604	40
Ca(OH) <sub>2</sub> (s)	-987	-899	83
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (s)	-4126	-3890	241
CaSO <sub>4</sub> (s)	-1433	-1320	107
CaSiO <sub>3</sub> (s)	-1630	-1550	84
<i>Carbon</i>			
C(s) (graphite)	0	0	6
C(s) (diamond)	2	3	2
CO(g)	-110.5	-137	198
CO <sub>2</sub> (g)	-393.5	-394	214
CH <sub>4</sub> (g)	-75	-51	186
CH <sub>3</sub> OH(g)	-201	-163	240
CH <sub>3</sub> OH(l)	-239	-166	127
H <sub>2</sub> CO(g)	-116	-110	219
HCOOH(g)	-363	-351	249
HCN(g)	135.1	125	202
C <sub>2</sub> H <sub>2</sub> (g)	227	209	201
C <sub>2</sub> H <sub>4</sub> (g)	52	68	219
CH <sub>3</sub> CHO(g)	-166	-129	250
C <sub>2</sub> H <sub>5</sub> OH(l)	-278	-175	161
C <sub>2</sub> H <sub>6</sub> (g)	-84.7	-32.9	229.5
C <sub>3</sub> H <sub>6</sub> (g)	20.9	62.7	266.9
C <sub>3</sub> H <sub>8</sub> (g)	-104	-24	270
C <sub>2</sub> H <sub>4</sub> O(g) (ethylene oxide)	-53	-13	242
CH <sub>2</sub> =CHCN(g)	185.0	195.4	274
CH <sub>3</sub> COOH(l)	-484	-389	160
C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> (s)	-1275	-911	212
CCl <sub>4</sub>	-135	-65	216
<i>Chlorine</i>			
Cl <sub>2</sub> (g)	0	0	223
Cl <sub>2</sub> (aq)	-23	7	121

<b>Substance and State</b>	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)	$S^\circ$ (J/K · mol)
<i>Chlorine, continued</i>			
Cl <sup>-</sup> (aq)	-167	-131	57
HCl(g)	-92	-95	187
<i>Chromium</i>			
Cr(s)	0	0	24
Cr <sub>2</sub> O <sub>3</sub> (s)	-1128	-1047	81
CrO <sub>3</sub> (s)	-579	-502	72
<i>Copper</i>			
Cu(s)	0	0	33
CuCO <sub>3</sub> (s)	-595	-518	88
Cu <sub>2</sub> O(s)	-170	-148	93
CuO(s)	-156	-128	43
Cu(OH) <sub>2</sub> (s)	-450	-372	108
CuS(s)	-49	-49	67
<i>Fluorine</i>			
F <sub>2</sub> (g)	0	0	203
F <sup>-</sup> (aq)	-333	-279	-14
HF(g)	-271	-273	174
<i>Hydrogen</i>			
H <sub>2</sub> (g)	0	0	131
H(g)	217	203	115
H <sup>+</sup> (aq)	0	0	0
OH <sup>-</sup> (aq)	-230	-157	-11
H <sub>2</sub> O(l)	-286	-237	70
H <sub>2</sub> O(g)	-242	-229	189
<i>Iodine</i>			
I <sub>2</sub> (s)	0	0	116
I <sub>2</sub> (g)	62	19	261
I <sub>2</sub> (aq)	23	16	137
I <sup>-</sup> (aq)	-55	-52	106
<i>Iron</i>			
Fe(s)	0	0	27
Fe <sub>3</sub> C(s)	21	15	108
Fe <sub>0.95</sub> O(s) (wustite)	-264	-240	59
FeO	-272	-255	61
Fe <sub>3</sub> O <sub>4</sub> (s) (magnetite)	-1117	-1013	146
Fe <sub>2</sub> O <sub>3</sub> (s) (hematite)	-826	-740	90
FeS(s)	-95	-97	67
FeS <sub>2</sub> (s)	-178	-166	53
FeSO <sub>4</sub> (s)	-929	-825	121
<i>Lead</i>			
Pb(s)	0	0	65
PbO <sub>2</sub> (s)	-277	-217	69
PbS(s)	-100	-99	91
PbSO <sub>4</sub> (s)	-920	-813	149
<i>Magnesium</i>			
Mg(s)	0	0	33
MgCO <sub>3</sub> (s)	-1113	-1029	66
MgO(s)	-602	-569	27
Mg(OH) <sub>2</sub> (s)	-925	-834	64
<i>Manganese</i>			
Mn(s)	0	0	32

## Appendix Four (continued)

Substance and State	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)	$S^\circ$ (J/K · mol)	Substance and State	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)	$S^\circ$ (J/K · mol)				
<b>Manganese, continued</b>											
MnO(s)	-385	-363	60	KClO <sub>3</sub> (s)	-391	-290	143				
Mn <sub>3</sub> O <sub>4</sub> (s)	-1387	-1280	149	KClO <sub>4</sub> (s)	-433	-304	151				
Mn <sub>2</sub> O <sub>3</sub> (s)	-971	-893	110	K <sub>2</sub> O(s)	-361	-322	98				
MnO <sub>2</sub> (s)	-521	-466	53	K <sub>2</sub> O <sub>2</sub> (s)	-496	-430	113				
MnO <sub>4</sub> <sup>-</sup> (aq)	-543	-449	190	KO <sub>2</sub> (s)	-283	-238	117				
<b>Mercury</b>											
Hg(l)	0	0	76	KOH(s)	-425	-379	79				
Hg <sub>2</sub> Cl <sub>2</sub> (s)	-265	-211	196	KOH(aq)	-481	-440	9.20				
HgCl <sub>2</sub> (s)	-230	-184	144	<b>Silicon</b>							
HgO(s)	-90	-59	70	SiO <sub>2</sub> (s) (quartz)	-911	-856	42				
HgS(s)	-58	-49	78	SiCl <sub>4</sub> (l)	-687	-620	240				
<b>Nickel</b>											
Ni(s)	0	0	30	<b>Silver</b>							
NiCl <sub>2</sub> (s)	-316	-272	107	Ag(s)	0	0	43				
NiO(s)	-241	-213	38	Ag <sup>+</sup> (aq)	105	77	73				
Ni(OH) <sub>2</sub> (s)	-538	-453	79	AgBr(s)	-100	-97	107				
NiS(s)	-93	-90	53	AgCN(s)	146	164	84				
<b>Nitrogen</b>											
N <sub>2</sub> (g)	0	0	192	AgCl(s)	-127	-110	96				
NH <sub>3</sub> (g)	-46	-17	193	Ag <sub>2</sub> CrO <sub>4</sub> (s)	-712	-622	217				
NH <sub>3</sub> (aq)	-80	-27	111	AgI(s)	-62	-66	115				
NH <sub>4</sub> <sup>+</sup> (aq)	-132	-79	113	Ag <sub>2</sub> O(s)	-31	-11	122				
NO(g)	90	87	211	Ag <sub>2</sub> S(s)	-32	-40	146				
NO <sub>2</sub> (g)	34	52	240	<b>Sodium</b>							
N <sub>2</sub> O(g)	82	104	220	Na(s)	0	0	51				
N <sub>2</sub> O <sub>4</sub> (g)	10	98	304	Na <sup>+</sup> (aq)	-240	-262	59				
N <sub>2</sub> O <sub>4</sub> (l)	-20	97	209	NaBr(s)	-360	-347	84				
N <sub>2</sub> O <sub>5</sub> (s)	-42	134	178	Na <sub>2</sub> CO <sub>3</sub> (s)	-1131	-1048	136				
N <sub>2</sub> H <sub>4</sub> (l)	51	149	121	NaHCO <sub>3</sub> (s)	-948	-852	102				
N <sub>2</sub> H <sub>3</sub> CH <sub>3</sub> (l)	54	180	166	NaCl(s)	-411	-384	72				
HNO <sub>3</sub> (aq)	-207	-111	146	NaH(s)	-56	-33	40				
HNO <sub>3</sub> (l)	-174	-81	156	NaI(s)	-288	-282	91				
NH <sub>4</sub> ClO <sub>4</sub> (s)	-295	-89	186	NaNO <sub>2</sub> (s)	-359						
NH <sub>4</sub> Cl(s)	-314	-203	96	NaNO <sub>3</sub> (s)	-467	-366	116				
<b>Oxygen</b>											
O <sub>2</sub> (g)	0	0	205	Na <sub>2</sub> O(s)	-416	-377	73				
O(g)	249	232	161	Na <sub>2</sub> O <sub>2</sub> (s)	-515	-451	95				
O <sub>3</sub> (g)	143	163	239	NaOH(s)	-427	-381	64				
<b>Phosphorus</b>											
P(s) (white)	0	0	41	NaOH(aq)	-470	-419	50				
P(s) (red)	-18	-12	23	<b>Sulfur</b>							
P(s) (black)	-39	-33	23	S(s) (rhombic)	0	0	32				
P <sub>4</sub> (g)	59	24	280	S(s) (monoclinic)	0.3	0.1	33				
PF <sub>5</sub> (g)	-1578	-1509	296	S <sup>2-</sup> (aq)	33	86	-15				
PH <sub>3</sub> (g)	5	13	210	S <sub>8</sub> (g)	102	50	431				
H <sub>3</sub> PO <sub>4</sub> (s)	-1279	-1119	110	SF <sub>6</sub> (g)	-1209	-1105	292				
H <sub>3</sub> PO <sub>4</sub> (l)	-1267	—	—	H <sub>2</sub> S(g)	-21	-34	206				
H <sub>3</sub> PO <sub>4</sub> (aq)	-1288	-1143	158	SO <sub>2</sub> (g)	-297	-300	248				
P <sub>4</sub> O <sub>10</sub> (s)	-2984	-2698	229	SO <sub>3</sub> (g)	-396	-371	257				
<b>Potassium</b>											
K(s)	0	0	64	SO <sub>4</sub> <sup>2-</sup> (aq)	-909	-745	20				
KCl(s)	-436	-408	83	H <sub>2</sub> SO <sub>4</sub> (l)	-814	-690	157				
<b>Tin</b>											
Sn(s) (white)											
Sn(s) (gray)											
SnO(s)											
SnO <sub>2</sub> (s)											

(continued)

**A22** Appendices

**Appendix Four (continued)**

Substance and State	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)	$S^\circ$ (J/K · mol)	Substance and State	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)	$S^\circ$ (J/K · mol)
Tin, <i>continued</i>				Xenon			
$\text{Sn}(\text{OH})_2(s)$	-561	-492	155	$\text{Xe}(g)$	0	0	170
Titanium				$\text{XeF}_2(g)$	-108	-48	254
$\text{TiCl}_4(g)$	-763	-727	355	$\text{XeF}_4(s)$	-251	-121	146
$\text{TiO}_2(s)$	-945	-890	50	$\text{XeF}_6(g)$	-294		
Uranium				$\text{XeO}_3(s)$	402		
$\text{U}(s)$	0	0	50	Zinc			
$\text{UF}_6(s)$	-2137	-2008	228	$\text{Zn}(s)$	0	0	42
$\text{UF}_6(g)$	-2113	-2029	380	$\text{ZnO}(s)$	-348	-318	44
$\text{UO}_2(s)$	-1084	-1029	78	$\text{Zn}(\text{OH})_2(s)$	-642		
$\text{U}_3\text{O}_8(s)$	-3575	-3393	282	$\text{ZnS}(s)$ (wurtzite)	-193		
$\text{UO}_3(s)$	-1230	-1150	99	$\text{ZnS}(s)$ (zinc blende)	-206	-201	58
				$\text{ZnSO}_4(s)$	-983	-874	120

## Equilibrium Constants and Reduction Potentials

**Appendix Five**

### A5.1 Values of $K_a$ for Some Common Monoprotic Acids

Name	Formula	Value of $K_a$
Hydrogen sulfate ion	$\text{HSO}_4^-$	$1.2 \times 10^{-2}$
Chlorous acid	$\text{HClO}_2$	$1.2 \times 10^{-2}$
Monochloracetic acid	$\text{HC}_2\text{H}_2\text{ClO}_2$	$1.35 \times 10^{-3}$
Hydrofluoric acid	HF	$7.2 \times 10^{-4}$
Nitrous acid	$\text{HNO}_2$	$4.0 \times 10^{-4}$
Formic acid	$\text{HCO}_2\text{H}$	$1.8 \times 10^{-4}$
Lactic acid	$\text{HC}_3\text{H}_5\text{O}_3$	$1.38 \times 10^{-4}$
Benzoic acid	$\text{HC}_7\text{H}_5\text{O}_2$	$6.4 \times 10^{-5}$
Acetic acid	$\text{HC}_2\text{H}_3\text{O}_2$	$1.8 \times 10^{-5}$
Hydrated aluminum(III) ion	$[\text{Al}(\text{H}_2\text{O})_6]^{3+}$	$1.4 \times 10^{-5}$
Propanoic acid	$\text{HC}_3\text{H}_5\text{O}_2$	$1.3 \times 10^{-5}$
Hypochlorous acid	HOCl	$3.5 \times 10^{-8}$
Hypobromous acid	HOBr	$2 \times 10^{-9}$
Hydrocyanic acid	HCN	$6.2 \times 10^{-10}$
Boric acid	$\text{H}_3\text{BO}_3$	$5.8 \times 10^{-10}$
Ammonium ion	$\text{NH}_4^+$	$5.6 \times 10^{-10}$
Phenol	$\text{HO}\text{C}_6\text{H}_5$	$1.6 \times 10^{-10}$
Hypoiodous acid	HOI	$2 \times 10^{-11}$

## A5.2 Stepwise Dissociation Constants for Several Common Polyprotic Acids

Name	Formula	$K_{a_1}$	$K_{a_2}$	$K_{a_3}$
Phosphoric acid	$H_3PO_4$	$7.5 \times 10^{-3}$	$6.2 \times 10^{-8}$	$4.8 \times 10^{-13}$
Arsenic acid	$H_3AsO_4$	$5 \times 10^{-3}$	$8 \times 10^{-8}$	$6 \times 10^{-10}$
Carbonic acid	$H_2CO_3$	$4.3 \times 10^{-7}$	$5.6 \times 10^{-11}$	
Sulfuric acid	$H_2SO_4$	Large	$1.2 \times 10^{-2}$	
Sulfurous acid	$H_2SO_3$	$1.5 \times 10^{-2}$	$1.0 \times 10^{-7}$	
Hydrosulfuric acid	$H_2S$	$1.0 \times 10^{-7}$	$\sim 10^{-19}$	
Oxalic acid	$H_2C_2O_4$	$6.5 \times 10^{-2}$	$6.1 \times 10^{-5}$	
Ascorbic acid (vitamin C)	$H_2C_6H_6O_6$	$7.9 \times 10^{-5}$	$1.6 \times 10^{-12}$	
Citric acid	$H_3C_6H_5O_7$	$8.4 \times 10^{-4}$	$1.8 \times 10^{-5}$	$4.0 \times 10^{-6}$

## A5.3 Values of $K_b$ for Some Common Weak Bases

Name	Conjugate Formula	Acid	$K_b$
Ammonia	$NH_3$	$NH_4^+$	$1.8 \times 10^{-5}$
Methylamine	$CH_3NH_2$	$CH_3NH_3^+$	$4.38 \times 10^{-4}$
Ethylamine	$C_2H_5NH_2$	$C_2H_5NH_3^+$	$5.6 \times 10^{-4}$
Diethylamine	$(C_2H_5)_2NH$	$(C_2H_5)_2NH_2^+$	$1.3 \times 10^{-3}$
Triethylamine	$(C_2H_5)_3N$	$(C_2H_5)_3NH^+$	$4.0 \times 10^{-4}$
Hydroxylamine	$HONH_2$	$HONH_3^+$	$1.1 \times 10^{-8}$
Hydrazine	$H_2NNH_2$	$H_2NNH_3^+$	$3.0 \times 10^{-6}$
Aniline	$C_6H_5NH_2$	$C_6H_5NH_3^+$	$3.8 \times 10^{-10}$
Pyridine	$C_5H_5N$	$C_5H_5NH^+$	$1.7 \times 10^{-9}$

## A5.4 $K_{sp}$ Values at 25°C for Common Ionic Solids

Ionic Solid	$K_{sp}$ (at 25°C)	Ionic Solid	$K_{sp}$ (at 25°C)	Ionic Solid	$K_{sp}$ (at 25°C)
Fluorides		$Hg_2CrO_4^*$	$2 \times 10^{-9}$	$Co(OH)_2$	$2.5 \times 10^{-16}$
$BaF_2$	$2.4 \times 10^{-5}$	$BaCrO_4$	$8.5 \times 10^{-11}$	$Ni(OH)_2$	$1.6 \times 10^{-16}$
$MgF_2$	$6.4 \times 10^{-9}$	$Ag_2CrO_4$	$9.0 \times 10^{-12}$	$Zn(OH)_2$	$4.5 \times 10^{-17}$
$PbF_2$	$4 \times 10^{-8}$	$PbCrO_4$	$2 \times 10^{-16}$	$Cu(OH)_2$	$1.6 \times 10^{-19}$
$SrF_2$	$7.9 \times 10^{-10}$			$Hg(OH)_2$	$3 \times 10^{-26}$
$CaF_2$	$4.0 \times 10^{-11}$			$Sn(OH)_2$	$3 \times 10^{-27}$
Chlorides		$NiCO_3$	$1.4 \times 10^{-7}$	$Cr(OH)_3$	$6.7 \times 10^{-31}$
		$CaCO_3$	$8.7 \times 10^{-9}$	$Al(OH)_3$	$2 \times 10^{-32}$
$PbCl_2$	$1.6 \times 10^{-5}$	$BaCO_3$	$1.6 \times 10^{-9}$	$Fe(OH)_3$	$4 \times 10^{-38}$
$AgCl$	$1.6 \times 10^{-10}$	$SrCO_3$	$7 \times 10^{-10}$	$Co(OH)_3$	$2.5 \times 10^{-43}$
$Hg_2Cl_2^*$	$1.1 \times 10^{-18}$	$CuCO_3$	$2.5 \times 10^{-10}$		
Bromides		$ZnCO_3$	$2 \times 10^{-10}$		
		$MnCO_3$	$8.8 \times 10^{-11}$	$MnS$	$2.3 \times 10^{-13}$
$PbBr_2$	$4.6 \times 10^{-6}$	$FeCO_3$	$2.1 \times 10^{-11}$	$FeS$	$3.7 \times 10^{-19}$
$AgBr$	$5.0 \times 10^{-13}$	$Ag_2CO_3$	$8.1 \times 10^{-12}$	$NiS$	$3 \times 10^{-21}$
$Hg_2Br_2^*$	$1.3 \times 10^{-22}$	$CdCO_3$	$5.2 \times 10^{-12}$	$CoS$	$5 \times 10^{-22}$
Iodides		$PbCO_3$	$1.5 \times 10^{-15}$	$ZnS$	$2.5 \times 10^{-22}$
		$MgCO_3$	$1 \times 10^{-5}$	$SnS$	$1 \times 10^{-26}$
$PbI_2$	$1.4 \times 10^{-8}$	$Hg_2CO_3^*$	$9.0 \times 10^{-15}$	$CdS$	$1.0 \times 10^{-28}$
$AgI$	$1.5 \times 10^{-16}$			$PbS$	$7 \times 10^{-29}$
$Hg_2I_2^*$	$4.5 \times 10^{-29}$			$CuS$	$8.5 \times 10^{-45}$
Sulfates		$Ba(OH)_2$	$5.0 \times 10^{-3}$	$Ag_2S$	$1.6 \times 10^{-49}$
		$Sr(OH)_2$	$3.2 \times 10^{-4}$	$HgS$	$1.6 \times 10^{-54}$
$CaSO_4$	$6.1 \times 10^{-5}$	$Ca(OH)_2$	$1.3 \times 10^{-6}$		
$Ag_2SO_4$	$1.2 \times 10^{-5}$	$AgOH$	$2.0 \times 10^{-8}$		
$SrSO_4$	$3.2 \times 10^{-7}$	$Mg(OH)_2$	$8.9 \times 10^{-12}$	$Ag_3PO_4$	$1.8 \times 10^{-18}$
$PbSO_4$	$1.3 \times 10^{-8}$	$Mn(OH)_2$	$2 \times 10^{-13}$	$Sr_3(PO_4)_2$	$1 \times 10^{-31}$
$BaSO_4$	$1.5 \times 10^{-9}$	$Cd(OH)_2$	$5.9 \times 10^{-15}$	$Ca_3(PO_4)_2$	$1.3 \times 10^{-32}$
Chromates		$Pb(OH)_2$	$1.2 \times 10^{-15}$	$Ba_3(PO_4)_2$	$6 \times 10^{-39}$
		$Fe(OH)_2$	$1.8 \times 10^{-15}$	$Pb_3(PO_4)_2$	$1 \times 10^{-54}$

\*Contains  $Hg_2^{2+}$  ions.  $K_{sp} = [Hg_2^{2+}][X^-]^2$  for  $Hg_2X_2$  salts.

## A5.5 Standard Reduction Potentials at 25°C (298 K) for Many Common Half-Reactions

Half-Reaction	$E^\circ$ (V)	Half-Reaction	$E^\circ$ (V)
$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	2.87	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$	0.40
$\text{Ag}^{2+} + \text{e}^- \rightarrow \text{Ag}^+$	1.99	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	0.34
$\text{Co}^{3+} + \text{e}^- \rightarrow \text{Co}^{2+}$	1.82	$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Hg} + 2\text{Cl}^-$	0.34
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$	1.78	$\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$	0.22
$\text{Ce}^{4+} + \text{e}^- \rightarrow \text{Ce}^{3+}$	1.70	$\text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{SO}_3 + \text{H}_2\text{O}$	0.20
$\text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{2-} + 2\text{e}^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$	1.69	$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$	0.16
$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	1.68	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.00
$2\text{e}^- + 2\text{H}^+ + \text{IO}_4^- \rightarrow \text{IO}_3^- + \text{H}_2\text{O}$	1.60	$\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$	-0.036
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.51	$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	-0.13
$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	1.50	$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$	-0.14
$\text{PbO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Pb}^{2+} + 2\text{H}_2\text{O}$	1.46	$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.23
$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	1.36	$\text{PbSO}_4 + 2\text{e}^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.35
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	1.33	$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$	-0.40
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	1.23	$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.44
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.21	$\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$	-0.50
$\text{IO}_3^- + 6\text{H}^+ + 5\text{e}^- \rightarrow \frac{1}{2}\text{I}_2 + 3\text{H}_2\text{O}$	1.20	$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$	-0.73
$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	1.09	$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.76
$\text{VO}_2^+ + 2\text{H}^+ + \text{e}^- \rightarrow \text{VO}^{2+} + \text{H}_2\text{O}$	1.00	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	-0.83
$\text{AuCl}_4^- + 3\text{e}^- \rightarrow \text{Au} + 4\text{Cl}^-$	0.99	$\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}$	-1.18
$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{NO} + 2\text{H}_2\text{O}$	0.96	$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.66
$\text{ClO}_2 + \text{e}^- \rightarrow \text{ClO}_2^-$	0.954	$\text{H}_2 + 2\text{e}^- \rightarrow 2\text{H}^-$	-2.23
$2\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}_2^{2+}$	0.91	$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	-2.37
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	0.80	$\text{La}^{3+} + 3\text{e}^- \rightarrow \text{La}$	-2.37
$\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow 2\text{Hg}$	0.80	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.71
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	0.77	$\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$	-2.76
$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$	0.68	$\text{Ba}^{2+} + 2\text{e}^- \rightarrow \text{Ba}$	-2.90
$\text{MnO}_4^- + \text{e}^- \rightarrow \text{MnO}_4^{2-}$	0.56	$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.92
$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	0.54	$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	-3.05
$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$	0.52		

## Appendix Six SI Units and Conversion Factors

### Length

*SI unit: meter (m)*

1 meter	= 1.0936 yards
1 centimeter	= 0.39370 inch
1 inch	= 2.54 centimeters (exactly)
1 kilometer	= 0.62137 mile
1 mile	= 5280 feet = 1.6093 kilometers
1 angstrom	= $10^{-10}$ meter = 100 picometers

### Mass

*SI unit: kilogram (kg)*

1 kilogram	= 1000 grams = 2.2046 pounds
1 pound	= 453.59 grams = 0.45359 kilogram
	= 16 ounces
1 ton	= 2000 pounds = 907.185 kilograms
1 metric ton	= 1000 kilograms = 2204.6 pounds
1 atomic mass unit	= $1.66056 \times 10^{-27}$ kilograms

### Volume

*SI unit: cubic meter ( $m^3$ )*

1 liter	= $10^{-3} m^3$ = 1 dm <sup>3</sup> = 1.0567 quarts
1 gallon	= 4 quarts = 8 pints = 3.7854 liters
1 quart	= 32 fluid ounces = 0.94633 liter

### Temperature

*SI unit: kelvin (K)*

$$\begin{aligned}0 \text{ K} &= -273.15^\circ\text{C} \\&= -459.67^\circ\text{F} \\K &= ^\circ\text{C} + 273.15 \\{}^\circ\text{C} &= \frac{5}{9}({}^\circ\text{F} - 32) \\{}^\circ\text{F} &= \frac{9}{5}({}^\circ\text{C}) + 32\end{aligned}$$

### Energy

*SI unit: joule (J)*

1 joule	= $1 \text{ kg} \cdot \text{m}^2/\text{s}^2$ = 0.23901 calorie = $9.4781 \times 10^{-4}$ btu (British thermal unit)
1 calorie	= 4.184 joules = $3.965 \times 10^{-3}$ btu
1 btu	= 1055.06 joules = 252.2 calories

### Pressure

*SI unit: pascal (Pa)*

1 pascal	= $1 \text{ N/m}^2$ = $1 \text{ kg}/\text{m} \cdot \text{s}^2$
1 atmosphere	= 101.325 kilopascals = 760 torr (mmHg) = 14.70 pounds per square inch
1 bar	= $10^5$ pascals

# Glossary

**Accuracy** the agreement of a particular value with the true value. (1.4)

**Acid** a substance that produces hydrogen ions in solution; a proton donor. (2.8; 4.2; 4.8)

**Acid-base indicator** a substance that marks the end point of an acid-base titration by changing color. (15.5)

**Acid dissociation constant ( $K_a$ )** the equilibrium constant for a reaction in which a proton is removed from an acid by  $H_2O$  to form the conjugate base and  $H_3O^+$ . (14.1)

**Acid rain** a result of air pollution by sulfur dioxide. (5.10)

**Acidic oxide** a covalent oxide that dissolves in water to give an acidic solution. (14.10)

**Actinide series** a group of 14 elements following actinium in the periodic table, in which the  $5f$  orbitals are being filled. (7.11; 19.1)

**Activated complex (transition state)** the arrangement of atoms found at the top of the potential energy barrier as a reaction proceeds from reactants to products. (12.7)

**Activation energy** the threshold energy that must be overcome to produce a chemical reaction. (12.7)

**Addition polymerization** a type of polymerization in which the monomers simply add together to form the polymer, with no other products. (22.5)

**Addition reaction** a reaction in which atoms add to a carbon–carbon multiple bond. (22.2)

**Adsorption** the collection of one substance on the surface of another. (12.8)

**Air pollution** contamination of the atmosphere, mainly by the gaseous products of transportation and production of electricity. (5.10)

**Alcohol** an organic compound in which the hydroxyl group is a substituent on a hydrocarbon. (22.4)

**Aldehyde** an organic compound containing the carbonyl group bonded to at least one hydrogen atom. (22.4)

**Alkali metal** a Group 1A metal. (2.7; 19.2)

**Alkaline earth metal** a Group 2A metal. (2.7; 19.4)

**Alkane** a saturated hydrocarbon with the general formula  $C_nH_{2n+2}$ . (22.1)

**Alkene** an unsaturated hydrocarbon containing a carbon–carbon double bond. The general formula is  $C_nH_{2n}$ . (22.2)

**Alkyne** an unsaturated hydrocarbon containing a triple carbon–carbon bond. The general formula is  $C_nH_{2n-2}$ . (22.2)

**Alloy** a substance that contains a mixture of elements and has metallic properties. (10.4)

**Alloy steel** a form of steel containing carbon plus other metals such as chromium, cobalt, manganese, and molybdenum. (21.8)

**Alpha ( $\alpha$ ) particle** a helium nucleus. (18.1)

**Alpha-particle production** a common mode of decay for radio-active nuclides in which the mass number changes. (18.1)

**Amine** an organic base derived from ammonia in which one or more of the hydrogen atoms are replaced by organic groups. (14.6; 22.4)

**$\alpha$ -Amino acid** an organic acid in which an amino group and an R group are attached to the carbon atom next to the carboxyl group. (22.6)

**Amorphous solid** a solid with considerable disorder in its structure. (10.3)

**Ampere** the unit of electric current equal to one coulomb of charge per second. (17.7)

**Amphoteric substance** a substance that can behave either as an acid or as a base. (14.2)

**Angular momentum quantum number ( $\ell$ )** the quantum number relating to the shape of an atomic orbital, which can assume any integral value from 0 to  $n - 1$  for each value of  $n$ . (7.6)

**Anion** a negative ion. (2.6)

**Anode** the electrode in a galvanic cell at which oxidation occurs. (17.1)

**Antibonding molecular orbital** an orbital higher in energy than the atomic orbitals of which it is composed. (9.2)

**Aqueous solution** a solution in which water is the dissolving medium or solvent. (4)

**Aromatic hydrocarbon** one of a special class of cyclic unsaturated hydrocarbons, the simplest of which is benzene. (22.3)

**Arrhenius concept** a concept postulating that acids produce hydrogen ions in aqueous solution, while bases produce hydroxide ions. (14.1)

**Arrhenius equation** the equation representing the rate constant as  $k = Ae^{-E_a/RT}$ , where  $A$  represents the product of the collision frequency and the steric factor, and  $e^{-E_a/RT}$  is the fraction of collisions with sufficient energy to produce a reaction. (12.7)

**Atactic chain** a polymer chain in which the substituent groups such as  $CH_3$  are randomly distributed along the chain. (22.5)

**Atmosphere** the mixture of gases that surrounds the earth's surface. (5.10)

**Atomic number** the number of protons in the nucleus of an atom. (2.5; 18)

**Atomic radius** half the distance between the nuclei in a molecule consisting of identical atoms. (7.12)

**Atomic solid** a solid that contains atoms at the lattice points. (10.3)

**Atomic weight** the weighted average mass of the atoms in a naturally occurring element. (2.3)

**Aufbau principle** the principle stating that as protons are added one by one to the nucleus to build up the elements, electrons are similarly added to hydrogen-like orbitals. (7.11)

**Autoionization** the transfer of a proton from one molecule to another of the same substance. (14.2)

**Avogadro's law** equal volumes of gases at the same temperature and pressure contain the same number of particles. (5.2)

**Avogadro's number** the number of atoms in exactly 12 grams of pure  $^{12}C$ , equal to  $6.022 \times 10^{23}$ . (3.3)

**Ball-and-stick model** a molecular model that distorts the sizes of atoms but shows bond relationships clearly. (2.6)

**Band model** a molecular model for metals in which the electrons are assumed to travel around the metal crystal in molecular orbitals formed from the valence atomic orbitals of the metal atoms. (10.4)

## A28 Glossary

- Barometer** a device for measuring atmospheric pressure. (5.1)
- Base** a substance that produces hydroxide ions in aqueous solution, a proton acceptor. (4.8)
- Basic oxide** an ionic oxide that dissolves in water to produce a basic solution. (14.10)
- Basic oxygen process** a process for producing steel by oxidizing and removing the impurities in iron using a high-pressure blast of oxygen. (21.8)
- Battery** a group of galvanic cells connected in series. (17.5)
- Beta ( $\beta$ ) particle** an electron produced in radioactive decay. (18.1)
- Beta-particle production** a decay process for radioactive nuclides in which the mass number remains constant and the atomic number changes. The net effect is to change a neutron to a proton. (18.1)
- Bidentate ligand** a ligand that can form two bonds to a metal ion. (21.3)
- Bimolecular step** a reaction involving the collision of two molecules. (12.6)
- Binary compound** a two-element compound. (2.8)
- Binding energy (nuclear)** the energy required to decompose a nucleus into its component nucleons. (18.5)
- Biomolecule** a molecule responsible for maintaining and/or reproducing life. (22)
- Blast furnace** a furnace in which iron oxide is reduced to iron metal by using a very strong blast of hot air to produce carbon monoxide from coke, and then using this gas as a reducing agent for the iron. (21.8)
- Bond energy** the energy required to break a given chemical bond. (8.1)
- Bond length** the distance between the nuclei of the two atoms connected by a bond; the distance where the total energy of a diatomic molecule is minimal. (8.1)
- Bond order** the difference between the number of bonding electrons and the number of antibonding electrons, divided by two. It is an index of bond strength. (9.2)
- Bonding molecular orbital** an orbital lower in energy than the atomic orbitals of which it is composed. (9.2)
- Bonding pair** an electron pair found in the space between two atoms. (8.9)
- Borane** a covalent hydride of boron. (19.5)
- Boyle's law** the volume of a given sample of gas at constant temperature varies inversely with the pressure. (5.2)
- Breeder reactor** a nuclear reactor in which fissionable fuel is produced while the reactor runs. (18.6)
- Brønsted-Lowry model** a model proposing that an acid is a proton donor, and a base is a proton acceptor. (14.1)
- Buffered solution** a solution that resists a change in its pH when either hydroxide ions or protons are added. (15.2)
- Buffering capacity** the ability of a buffered solution to absorb protons or hydroxide ions without a significant change in pH; determined by the magnitudes of  $[HA]$  and  $[A^-]$  in the solution. (15.3)
- Calorimetry** the science of measuring heat flow. (6.2)
- Capillary action** the spontaneous rising of a liquid in a narrow tube. (10.2)
- Carbohydrate** a polyhydroxyl ketone or polyhydroxyl aldehyde or a polymer composed of these. (22.6)
- Carbon steel** an alloy of iron containing up to about 1.5% carbon. (21.8)
- Carboxyhemoglobin** a stable complex of hemoglobin and carbon monoxide that prevents normal oxygen uptake in the blood. (21.7)
- Carboxyl group** the  $-COOH$  group in an organic acid. (14.2; 22.4)
- Carboxylic acid** an organic compound containing the carboxyl group; an acid with the general formula  $RCOOH$ . (22.4)
- Catalyst** a substance that speeds up a reaction without being consumed. (12.8)
- Cathode** the electrode in a galvanic cell at which reduction occurs. (17.1)
- Cathode rays** the "rays" emanating from the negative electrode (cathode) in a partially evacuated tube; a stream of electrons. (2.4)
- Cathodic protection** a method in which an active metal, such as magnesium, is connected to steel to protect it from corrosion. (17.6)
- Cation** a positive ion. (2.6)
- Cell potential (electromotive force)** the driving force in a galvanic cell that pulls electrons from the reducing agent in one compartment to the oxidizing agent in the other. (17.1)
- Ceramic** a nonmetallic material made from clay and hardened by firing at high temperature; it contains minute silicate crystals suspended in a glassy cement. (10.5)
- Chain reaction (nuclear)** a self-sustaining fission process caused by the production of neutrons that proceed to split other nuclei. (18.6)
- Charles's law** the volume of a given sample of gas at constant pressure is directly proportional to the temperature in kelvins. (5.2)
- Chelating ligand (chelate)** a ligand having more than one atom with a lone pair that can be used to bond to a metal ion. (21.3)
- Chemical bond** the force or, more accurately, the energy, that holds two atoms together in a compound. (2.6)
- Chemical change** the change of substances into other substances through a reorganization of the atoms; a chemical reaction. (1.9)
- Chemical equation** a representation of a chemical reaction showing the relative numbers of reactant and product molecules. (3.7)
- Chemical equilibrium** a dynamic reaction system in which the concentrations of all reactants and products remain constant as a function of time. (13)
- Chemical formula** the representation of a molecule in which the symbols for the elements are used to indicate the types of atoms present and subscripts are used to show the relative numbers of atoms. (2.6)
- Chemical kinetics** the area of chemistry that concerns reaction rates. (12)
- Chemical stoichiometry** the calculation of the quantities of material consumed and produced in chemical reactions. (3)
- Chirality** the quality of having nonsuperimposable mirror images. (21.4)
- Chlor-alkali process** the process for producing chlorine and sodium hydroxide by electrolyzing brine in a mercury cell. (17.8)
- Chromatography** the general name for a series of methods for separating mixtures by employing a system with a mobile phase and a stationary phase. (1.9)
- Coagulation** the destruction of a colloid by causing particles to aggregate and settle out. (11.8)
- Codons** organic bases in sets of three that form the genetic code. (22.6)
- Colligative properties** properties of a solution that depend only on the number, and not on the identity, of the solute particles. (11.5)
- Collision model** a model based on the idea that molecules must collide to react; used to account for the observed characteristics of reaction rates. (12.7)

**Colloid (colloidal dispersion)** a suspension of particles in a dispersing medium. (11.8)

**Combustion reaction** the vigorous and exothermic reaction that takes place between certain substances, particularly organic compounds, and oxygen. (22.1)

**Common ion effect** the shift in an equilibrium position caused by the addition or presence of an ion involved in the equilibrium reaction. (15.1)

**Complete ionic equation** an equation that shows all substances that are strong electrolytes as ions. (4.6)

**Complex ion** a charged species consisting of a metal ion surrounded by ligands. (15.8; 21.1)

**Compound** a substance with constant composition that can be broken down into elements by chemical processes. (1.9)

**Concentration cell** a galvanic cell in which both compartments contain the same components, but at different concentrations. (17.4)

**Condensation** the process by which vapor molecules reform a liquid. (10.8)

**Condensation polymerization** a type of polymerization in which the formation of a small molecule, such as water, accompanies the extension of the polymer chain. (22.5)

**Condensation reaction** a reaction in which two molecules are joined, accompanied by the elimination of a water molecule. (20.3)

**Condensed states of matter** liquids and solids. (10.1)

**Conjugate acid** the species formed when a proton is added to a base. (14.1)

**Conjugate acid-base pair** two species related to each other by the donating and accepting of a single proton. (14.1)

**Conjugate base** what remains of an acid molecule after a proton is lost. (14.1)

**Continuous spectrum** a spectrum that exhibits all the wavelengths of visible light. (7.3)

**Control rods** rods in a nuclear reactor composed of substances that absorb neutrons. These rods regulate the power level of the reactor. (18.6)

**Coordinate covalent bond** a metal-ligand bond resulting from the interaction of a Lewis base (the ligand) and a Lewis acid (the metal ion). (21.3)

**Coordination compound** a compound composed of a complex ion and counter ions sufficient to give no net charge. (21.3)

**Coordination isomerism** isomerism in a coordination compound in which the composition of the coordination sphere of the metal ion varies. (21.4)

**Coordination number** the number of bonds formed between the metal ion and the ligands in a complex ion. (21.3)

**Copolymer** a polymer formed from the polymerization of more than one type of monomer. (22.5)

**Core electron** an inner electron in an atom; one not in the outermost (valence) principal quantum level. (7.11)

**Corrosion** the process by which metals are oxidized in the atmosphere. (17.6)

**Coulomb's law**  $E = 2.31 \times 10^{-19} \left( \frac{Q_1 Q_2}{r} \right)$ , where  $E$  is the energy of interaction between a pair of ions, expressed in joules;  $r$  is the distance between the ion centers in nm; and  $Q_1$  and  $Q_2$  are the numerical ion charges. (8.1)

**Counterions** anions or cations that balance the charge on the complex ion in a coordination compound. (21.3)

**Covalent bonding** a type of bonding in which electrons are shared by atoms. (2.6; 8.1)

**Critical mass** the mass of fissionable material required to produce a self-sustaining chain reaction. (18.6)

**Critical point** the point on a phase diagram at which the temperature and pressure have their critical values; the end point of the liquid-vapor line. (10.9)

**Critical pressure** the minimum pressure required to produce liquefaction of a substance at the critical temperature. (10.9)

**Critical reaction (nuclear)** a reaction in which exactly one neutron from each fission event causes another fission event, thus sustaining the chain reaction. (18.6)

**Critical temperature** the temperature above which vapor cannot be liquefied no matter what pressure is applied. (10.9)

**Crosslinking** the existence of bonds between adjacent chains in a polymer, thus adding strength to the material. (22.5)

**Crystal field model** a model used to explain the magnetism and colors of coordination complexes through the splitting of the  $d$  orbital energies. (21.6)

**Crystalline solid** a solid with a regular arrangement of its components. (10.3)

**Cubic closest packed (ccp) structure** a solid modeled by the closest packing of spheres with an  $abcabc$  arrangement of layers; the unit cell is face-centered cubic. (10.4)

**Cyanidation** a process in which crushed gold ore is treated with an aqueous cyanide solution in the presence of air to dissolve the gold. Pure gold is recovered by reduction of the ion to the metal. (21.8)

**Cyclotron** a type of particle accelerator in which an ion introduced at the center is accelerated in an expanding spiral path by the use of alternating electrical fields in the presence of a magnetic field. (18.3)

**Cytochromes** a series of iron-containing species composed of heme and a protein. Cytochromes are the principal electron-transfer molecules in the respiratory chain. (21.7)

**Dalton's law of partial pressures** for a mixture of gases in a container, the total pressure exerted is the sum of the pressures that each gas would exert if it were alone. (5.5)

**Degenerate orbitals** a group of orbitals with the same energy. (7.7)

**Dehydrogenation reaction** a reaction in which two hydrogen atoms are removed from adjacent carbons of a saturated hydrocarbon, giving an unsaturated hydrocarbon. (22.1)

**Denaturation** the breaking down of the three-dimensional structure of a protein resulting in the loss of its function. (22.6)

**Denitrification** the return of nitrogen from decomposed matter to the atmosphere by bacteria that change nitrates to nitrogen gas. (20.2)

**Density** a property of matter representing the mass per unit volume. (1.8)

**Deoxyribonucleic acid (DNA)** a huge nucleotide polymer having a double-helical structure with complementary bases on the two strands. Its major functions are protein synthesis and the storage and transport of genetic information. (22.6)

**Desalination** the removal of dissolved salts from an aqueous solution. (11.6)

**Dialysis** a phenomenon in which a semipermeable membrane allows transfer of both solvent molecules and small solute molecules and ions. (11.6)

**Diamagnetism** a type of magnetism, associated with paired electrons, that causes a substance to be repelled from the inducing magnetic field. (9.3)

**Differential rate law** an expression that gives the rate of a reaction as a function of concentrations; often called the rate law. (12.2)

## A30 Glossary

- Diffraction** the scattering of light from a regular array of points or lines, producing constructive and destructive interference. (7.2)
- Diffusion** the mixing of gases. (5.7)
- Dilution** the process of adding solvent to lower the concentration of solute in a solution. (4.3)
- Dimer** a molecule formed by the joining of two identical monomers. (22.5)
- Dipole–dipole attraction** the attractive force resulting when polar molecules line up so that the positive and negative ends are close to each other. (10.1)
- Dipole moment** a property of a molecule whose charge distribution can be represented by a center of positive charge and a center of negative charge. (8.3)
- Direct reduction furnace** a furnace in which iron oxide is reduced to iron metal using milder reaction conditions than in a blast furnace. (21.8)
- Disaccharide** a sugar formed from two monosaccharides joined by a glycoside linkage. (22.6)
- Disproportionation reaction** a reaction in which a given element is both oxidized and reduced. (20.7)
- Distillation** a method for separating the components of a liquid mixture that depends on differences in the ease of vaporization of the components. (1.9)
- Disulfide linkage** an S—S bond that stabilizes the tertiary structure of many proteins. (22.6)
- Double bond** a bond in which two pairs of electrons are shared by two atoms. (8.8)
- Downs cell** a cell used for electrolyzing molten sodium chloride. (17.8)
- Dry cell battery** a common battery used in calculators, watches, radios, and tape players. (17.5)
- Dual nature of light** the statement that light exhibits both wave and particulate properties. (7.2)
- Effusion** the passage of a gas through a tiny orifice into an evacuated chamber. (5.7)
- Electrical conductivity** the ability to conduct an electric current. (4.2)
- Electrochemistry** the study of the interchange of chemical and electrical energy. (17)
- Electrolysis** a process that involves forcing a current through a cell to cause a nonspontaneous chemical reaction to occur. (17.7)
- Electrolyte** a material that dissolves in water to give a solution that conducts an electric current. (4.2)
- Electrolytic cell** a cell that uses electrical energy to produce a chemical change that would otherwise not occur spontaneously. (17.7)
- Electromagnetic radiation** radiant energy that exhibits wavelike behavior and travels through space at the speed of light in a vacuum. (7.1)
- Electron** a negatively charged particle that moves around the nucleus of an atom. (2.4)
- Electron affinity** the energy change associated with the addition of an electron to a gaseous atom. (7.12)
- Electron capture** a process in which one of the inner-orbital electrons in an atom is captured by the nucleus. (18.1)
- Electron spin quantum number** a quantum number representing one of the two possible values for the electron spin; either  $+\frac{1}{2}$  or  $-\frac{1}{2}$ . (7.8)
- Electronegativity** the tendency of an atom in a molecule to attract shared electrons to itself. (8.2)
- Element** a substance that cannot be decomposed into simpler substances by chemical or physical means. (1.9)
- Elementary step** a reaction whose rate law can be written from its molecularity. (12.6)
- $E = mc^2$**  Einstein's equation proposing that energy has mass;  $E$  is energy,  $m$  is mass, and  $c$  is the speed of light. (7.2)
- Empirical formula** the simplest whole number ratio of atoms in a compound. (3.6)
- Enantiomers** isomers that are nonsuperimposable mirror images of each other. (21.4)
- Endpoint** the point in a titration at which the indicator changes color. (4.8)
- Endothermic** refers to a reaction where energy (as heat) flows into the system. (6.1)
- Energy** the capacity to do work or to cause heat flow. (6.1)
- Enthalpy** a property of a system equal to  $E + PV$ , where  $E$  is the internal energy of the system,  $P$  is the pressure of the system, and  $V$  is the volume of the system. At constant pressure the change in enthalpy equals the energy flow as heat. (6.2)
- Enthalpy (heat) of fusion** the enthalpy change that occurs to melt a solid at its melting point. (10.8)
- Entropy** a thermodynamic function that measures randomness or disorder. (16.1)
- Enzyme** a large molecule, usually a protein, that catalyzes biological reactions. (12.8)
- Equilibrium constant** the value obtained when equilibrium concentrations of the chemical species are substituted in the equilibrium expression. (13.2)
- Equilibrium expression** the expression (from the law of mass action) obtained by multiplying the product concentrations and dividing by the multiplied reactant concentrations, with each concentration raised to a power represented by the coefficient in the balanced equation. (13.2)
- Equilibrium point (thermodynamic definition)** the position where the free energy of a reaction system has its lowest possible value. (16.8)
- Equilibrium position** a particular set of equilibrium concentrations. (13.2)
- Equivalence point (stoichiometric point)** the point in a titration when enough titrant has been added to react exactly with the substance in solution being titrated. (4.9; 15.4)
- Ester** an organic compound produced by the reaction between a carboxylic acid and an alcohol. (22.4)
- Exothermic** refers to a reaction where energy (as heat) flows out of the system. (6.1)
- Exponential notation** expresses a number as  $N \times 10^M$ , a convenient method for representing a very large or very small number and for easily indicating the number of significant figures. (1.5)
- Faraday** a constant representing the charge on one mole of electrons; 96,485 coulombs. (17.3)
- Filtration** a method for separating the components of a mixture containing a solid and a liquid. (1.9)
- First law of thermodynamics** the energy of the universe is constant; same as the law of conservation of energy. (6.1)
- Fission** the process of using a neutron to split a heavy nucleus into two nuclei with smaller mass numbers. (18.6)
- Flotation process** a method of separating the mineral particles in an ore from the gangue that depends on the greater wettability of the mineral pieces. (21.8)

**Formal charge** the charge assigned to an atom in a molecule or polyatomic ion derived from a specific set of rules. (8.12)

**Formation constant (stability constant)** the equilibrium constant for each step of the formation of a complex ion by the addition of an individual ligand to a metal ion or complex ion in aqueous solution. (15.8)

**Formula equation** an equation representing a reaction in solution showing the reactants and products in undissociated form, whether they are strong or weak electrolytes. (4.6)

**Fossil fuel** coal, petroleum, or natural gas; consists of carbon-based molecules derived from decomposition of once-living organisms. (6.5)

**Frasch process** the recovery of sulfur from underground deposits by melting it with hot water and forcing it to the surface by air pressure. (20.6)

**Free energy** a thermodynamic function equal to the enthalpy ( $H$ ) minus the product of the entropy ( $S$ ) and the Kelvin temperature ( $T$ );  $G = H - TS$ . Under certain conditions the change in free energy for a process is equal to the maximum useful work. (16.4)

**Free radical** a species with an unpaired electron. (22.5)

**Frequency** the number of waves (cycles) per second that pass a given point in space. (7.1)

**Fuel cell** a galvanic cell for which the reactants are continuously supplied. (17.5)

**Functional group** an atom or group of atoms in hydrocarbon derivatives that contains elements in addition to carbon and hydrogen. (22.4)

**Fusion** the process of combining two light nuclei to form a heavier, more stable nucleus. (18.6)

**Galvanic cell** a device in which chemical energy from a spontaneous redox reaction is changed to electrical energy that can be used to do work. (17.1)

**Galvanizing** a process in which steel is coated with zinc to prevent corrosion. (17.6)

**Gamma ( $\gamma$ ) ray** a high-energy photon. (18.1)

**Gangue** the impurities (such as clay or sand) in an ore. (21.8)

**Geiger–Müller counter (Geiger counter)** an instrument that measures the rate of radioactive decay based on the ions and electrons produced as a radioactive particle passes through a gas-filled chamber. (18.4)

**Gene** a given segment of the DNA molecule that contains the code for a specific protein. (22.6)

**Geometrical (*cis-trans*) isomerism** isomerism in which atoms or groups of atoms can assume different positions around a rigid ring or bond. (21.4; 22.2)

**Glass** an amorphous solid obtained when silica is mixed with other compounds, heated above its melting point, and then cooled rapidly. (10.5)

**Glass electrode** an electrode for measuring pH from the potential difference that develops when it is dipped into an aqueous solution containing  $H^+$  ions. (17.4)

**Glycoside linkage** a C—O—C bond formed between the rings of two cyclic monosaccharides by the elimination of water. (22.6)

**Graham's law of effusion** the rate of effusion of a gas is inversely proportional to the square root of the mass of its particles. (5.7)

**Greenhouse effect** a warming effect exerted by the earth's atmosphere (particularly  $CO_2$  and  $H_2O$ ) due to thermal energy retained by absorption of infrared radiation. (6.5)

**Ground state** the lowest possible energy state of an atom or molecule. (7.4)

**Group (of the periodic table)** a vertical column of elements having the same valence electron configuration and showing similar properties. (2.7)

**Haber process** the manufacture of ammonia from nitrogen and hydrogen, carried out at high pressure and high temperature with the aid of a catalyst. (3.10; 20.2)

**Half-life (of a radioactive sample)** the time required for the number of nuclides in a radioactive sample to reach half of the original value. (18.2)

**Half-life (of a reactant)** the time required for a reactant to reach half of its original concentration. (12.4)

**Half-reactions** the two parts of an oxidation–reduction reaction, one representing oxidation, the other reduction. (4.10; 17.1)

**Halogen** a Group 7A element. (2.7; 20.7)

**Halogenation** the addition of halogen atoms to unsaturated hydrocarbons. (22.2)

**Hard water** water from natural sources that contains relatively large concentrations of calcium and magnesium ions. (19.4)

**Heat** energy transferred between two objects due to a temperature difference between them. (6.1)

**Heat capacity** the amount of energy required to raise the temperature of an object by one degree Celsius. (6.2)

**Heat of fusion** the enthalpy change that occurs to melt a solid at its melting point. (10.8)

**Heat of hydration** the enthalpy change associated with placing gaseous molecules or ions in water; the sum of the energy needed to expand the solvent and the energy released from the solvent–solute interactions. (11.2)

**Heat of solution** the enthalpy change associated with dissolving a solute in a solvent; the sum of the energies needed to expand both solvent and solute in a solution and the energy released from the solvent–solute interactions. (11.2)

**Heat of vaporization** the energy required to vaporize one mole of a liquid at a pressure of one atmosphere. (10.8)

**Heating curve** a plot of temperature versus time for a substance where energy is added at a constant rate. (10.8)

**Heisenberg uncertainty principle** a principle stating that there is a fundamental limitation to how precisely both the position and momentum of a particle can be known at a given time. (7.5)

**Heme** an iron complex. (21.7)

**Hemoglobin** a biomolecule composed of four myoglobin-like units (proteins plus heme) that can bind and transport four oxygen molecules in the blood. (21.7)

**Henderson–Hasselbalch equation** an equation giving the relationship between the pH of an acid–base system and the concentrations

$$\text{of base and acid: } \text{pH} = \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right). \quad (15.2)$$

**Henry's law** the amount of a gas dissolved in a solution is directly proportional to the pressure of the gas above the solution. (11.3)

**Hess's law** in going from a particular set of reactants to a particular set of products, the enthalpy change is the same whether the reaction takes place in one step or in a series of steps; in summary, enthalpy is a state function. (6.3)

**Heterogeneous equilibrium** an equilibrium involving reactants and/or products in more than one phase. (13.4)

## A32 Glossary

**Hexagonal closest packed (hcp) structure** a structure composed of closest packed spheres with an *ababab* arrangement of layers; the unit cell is hexagonal. (10.4)

**Homogeneous equilibrium** an equilibrium system where all reactants and products are in the same phase. (13.4)

**Homopolymer** a polymer formed from the polymerization of only one type of monomer. (22.5)

**Hund's rule** the lowest energy configuration for an atom is the one having the maximum number of unpaired electrons allowed by the Pauli exclusion principle in a particular set of degenerate orbitals, with all unpaired electrons having parallel spins. (7.11)

**Hybrid orbitals** a set of atomic orbitals adopted by an atom in a molecule different from those of the atom in the free state. (9.1)

**Hybridization** a mixing of the native orbitals on a given atom to form special atomic orbitals for bonding. (9.1)

**Hydration** the interaction between solute particles and water molecules. (4.1)

**Hydride** a binary compound containing hydrogen. The hydride ion,  $\text{H}^-$ , exists in ionic hydrides. The three classes of hydrides are covalent, interstitial, and ionic. (19.3)

**Hydrocarbon** a compound composed of carbon and hydrogen. (22.1)

**Hydrocarbon derivative** an organic molecule that contains one or more elements in addition to carbon and hydrogen. (22.4)

**Hydrogen bonding** unusually strong dipole–dipole attractions that occur among molecules in which hydrogen is bonded to a highly electronegative atom. (10.1)

**Hydrogenation reaction** a reaction in which hydrogen is added, with a catalyst present, to a carbon–carbon multiple bond. (22.2)

**Hydrohalic acid** an aqueous solution of a hydrogen halide. (20.7)

**Hydrometallurgy** a process for extracting metals from ores by use of aqueous chemical solutions. Two steps are involved: selective leaching and selective precipitation. (21.8)

**Hydronium ion** the  $\text{H}_3\text{O}^+$  ion; a hydrated proton. (14.1)

**Hypothesis** one or more assumptions put forth to explain the observed behavior of nature. (1.2)

**Ideal gas law** an equation of state for a gas, where the state of the gas is its condition at a given time; expressed by  $PV = nRT$ , where  $P$  = pressure,  $V$  = volume,  $n$  = moles of the gas,  $R$  = the universal gas constant, and  $T$  = absolute temperature. This equation expresses behavior approached by real gases at high  $T$  and low  $P$ . (5.3)

**Ideal solution** a solution whose vapor pressure is directly proportional to the mole fraction of solvent present. (11.4)

**Indicator** a chemical that changes color and is used to mark the end point of a titration. (4.8; 15.5)

**Integrated rate law** an expression that shows the concentration of a reactant as a function of time. (12.2)

**Interhalogen compound** a compound formed by the reaction of one halogen with another. (20.7)

**Intermediate** a species that is neither a reactant nor a product but that is formed and consumed in the reaction sequence. (12.6)

**Intermolecular forces** relatively weak interactions that occur between molecules. (10.1)

**Internal energy** a property of a system that can be changed by a flow of work, heat or both;  $\Delta E = q + w$ , where  $\Delta E$  is the change in the internal energy of the system,  $q$  is heat, and  $w$  is work. (6.1)

**Ion** an atom or a group of atoms that has a net positive or negative charge. (2.6)

**Ion exchange (water softening)** the process in which an ion-exchange resin removes unwanted ions (for example,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) and replaces them with  $\text{Na}^+$  ions, which do not interfere with soap and detergent action. (19.4)

**Ion pairing** a phenomenon occurring in solution when oppositely charged ions aggregate and behave as a single particle. (11.7)

**Ion-product (dissociation) constant ( $K_w$ )** the equilibrium constant for the auto-ionization of water;  $K_w = [\text{H}^+][\text{OH}^-]$ . At  $25^\circ\text{C}$ ,  $K_w$  equals  $1.0 \times 10^{-14}$ . (14.2)

**Ion-selective electrode** an electrode sensitive to the concentration of a particular ion in solution. (17.4)

**Ionic bonding** the electrostatic attraction between oppositely charged ions. (2.6; 8.1)

**Ionic compound (binary)** a compound that results when a metal reacts with a nonmetal to form a cation and an anion. (8.1)

**Ionic solid (salt)** a solid containing cations and anions that dissolves in water to give a solution containing the separated ions which are mobile and thus free to conduct electrical current. (2.6; 10.3)

**Irreversible process** any real process. When a system undergoes the changes State 1  $\rightarrow$  State 2  $\rightarrow$  State 1 by any real pathway, the universe is different than before the cyclic process took place in the system. (16.9)

**Isoelectronic ions** ions containing the same number of electrons. (8.4)

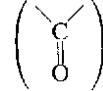
**Isomers** species with the same formula but different properties. (21.4)

**Isotactic chain** a polymer chain in which the substituent groups such as  $\text{CH}_3$  are all arranged on the same side of the chain. (22.5)

**Isotonic solutions** solutions having identical osmotic pressures. (11.6)

**Isotopes** atoms of the same element (the same number of protons) with different numbers of neutrons. They have identical atomic numbers but different mass numbers. (2.5; 18)

**Ketone** an organic compound containing the carbonyl group bonded



to two carbon atoms. (22.4)

**Kinetic energy** ( $\frac{1}{2}mv^2$ ) energy due to the motion of an object; dependent on the mass of the object and the square of its velocity. (6.1)

**Kinetic molecular theory (KMT)** a model that assumes that an ideal gas is composed of tiny particles (molecules) in constant motion. (5.6)

**Lanthanide contraction** the decrease in the atomic radii of the lanthanide series elements, going from left to right in the periodic table. (21.1)

**Lanthanide series** a group of 14 elements following lanthanum in the periodic table, in which the  $4f$  orbitals are being filled. (7.11; 19.1; 21.1)

**Lattice** a three-dimensional system of points designating the positions of the centers of the components of a solid (atoms, ions, or molecules). (10.3)

**Lattice energy** the energy change occurring when separated gaseous ions are packed together to form an ionic solid. (8.5)

**Law of conservation of energy** energy can be converted from one form to another but can be neither created nor destroyed. (6.1)

**Law of conservation of mass** mass is neither created nor destroyed. (1.2; 2.2)

**Law of definite proportion** a given compound always contains exactly the same proportion of elements by mass. (2.2)

**Law of mass action** a general description of the equilibrium condition; it defines the equilibrium constant expression. (13.2)

**Law of multiple proportions** a law stating that when two elements form a series of compounds, the ratios of the masses of the second element that combine with one gram of the first element can always be reduced to small whole numbers. (2.2)

**Leaching** the extraction of metals from ores using aqueous chemical solutions. (21.8)

**Lead storage battery** a battery (used in cars) in which the anode is lead, the cathode is lead coated with lead dioxide, and the electrolyte is a sulfuric acid solution. (17.5)

**Le Châtelier's principle** if a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce the effect of that change. (13.7)

**Lewis acid** an electron-pair acceptor. (14.11)

**Lewis base** an electron-pair donor. (14.11)

**Lewis structure** a diagram of a molecule showing how the valence electrons are arranged among the atoms in the molecule. (8.10)

**Ligand** a neutral molecule or ion having a lone pair of electrons that can be used to form a bond to a metal ion; a Lewis base. (21.3)

**Lime-soda process** a water-softening method in which lime and soda ash are added to water to remove calcium and magnesium ions by precipitation. (14.6)

**Limiting reactant (limiting reagent)** the reactant that is completely consumed when a reaction is run to completion. (3.10)

**Line spectrum** a spectrum showing only certain discrete wavelengths. (7.3)

**Linear accelerator** a type of particle accelerator in which a changing electrical field is used to accelerate a positive ion along a linear path. (18.3)

**Linkage isomerism** isomerism involving a complex ion where the ligands are all the same but the point of attachment of at least one of the ligands differs. (21.4)

**Liquefaction** the transformation of a gas into a liquid. (19.1)

**Localized electron (LE) model** a model which assumes that a molecule is composed of atoms that are bound together by sharing pairs of electrons using the atomic orbitals of the bound atoms. (8.9)

**London dispersion forces** the forces, existing among noble gas atoms and nonpolar molecules, that involve an accidental dipole that induces a momentary dipole in a neighbor. (10.1)

**Lone pair** an electron pair that is localized on a given atom; an electron pair not involved in bonding. (8.9)

**Magnetic quantum number**  $m_\ell$ , the quantum number relating to the orientation of an orbital in space relative to the other orbitals with the same  $\ell$  quantum number. It can have integral values between  $\ell$  and  $-\ell$ , including zero. (7.6)

**Main-group (representative) elements** elements in the groups labeled 1A, 2A, 3A, 4A, 5A, 6A, 7A, and 8A in the periodic table. The group number gives the sum of the valence  $s$  and  $p$  electrons. (7.11; 18.1)

**Major species** the components present in relatively large amounts in a solution. (14.3)

**Manometer** a device for measuring the pressure of a gas in a container. (5.1)

**Mass** the quantity of matter in an object. (1.3)

**Mass defect** the change in mass occurring when a nucleus is formed from its component nucleons. (18.5)

**Mass number** the total number of protons and neutrons in the atomic nucleus of an atom. (2.5; 18)

**Mass percent** the percent by mass of a component of a mixture (11.1) or of a given element in a compound. (3.5)

**Mass spectrometer** an instrument used to determine the relative masses of atoms by the deflection of their ions on a magnetic field. (3.2)

**Matter** the material of the universe. (1.9)

**Messenger RNA (mRNA)** a special RNA molecule built in the cell nucleus that migrates into the cytoplasm and participates in protein synthesis. (22.6)

**Metal** an element that gives up electrons relatively easily and is lustrous, malleable, and a good conductor of heat and electricity. (2.7)

**Metalloids (semimetals)** elements along the division line in the periodic table between metals and nonmetals. These elements exhibit both metallic and nonmetallic properties. (7.13; 19.1)

**Metallurgy** the process of separating a metal from its ore and preparing it for use. (19.1; 21.8)

**Millimeters of mercury** (mmHg) a unit of pressure, also called a torr, 760 mm Hg = 760 torr = 101,325 Pa = 1 standard atmosphere. (5.1)

**Mineral** a relatively pure compound as found in nature. (21.8)

**Model (theory)** a set of assumptions put forth to explain the observed behavior of matter. The models of chemistry usually involve assumptions about the behavior of individual atoms or molecules. (1.2)

**Moderator** a substance used in a nuclear reactor to slow down the neutrons. (18.6)

**Molal boiling-point elevation constant** a constant characteristic of a particular solvent that gives the change in boiling point as a function of solution molality; used in molecular weight determinations. (11.5)

**Molal freezing-point depression constant** a constant characteristic of a particular solvent that gives the change in freezing point as a function of the solution molality; used in molecular weight determinations (11.5)

**Molality** the number of moles of solute per kilogram of solvent in a solution. (11.1)

**Molar heat capacity** the energy required to raise the temperature of one mole of a substance by one degree Celsius. (6.2)

**Molar mass** the mass in grams of one mole of molecules or formula units of a substance; also called *molecular weight*. (3.4)

**Molar volume** the volume of one mole of an ideal gas; equal to 22.42 liters at STP. (5.4)

**Molarity** moles of solute per volume of solution in liters. (4.3; 11.1)

**Mole (mol)** the number equal to the number of carbon atoms in exactly 12 grams of pure  $^{12}\text{C}$ : Avogadro's number. One mole represents  $6.022 \times 10^{23}$  units. (3.3)

**Mole fraction** the ratio of the number of moles of a given component in a mixture to the total number of moles in the mixture. (5.5; 11.1)

**Mole ratio (stoichiometry)** the ratio of moles of one substance to moles of another substance in a balanced chemical equation. (3.9)

**Molecular formula** the exact formula of a molecule, giving the types of atoms and the number of each type. (3.6)

**Molecular orbital (MO) model** a model that regards a molecule as a collection of nuclei and electrons, where the electrons are assumed to occupy orbitals much as they do in atoms, but having the orbitals extend over the entire molecule. In this model the electrons are assumed to be delocalized rather than always located between a given pair of atoms. (9.2; 10.4)

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**Molecular orientations (kinetics)** orientations of molecules during collisions, some of which can lead to reaction while others cannot. (12.7)

**Molecular solid** a solid composed of neutral molecules at the lattice points. (10.3)

**Molecular structure** the three-dimensional arrangement of atoms in a molecule. (8.13)

**Molecularity** the number of species that must collide to produce the reaction represented by an elementary step in a reaction mechanism. (12.6)

**Molecule** a bonded collection of two or more atoms of the same or different elements. (2.6)

**Monodentate (unidentate) ligand** a ligand that can form one bond to a metal ion. (21.3)

**Monoprotic acid** an acid with one acidic proton. (14.2)

**Monosaccharide (simple sugar)** a polyhydroxy ketone or aldehyde containing from three to nine carbon atoms. (22.6)

**Myoglobin** an oxygen-storing biomolecule consisting of a heme complex and a proton. (21.7)

**Natural law** a statement that expresses generally observed behavior. (1.2)

**Nernst equation** an equation relating the potential of an electrochemical cell to the concentrations of the cell components:

$$\mathcal{E} = \mathcal{E}^\circ - \frac{0.0591}{n} \log(Q) \text{ at } 25^\circ\text{C} \quad (17.4)$$

**Net ionic equation** an equation for a reaction in solution, where strong electrolytes are written as ions, showing only those components that are directly involved in the chemical change. (4.6)

**Network solid** an atomic solid containing strong directional covalent bonds. (10.5)

**Neutralization reaction** an acid–base reaction. (4.8)

**Neutron** a particle in the atomic nucleus with mass virtually equal to the proton's but with no charge. (2.5; 18)

**Nitrogen cycle** the conversion of N<sub>2</sub> to nitrogen-containing compounds, followed by the return of nitrogen gas to the atmosphere by natural decay processes. (20.2)

**Nitrogen fixation** the process of transforming N<sub>2</sub> to nitrogen-containing compounds useful to plants. (20.2)

**Nitrogen-fixing bacteria** bacteria in the root nodules of plants that can convert atmospheric nitrogen to ammonia and other nitrogen-containing compounds useful to plants. (20.2)

**Noble gas** a Group 8A element. (2.7; 20.8)

**Node** an area of an orbital having zero electron probability. (7.7)

**Nonelectrolyte** a substance that, when dissolved in water, gives a nonconducting solution. (4.2)

**Nonmetal** an element not exhibiting metallic characteristics. Chemically, a typical nonmetal accepts electrons from a metal. (2.7)

**Normal boiling point** the temperature at which the vapor pressure of a liquid is exactly one atmosphere. (10.8)

**Normal melting point** the temperature at which the solid and liquid states have the same vapor pressure under conditions where the total pressure on the system is one atmosphere. (10.8)

**Normality** the number of equivalents of a substance dissolved in a liter of solution. (11.1)

**Nuclear atom** an atom having a dense center of positive charge (the nucleus) with electrons moving around the outside. (2.4)

**Nuclear transformation** the change of one element into another. (18.3)

**Nucleon** a particle in an atomic nucleus, either a neutron or a proton. (18)

**Nucleotide** a monomer of the nucleic acids composed of a five-carbon sugar, a nitrogen-containing base, and phosphoric acid. (22.6)

**Nucleus** the small, dense center of positive charge in an atom. (2.4)

**Nuclide** the general term applied to each unique atom; represented by <sup>A</sup><sub>Z</sub>X, where X is the symbol for a particular element. (18)

**Octet rule** the observation that atoms of nonmetals tend to form the most stable molecules when they are surrounded by eight electrons (to fill their valence orbitals). (8.10)

**Open hearth process** a process for producing steel by oxidizing and removing the impurities in molten iron using external heat and a blast of air or oxygen. (21.8)

**Optical isomerism** isomerism in which the isomers have opposite effects on plane-polarized light. (21.4)

**Orbital** a specific wave function for an electron in an atom. The square of this function gives the probability distribution for the electron. (7.5)

**d-Orbital splitting** a splitting of the d orbitals of the metal ion in a complex such that the orbitals pointing at the ligands have higher energies than those pointing between the ligands. (21.6)

**Order (of reactant)** the positive or negative exponent, determined by experiment, of the reactant concentration in a rate law. (12.2)

**Organic acid** an acid with a carbon-atom backbone; often contains the carboxyl group. (14.2)

**Organic chemistry** the study of carbon-containing compounds (typically chains of carbon atoms) and their properties. (22)

**Osmosis** the flow of solvent into a solution through a semipermeable membrane. (11.6)

**Osmotic pressure ( $\pi$ )** the pressure that must be applied to a solution to stop osmosis;  $\pi = MRT$ . (11.6)

**Ostwald process** a commercial process for producing nitric acid by the oxidation of ammonia. (20.2)

**Oxidation** an increase in oxidation state (a loss of electrons). (4.9; 17.1)

**Oxidation-reduction (redox) reaction** a reaction in which one or more electrons are transferred. (4.9; 17.1)

**Oxidation states** a concept that provides a way to keep track of electrons in oxidation-reduction reactions according to certain rules. (4.9; 21.3)

**Oxidizing agent (electron acceptor)** a reactant that accepts electrons from another reactant. (4.9; 17.1)

**Oxyacid** an acid in which the acidic proton is attached to an oxygen atom. (14.2)

**Ozone** O<sub>3</sub>, the form of elemental oxygen in addition to the much more common O<sub>2</sub>. (20.5)

**Paramagnetism** a type of induced magnetism, associated with unpaired electrons, that causes a substance to be attracted into the inducing magnetic field. (9.3)

**Partial pressures** the independent pressures exerted by different gases in a mixture. (5.5)

**Particle accelerator** a device used to accelerate nuclear particles to very high speeds. (18.3)

**Pascal** the SI unit of pressure; equal to newtons per meter squared. (5.1)

**Pauli exclusion principle** in a given atom no two electrons can have the same set of four quantum numbers. (7.8)

**Peptide linkage** the bond resulting from the condensation reaction between amino acids; represented by:



**Percent dissociation** the ratio of the amount of a substance that is dissociated at equilibrium to the initial concentration of the substance in a solution, multiplied by 100. (14.5)

**Percent yield** the actual yield of a product as a percentage of the theoretical yield. (3.10)

**Periodic table** a chart showing all the elements arranged in columns with similar chemical properties. (2.7)

**pH curve (titration curve)** a plot showing the pH of a solution being analyzed as a function of the amount of titrant added. (15.4)

**pH scale** a log scale based on 10 and equal to  $-\log[\text{H}^+]$ ; a convenient way to represent solution acidity. (14.3)

**Phase diagram** a convenient way of representing the phases of a substance in a closed system as a function of temperature and pressure. (10.9)

**Phenyl group** the benzene molecule minus one hydrogen atom. (22.3)

**Photochemical smog** air pollution produced by the action of light on oxygen, nitrogen oxides, and unburned fuel from auto exhaust to form ozone and other pollutants. (5.10)

**Photon** a quantum of electromagnetic radiation. (7.2)

**Physical change** a change in the form of a substance, but not in its chemical composition; chemical bonds are not broken in a physical change. (1.9)

**Pi ( $\pi$ ) bond** a covalent bond in which parallel  $p$  orbitals share an electron pair occupying the space above and below the line joining the atoms. (9.1)

**Planck's constant** the constant relating the change in energy for a system to the frequency of the electromagnetic radiation absorbed or emitted; equal to  $6.626 \times 10^{-34}$  J s. (7.2)

**Polar covalent bond** a covalent bond in which the electrons are not shared equally because one atom attracts them more strongly than the other. (8.1)

**Polar molecule** a molecule that has a permanent dipole moment. (4.1)

**Polyatomic ion** an ion containing a number of atoms. (2.6)

**Polyelectronic atom** an atom with more than one electron. (7.9)

**Polymer** a large, usually chainlike molecule built from many small molecules (monomers). (22.5)

**Polymerization** a process in which many small molecules (monomers) are joined together to form a large molecule. (22.2)

**Polypeptide** a polymer formed from amino acids joined together by peptide linkages. (22.6)

**Polyprotic acid** an acid with more than one acidic proton. It dissociates in a stepwise manner, one proton at a time. (14.7)

**Porous disk** a disk in a tube connecting two different solutions in a galvanic cell that allows ion flow without extensive mixing of the solutions. (17.1)

**Porphyrin** a planar ligand with a central ring structure and various substituent groups at the edges of the ring. (21.7)

**Positional probability** a type of probability that depends on the number of arrangements in space that yield a particular state. (16.1)

**Positron production** a mode of nuclear decay in which a particle is formed having the same mass as an electron but opposite charge. The net effect is to change a proton to a neutron. (18.1)

**Potential energy** energy due to position or composition. (6.1)

**Precipitation reaction** a reaction in which an insoluble substance forms and separates from the solution. (4.5)

**Precision** the degree of agreement among several measurements of the same quantity; the reproducibility of a measurement. (1.4)

**Primary structure (of a protein)** the order (sequence) of amino acids in the protein chain. (22.6)

**Principal quantum number ( $n$ )** the quantum number relating to the size and energy of an orbital; it can have any positive integer value. (7.6)

**Probability distribution** the square of the wave function indicating the probability of finding an electron at a particular point in space. (7.5)

**Product** a substance resulting from a chemical reaction. It is shown to the right of the arrow in a chemical equation. (3.7)

**Protein** a natural high-molecular-weight polymer formed by condensation reactions between amino acids. (22.6)

**Proton** a positively charged particle in an atomic nucleus. (2.5; 18)

**Pure substance** a substance with constant composition. (1.9)

**Pyrometallurgy** recovery of a metal from its ore by treatment at high temperatures. (21.8)

**Quantization** the concept that energy can occur only in discrete units called *quanta*. (7.2)

**Rad** a unit of radiation dosage corresponding to  $10^{-2}$  J of energy deposited per kilogram of tissue (from *radiation absorbed dose*). (18.7)

**Radioactive decay (radioactivity)** the spontaneous decomposition of a nucleus to form a different nucleus. (2.4; 18.1)

**Radiocarbon dating (carbon-14 dating)** a method for dating ancient wood or cloth based on the rate of radioactive decay of the nuclide  $^{14}_6\text{C}$ . (18.4)

**Radiotracer** a radioactive nuclide, introduced into an organism for diagnostic purposes, whose pathway can be traced by monitoring its radioactivity. (18.4)

**Random error** an error that has an equal probability of being high or low. (1.4)

**Raoult's law** the vapor pressure of a solution is directly proportional to the mole fraction of solvent present. (11.4)

**Rate constant** the proportionality constant in the relationship between reaction rate and reactant concentrations. (12.2)

**Rate of decay** the change in the number of radioactive nuclides in a sample per unit time. (18.2)

**Rate-determining step** the slowest step in a reaction mechanism, the one determining the overall rate. (12.6)

**Rate law (differential rate law)** an expression that shows how the rate of reaction depends on the concentration of reactants. (12.2)

**Reactant** a starting substance in a chemical reaction. It appears to the left of the arrow in a chemical equation. (3.7)

**Reaction mechanism** the series of elementary steps involved in a chemical reaction. (12.6)

**Reaction quotient,  $Q$**  a quotient obtained by applying the law of mass action to initial concentrations rather than to equilibrium concentrations. (13.5)

**Reaction rate** the change in concentration of a reactant or product per unit time. (12.1)

**Reactor core** the part of a nuclear reactor where the fission reaction takes place. (18.6)

**Reducing agent (electron donor)** a reactant that donates electrons to another substance to reduce the oxidation state of one of its atoms. (4.9; 17.1)

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**Reduction** a decrease in oxidation state (a gain of electrons). (4.9; 17.1)

**Rem** a unit of radiation dosage that accounts for both the energy of the dose and its effectiveness in causing biological damage (from roentgen equivalent for man). (18.7)

**Resonance** a condition occurring when more than one valid Lewis structure can be written for a particular molecule. The actual electronic structure is not represented by any one of the Lewis structures but by the average of all of them. (8.12)

**Reverse osmosis** the process occurring when the external pressure on a solution causes a net flow of solvent through a semipermeable membrane from the solution to the solvent. (11.6)

**Reversible process** a cyclic process carried out by a hypothetical pathway, which leaves the universe exactly the same as it was before the process. No real process is reversible. (16.9)

**Ribonucleic acid (RNA)** a nucleotide polymer that transmits the genetic information stored in DNA to the ribosomes for protein synthesis. (22.6)

**Roasting** a process of converting sulfide minerals to oxides by heating in air at temperatures below their melting points. (21.8)

**Root mean square velocity** the square root of the average of the squares of the individual velocities of gas particles. (5.6)

**Salt** an ionic compound. (14.8)

**Salt bridge** a U-tube containing an electrolyte that connects the two compartments of a galvanic cell, allowing ion flow without extensive mixing of the different solutions. (17.1)

**Scientific method** the process of studying natural phenomena, involving observations, forming laws and theories, and testing of theories by experimentation. (1.2)

**Scintillation counter** an instrument that measures radioactive decay by sensing the flashes of light produced in a substance by the radiation. (18.4)

**Second law of thermodynamics** in any spontaneous process, there is always an increase in the entropy of the universe. (16.2)

**Secondary structure (of a protein)** the three-dimensional structure of the protein chain (for example,  $\alpha$ -helix, random coil, or pleated sheet). (22.6)

**Selective precipitation** a method of separating metal ions from an aqueous mixture by using a reagent whose anion forms a precipitate with only one or a few of the ions in the mixture. (4.7; 15.7)

**Semiconductor** a substance conducting only a slight electrical current at room temperature, but showing increased conductivity at higher temperatures. (10.5)

**Semipermeable membrane** a membrane that allows solvent but not solute molecules to pass through. (11.6)

**SI system** International System of units based on the metric system and units derived from the metric system. (1.3)

**Side chain (of amino acid)** the hydrocarbon group on an amino acid represented by H, CH<sub>3</sub>, or a more complex substituent. (22.6)

**Sigma ( $\sigma$ ) bond** a covalent bond in which the electron pair is shared in an area centered on a line running between the atoms. (9.1)

**Significant figures** the certain digits and the first uncertain digit of a measurement. (1.4)

**Silica** the fundamental silicon–oxygen compound, which has the empirical formula SiO<sub>2</sub>, and forms the basis of quartz and certain types of sand. (10.5)

**Silicates** salts that contain metal cations and polyatomic silicon–oxygen anions that are usually polymeric. (10.5)

**Single bond** a bond in which one pair of electrons is shared by two atoms. (8.8)

**Smelting** a metallurgical process that involves reducing metal ions to the free metal. (21.8)

**Solubility** the amount of a substance that dissolves in a given volume of solvent at a given temperature. (4.2)

**Solubility product constant** the constant for the equilibrium expression representing the dissolving of an ionic solid in water. (15.6)

**Solute** a substance dissolved in a liquid to form a solution. (4.2; 11.1)

**Solution** a homogeneous mixture. (1.9)

**Solvent** the dissolving medium in a solution. (4.2)

**Somatic damage** radioactive damage to an organism resulting in its sickness or death. (18.7)

**Space-filling model** a model of a molecule showing the relative sizes of the atoms and their relative orientations. (2.6)

**Specific heat capacity** the energy required to raise the temperature of one gram of a substance by one degree Celsius. (6.2)

**Spectator ions** ions present in solution that do not participate directly in a reaction. (4.6)

**Spectrochemical series** a listing of ligands in order based on their ability to produce *d*-orbital splitting. (21.6)

**Spontaneous fission** the spontaneous splitting of a heavy nuclide into two lighter nuclides. (18.1)

**Spontaneous process** a process that occurs without outside intervention. (16.1)

**Standard atmosphere** a unit of pressure equal to 760 mm Hg. (5.1)

**Standard enthalpy of formation** the enthalpy change that accompanies the formation of one mole of a compound at 25°C from its elements, with all substances in their standard states at that temperature. (6.4)

**Standard free energy change** the change in free energy that will occur for one unit of reaction if the reactants in their standard states are converted to products in their standard states. (16.6)

**Standard free energy of formation** the change in free energy that accompanies the formation of one mole of a substance from its constituent elements with all reactants and products in their standard states. (16.6)

**Standard hydrogen electrode** a platinum conductor in contact with 1 M H<sup>+</sup> ions and bathed by hydrogen gas at one atmosphere. (17.2)

**Standard reduction potential** the potential of a half-reaction under standard state conditions, as measured against the potential of the standard hydrogen electrode. (17.2)

**Standard solution** a solution whose concentration is accurately known. (4.3)

**Standard state** a reference state for a specific substance defined according to a set of conventional definitions. (6.4)

**Standard temperature and pressure (STP)** the condition 0°C and 1 atmosphere of pressure. (5.4)

**Standing wave** a stationary wave as on a string of a musical instrument; in the wave mechanical model, the electron in the hydrogen atom is considered to be a standing wave. (7.5)

**State function (property)** a property that is independent of the pathway. (6.1)

**States of matter** the three different forms in which matter can exist; solid, liquid, and gas. (1.9)

**Stereoisomerism** isomerism in which all the bonds in the isomers are the same but the spatial arrangements of the atoms are different. (21.4)

**Steric factor** the factor (always less than 1) that reflects the fraction of collisions with orientations that can produce a chemical reaction. (12.7)

**Stoichiometric quantities** quantities of reactants mixed in exactly the correct amounts so that all are used up at the same time. (3.10)

**Strong acid** an acid that completely dissociates to produce an H<sup>+</sup> ion and the conjugate base. (4.2; 14.2)

**Strong base** a metal hydroxide salt that completely dissociates into its ions in water. (4.2; 14.6)

**Strong electrolyte** a material that, when dissolved in water, gives a solution that conducts an electric current very efficiently. (4.2)

**Structural formula** the representation of a molecule in which the relative positions of the atoms are shown and the bonds are indicated by lines. (2.6)

**Structural isomerism** isomerism in which the isomers contain the same atoms but one or more bonds differ. (21.4; 22.1)

**Subcritical reaction (nuclear)** a reaction in which less than one neutron causes another fission event and the process dies out. (18.6)

**Sublimation** the process by which a substance goes directly from the solid to the gaseous state without passing through the liquid state. (10.8)

**Subshell** a set of orbitals with a given azimuthal quantum number. (7.6)

**Substitution reaction (hydrocarbons)** a reaction in which an atom, usually a halogen, replaces a hydrogen atom in a hydrocarbon. (22.1)

**Supercooling** the process of cooling a liquid below its freezing point without its changing to a solid. (10.8)

**Supercritical reaction (nuclear)** a reaction in which more than one neutron from each fission event causes another fission event. The process rapidly escalates to a violent explosion. (18.6)

**Superheating** the process of heating a liquid above its boiling point without its boiling. (10.8)

**Superoxide** a compound containing the O<sub>2</sub><sup>-</sup> anion. (19.2)

**Surface tension** the resistance of a liquid to an increase in its surface area. (10.2)

**Surroundings** everything in the universe surrounding a thermodynamic system. (6.1)

**Syndiotactic chain** a polymer chain in which the substituent groups such as CH<sub>3</sub> are arranged on alternate sides of the chain. (22.5)

**Syngas** synthetic gas, a mixture of carbon monoxide and hydrogen, obtained by coal gasification. (6.6)

**System (thermodynamic)** that part of the universe on which attention is to be focused. (6.1)

**Systematic error** an error that always occurs in the same direction. (1.4)

**Tempering** a process in steel production that fine-tunes the proportions of carbon crystals and cementite by heating to intermediate temperatures followed by rapid cooling. (21.8)

**Termolecular step** a reaction involving the simultaneous collision of three molecules. (12.6)

**Tertiary structure (of a protein)** the overall shape of a protein, long and narrow or globular, maintained by different types of intramolecular interactions. (22.6)

**Theoretical yield** the maximum amount of a given product that can be formed when the limiting reactant is completely consumed. (3.10)

**Theory** a set of assumptions put forth to explain some aspect of the observed behavior of matter. (1.2)

**Thermal pollution** the oxygen-depleting effect on lakes and rivers of using water for industrial cooling and returning it to its natural source at a higher temperature. (11.3)

**Thermodynamic stability (nuclear)** the potential energy of a particular nucleus as compared to the sum of the potential energies of its component protons and neutrons. (18.1)

**Thermodynamics** the study of energy and its interconversions. (6.1)

**Thermoplastic polymer** a substance that when molded to a certain shape under appropriate conditions can later be remelted. (22.5)

**Thermoset polymer** a substance that when molded to a certain shape under pressure and high temperatures cannot be softened again or dissolved. (22.5)

**Third law of thermodynamics** the entropy of a perfect crystal at 0 K is zero. (16.5)

**Titration** a technique in which one solution is used to analyze another. (4.8)

**Torr** another name for millimeter of mercury (mm Hg). (5.1)

**Transfer RNA (tRNA)** a small RNA fragment that finds specific amino acids and attaches them to the protein chain as dictated by the codons in mRNA. (22.6)

**Transition metals** several series of elements in which inner orbitals (*d* or *f* orbitals) are being filled. (7.11; 19.1)

**Transuranium elements** the elements beyond uranium that are made artificially by particle bombardment. (18.3)

**Triple bond** a bond in which three pairs of electrons are shared by two atoms. (8.8)

**Triple point** the point on a phase diagram at which all three states of a substance are present. (10.9)

**Tyndall effect** the scattering of light by particles in a suspension. (11.8)

**Uncertainty (in measurement)** the characteristic that any measurement involves estimates and cannot be exactly reproduced. (1.4)

**Unimolecular step** a reaction step involving only one molecule. (12.6)

**Unit cell** the smallest repeating unit of a lattice. (10.3)

**Unit factor method** an equivalence statement between units used for converting from one unit to another. (1.6)

**Universal gas constant** the combined proportionality constant in the ideal gas law; 0.08206 L · atm/K · mol or 8.3145 J/K · mol. (5.3)

**Valence electrons** the electrons in the outermost principal quantum level of an atom. (7.11)

**Valence shell electron-pair repulsion (VSEPR) model** a model whose main postulate is that the structure around a given atom in a molecule is determined principally by minimizing electron-pair repulsions. (8.13)

**Van der Waals equation** a mathematical expression for describing the behavior of real gases. (5.8)

**Van't Hoff factor** the ratio of moles of particles in solution to moles of solute dissolved. (11.7)

**Vapor pressure** the pressure of the vapor over a liquid at equilibrium. (10.8)

**Vaporization (evaporation)** the change in state that occurs when a liquid evaporates to form a gas. (10.8)

**Viscosity** the resistance of a liquid to flow. (10.2)

**Volt** the unit of electrical potential defined as one joule of work per coulomb of charge transferred. (17.1)

**Voltmeter** an instrument that measures cell potential by drawing electric current through a known resistance. (17.1)

**Volumetric analysis** a process involving titration of one solution with another. (4.8)

**A38** Glossary

**Vulcanization** a process in which sulfur is added to rubber and the mixture is heated, causing crosslinking of the polymer chains and thus adding strength to the rubber. (22.5)

**Wave function** a function of the coordinates of an electron's position in three-dimensional space that describes the properties of the electron. (7.5)

**Wave mechanical model** a model for the hydrogen atom in which the electron is assumed to behave as a standing wave. (7.5)

**Wavelength** the distance between two consecutive peaks or troughs in a wave. (7.1)

**Weak acid** an acid that dissociates only slightly in aqueous solution. (4.2; 14.2)

**Weak base** a base that reacts with water to produce hydroxide ions to only a slight extent in aqueous solution. (4.2; 14.6)

**Weak electrolyte** a material which, when dissolved in water, gives a solution that conducts only a small electric current. (4.2)

**Weight** the force exerted on an object by gravity. (1.3)

**Work** force acting over a distance. (6.1)

**X-ray diffraction** a technique for establishing the structure of crystalline solids by directing X rays of a single wavelength at a crystal and obtaining a diffraction pattern from which interatomic spaces can be determined. (10.3)

**Zone of nuclear stability** the area encompassing the stable nuclides on a plot of their positions as a function of the number of protons and the number of neutrons in the nucleus. (18.1)

**Zone refining** a metallurgical process for obtaining a highly pure metal that depends on continuously melting the impure material and recrystallizing the pure metal. (21.8)

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The answers listed here are from the *Complete Solutions Guide*, in which rounding is carried out at each intermediate step in a calculation in order to show the correct number of significant figures for that step. Therefore, an answer given here may differ in the last digit from the result obtained by carrying extra digits throughout the entire calculation and rounding at the end (the procedure you should follow).

## Chapter 1

**17.** A law summarizes what happens, e.g., law of conservation of mass in a chemical reaction or the ideal gas law,  $PV = nRT$ . A theory (model) is an attempt to explain why something happens. Dalton's atomic theory explains why mass is conserved in a chemical reaction. The kinetic molecular theory explains why pressure and volume are inversely related at constant temperature and moles of gas. **19.** A qualitative observation expresses what makes something what it is; it does not involve a number; e.g., the air we breathe is a mixture of gases, ice is less dense than water, rotten milk stinks. The SI units are mass in grams, length in meters, and volume in the derived units of  $\text{m}^3$ . The assumed uncertainty in a number is  $\pm 1$  in the last significant figure of the number. The precision of an instrument is related to the number of significant figures associated with an experimental reading on that instrument. Different instruments for measuring mass, length, or volume have varying degrees of precision. Some instruments only give a few significant figures for a measurement while others will give more significant figures. **21.** Significant figures are the digits we associate with a number. They contain all of the certain digits and the first uncertain digit (the first estimated digit). What follows is one thousand indicated to varying numbers of significant figures: 1000 or  $1 \times 10^3$  (1 S.F.);  $1.0 \times 10^3$  (2 S.F.);  $1.00 \times 10^3$  (3 S.F.); 1000. or  $1.000 \times 10^3$  (4 S.F.). To perform the calculation, the addition/subtraction significant rule is applied to  $1.5 - 1.0$ . The result of this is the one significant figure answer of 0.5. Next, the multiplication/division rule is applied to  $0.5/0.50$ . A one significant number divided by a two significant number yields an answer with one significant figure (answer = 1). **23.** The slope of the  $T_F$  vs.  $T_C$  plot is 1.8 ( $= 9/5$ ) and the y-intercept is  $32^\circ\text{F}$ . The slope of  $T_C$  vs.  $T_K$  plot is one and the y-intercept is  $-273^\circ\text{C}$ . **25.** **a.** exact; **b.** inexact; **c.** exact; **d.** inexact **27.** **a.** 3; **b.** 4; **c.** 4; **d.** 1; **e.** 7; **f.** 1; **g.** 3; **h.** 3 **29.** **a.**  $3.42 \times 10^{-4}$ ; **b.**  $1.034 \times 10^4$ ; **c.**  $1.7992 \times 10^1$ ; **d.**  $3.37 \times 10^5$  **31.** **a.** 641.0; **b.** 1.327; **c.** 77.34; **d.** 3215; **e.** 0.420 **33.** **a.** 188.1; **b.** 12.; **c.**  $4 \times 10^{-7}$ ; **d.**  $6.3 \times 10^{-26}$ ; **e.** 4.9; Uncertainty appears in the first decimal place. The average of several numbers can be only as precise as the least precise number. Averages can be exceptions to the significant figure rules. **f.** 0.22 **35.** **a.** 84.3 mm; **b.** 2.41 m; **c.**  $2.945 \times 10^{-5}$  cm; **d.** 14.45 km; **e.**  $2.353 \times 10^5$  mm; **f.** 0.9033  $\mu\text{m}$  **37.** **a.** 8 lb and 9.9 oz;  $20\frac{1}{4}$  in; **b.**  $4.0 \times 10^4$  km,  $4.0 \times 10^7$  m; **c.**  $1.2 \times 10^{-2}$   $\text{m}^3$ , 12 L,  $730 \text{ in}^3$ ,  $0.42 \text{ ft}^3$  **39.** **a.**  $4.00 \times 10^2$  rods; 10.0 furlongs;  $2.01 \times 10^3$  m; 2.01 km; **b.** 8390.0 rods; 209.75 furlongs; 42,195 m; 42.195 km **41.** **a.** 0.373 kg, 0.822 lb; **b.** 31.1 g, 156 carats; **c.**  $19.3 \text{ cm}^3$  **43.**  $2.95 \times 10^9$  knots;  $3.36 \times 10^9$  mi/h **45.** To the proper number of significant figures, the car is traveling at 40. mi/h, which would not violate the speed limit. **47.** 0.68 Canadian/L **49.** **a.**  $-273^\circ\text{C}$ , 0 K; **b.**  $-40^\circ\text{C}$ , 233 K; **c.**  $20^\circ\text{C}$ , 293 K; **d.**  $4 \times 10^7$  °C,  $4 \times 10^7$  K **51.** **a.** 312.4 K;  $102.6^\circ\text{F}$ ; **b.** 248 K;  $-13^\circ\text{F}$ ; **c.** 0 K;  $-459^\circ\text{F}$ ; **d.** 1074 K;  $1470^\circ\text{F}$  **53.** It will float (density =  $0.80 \text{ g/cm}^3$ ). **55.**  $1 \times 10^6 \text{ g/cm}^3$  **57.**  $0.28 \text{ cm}^3$  **59.**  $3.8 \text{ g/cm}^3$  **61.** **a.** Both are the same mass; **b.** 1.0 mL mercury; **c.** Both are the same mass; **d.** 1.0 L benzene **63.** **a.** 1.0 kg feather; **b.** 100 g water; **c.** same **65.** 2.77 cm **67.** **a.** Picture iv represents a gaseous compound. Pictures ii and iii also contain a gaseous compound but have a gaseous element present. **b.** Picture vi represents a mixture of two elemental gases. **c.** Picture v represents a solid element. **d.** Pictures ii and iii both represent a mixture of a gaseous element and a gaseous compound. **69.** **a.** heterogeneous;

**b.** homogeneous (hopefully); **c.** homogeneous; **d.** homogeneous (hopefully); **e.** heterogeneous; **f.** heterogeneous **71.** **a.** physical; **b.** chemical; **c.** physical; **d.** chemical **73.** 24 capsules **75.**  $1.0 \times 10^5$  bags **77.**  $56.56^\circ\text{C}$  **79.** **a.** Volume  $\times$  density = mass; the orange block is more dense. Since mass (orange)  $>$  mass (blue) and volume (orange)  $<$  volume (blue), then the density of the orange block must be greater to account for the larger mass of the orange block. **b.** Which block is more dense cannot be determined. Since mass (orange)  $>$  mass (blue) and volume (orange)  $>$  volume (blue), then the density of the orange block may or may not be larger than the blue block. If the blue block is more dense, then its density cannot be so large that the mass of the smaller blue block becomes larger than the orange block mass. **c.** The blue block is more dense. Since mass (blue) = mass (orange) and volume (blue)  $<$  volume (orange), then the density of the blue block must be larger to equate the masses. **d.** The blue block is more dense. Since mass (blue)  $>$  mass (orange) and the volumes are equal, then the density of the blue block must be larger to give the blue block the larger mass. **81.**  $8.5 \pm 0.5 \text{ g/cm}^3$  **83.** **a.** 2%; **b.** 2.2%; **c.** 0.2% **85.**  $d_{\text{old}} = 8.8 \text{ g/cm}^3$ ,  $d_{\text{new}} = 7.17 \text{ g/cm}^3$ ;  $d_{\text{new}}/d_{\text{old}} = \text{mass}_{\text{new}}/\text{mass}_{\text{old}} = 0.81$ ; The difference in mass is accounted for by the difference in the alloy used (if the assumptions are correct). **87.** 7.0% **89.** **a.** One possibility is that rope B is not attached to anything and rope A and rope C are connected via a pair of pulleys and/or gears; **b.** Try to pull rope B out of the box. Measure the distance moved by C for a given movement of A. Hold either A or C firmly while pulling on the other rope. **91.** \$160/person;  $3.20 \times 10^3$  nickels/person; 85.6 £/person **93.**  $200.0^\circ\text{F} = 93.33^\circ\text{C}$ ;  $-100.0^\circ\text{F} = -73.3^\circ\text{C}$ ;  $93.33^\circ\text{C} = 366.48 \text{ K}$ ;  $-73.3^\circ\text{C} = 199.9 \text{ K}$ ; difference of temperatures in °C = 166.6; difference of temperatures in K = 166.6; No, there is not a difference of 300 degrees in °C or K.

## Chapter 2

**15.** A compound will always contain the same numbers (and types) of atoms. A given amount of hydrogen will react only with a specific amount of oxygen. Any excess oxygen will remain unreacted. **17.** Law of conservation of mass: mass is neither created nor destroyed. The mass before a chemical reaction always equals the mass after a chemical reaction. Law of definite proportion: a given compound always contains exactly the same proportion of elements by mass. Water is always 1 g H for every 8 g oxygen. Law of multiple proportions: When two elements form a series of compounds, the ratios of the mass of the second element that combine with one gram of the first element can always be reduced to small whole numbers. For  $\text{CO}_2$  and CO discussed in section 2.2, the mass ratios of oxygen that react with 1 g of carbon in each compound are in a 2:1 ratio. **19.** J. J. Thomson's study of cathode-ray tubes led him to postulate the existence of negatively charged particles which we now call electrons. Ernest Rutherford and his alpha bombardment of metal foil experiments led him to postulate the nuclear atom—an atom with a tiny dense center of positive charge (the nucleus) with electrons moving about the nucleus at relatively large distances away; the distance is so large that an atom is mostly empty space. **21.** The number and arrangement of electrons in an atom determines how the atom will react with other atoms. The electrons determine the chemical properties of an atom. The number of neutrons present determine the isotope identity. **23.** Statements a and b are true. Counting over in the periodic table, element 118 will be the next noble gas (a nonmetal). For statement c, hydrogen has mostly nonmetallic properties. For statement d, a family of elements is also known as a group of elements. For statement e, two items are incorrect. When a metal reacts with a nonmetal, an ionic compound is produced and the formula of the compound would be  $\text{AX}_2$  (since alkaline earth metals for +2 ions and halogens form -1 ions in ionic compounds). The correct statement would be: When alkaline earth metal, A reacts with a

## A42 Answers to Selected Exercises

halogen, X, the formula of the ionic compound formed should be AX<sub>2</sub>.

- 25.** **a.** The composition of a substance depends on the number of atoms of each element making up the compound (depends on the formula of the compound) and not on the composition of the mixture from which it was formed. **b.** Avogadro's hypothesis implies that volume ratios are equal to molecule ratios at constant temperature and pressure. H<sub>2</sub>(g) + Cl<sub>2</sub>(g) → 2 HCl(g); from the balanced equation, the volume of HCl produced will be twice the volume of H<sub>2</sub> (or Cl<sub>2</sub>) reacted. **27.** All the masses of hydrogen in these three compounds can be expressed as simple whole-number ratios. The g H/g N in hydrazine, ammonia, and hydrogen azide are in the ratios 6:9:1. **29.** O, 7.94; Na, 22.8; Mg, 11.9; O and Mg are incorrect by a factor of ≈2; correct formulas are H<sub>2</sub>O, Na<sub>2</sub>O, and MgO. **31.** Using  $r = 5 \times 10^{-14}$  cm,  $d_{\text{nucleus}} = 3 \times 10^{15}$  g/cm<sup>3</sup>; using  $r = 1 \times 10^{-8}$  cm,  $d_{\text{atom}} = 0.4$  g/cm<sup>3</sup>. **33.** 37 **35.** sodium, Na; radium, Ra; iron, Fe; gold, Au; manganese, Mn; lead, Pb **37.** Sn, tin; Pt, platinum; Hg, mercury; Mg, magnesium; K, potassium; Ag, silver **39.** **a.** Metals: Mg, Ti, Au, Bi, Ge, Eu, Am; nonmetals: Si, B, At, Rn, Br; **b.** metalloids: Si, Ge, B, At. The elements at the boundary between the metals and the nonmetals are B, Si, Ge, As, Sb, Te, Po, and At. These elements are all considered metalloids. Aluminum has mostly properties of metals. **41.** **a.** 6; **b.** 5; **c.** 4; **d.** 6 **43.** **a.** 35 p, 44 n, 35 e; **b.** 35 p, 46 n, 35 e; **c.** 94 p, 145 n, 94 e; **d.** 55 p, 78 n, 55 e; **e.** 1 p, 2 n, 1 e; **f.** 26 p, 30 n, 26 e **45.** **a.** <sup>17</sup>O; **b.** <sup>37</sup>Cl; **c.** <sup>60</sup>Co; **d.** <sup>57</sup>Fe; **e.** <sup>131</sup>I; **f.** <sup>7</sup>Li **47.** <sup>151</sup>Eu<sup>3+</sup>; <sup>118</sup>Sn<sup>2+</sup> **49.** <sup>238</sup>U, 92 p, 146 n, 92 e, 0; <sup>40</sup>Ca<sup>2+</sup>, 20 p, 20 n, 18 e, 2+; <sup>23</sup>V<sup>3+</sup>, 23 p, 28 n, 20 e, 3+; <sup>89</sup>Y, 39 p, 50 n, 39 e, 0; <sup>79</sup>Br<sup>-</sup>, 35 p, 44 n, 36 e, 1-; <sup>15</sup>F<sup>3-</sup>, 15 p, 16 n, 18 e, 3- **51.** **a.** transition metals; **b.** alkaline earth metals; **c.** alkali metals; **d.** noble gases; **e.** halogens **53.** **a.** lose 2 e<sup>-</sup> to form Ra<sup>2+</sup>; **b.** lose 3 e<sup>-</sup> to form In<sup>3+</sup>; **c.** gain 3 e<sup>-</sup> to form P<sup>3-</sup>; **d.** gain 2 e<sup>-</sup> to form Te<sup>2-</sup>; **e.** gain 1 e<sup>-</sup> to form Br<sup>-</sup>; **f.** lose 1 e<sup>-</sup> to form Rb<sup>+</sup> **55.** **a.** sodium bromide; **b.** rubidium oxide; **c.** calcium sulfide; **d.** aluminum iodide; **e.** SrF<sub>2</sub>; **f.** Al<sub>2</sub>Se<sub>3</sub>; **g.** K<sub>3</sub>N; **h.** Mg<sub>3</sub>P<sub>2</sub> **57.** **a.** cesium fluoride; **b.** lithium nitride; **c.** silver sulfide (Silver forms only +1 ions so no Roman numerals are needed); **d.** manganese(IV) oxide; **e.** titanium(IV) oxide; **f.** strontium phosphide **59.** **a.** barium sulfate; **b.** sodium nitrite; **c.** potassium permanganate; **d.** potassium dichromate **61.** **a.** dinitrogen tetroxide; **b.** iodine trichloride; **c.** sulfur dioxide; **d.** diphosphorus pentasulfide **63.** **a.** copper(I) iodide; **b.** copper(II) iodide; **c.** cobalt(II) iodide; **d.** sodium carbonate; **e.** sodium hydrogen carbonate or sodium bicarbonate; **f.** tetrasulfur tetranitride; **g.** sulfur hexafluoride; **h.** sodium hypochlorite; **i.** barium chromate; **j.** ammonium nitrate **65.** **a.** SF<sub>2</sub>; **b.** SF<sub>6</sub>; **c.** NaH<sub>2</sub>PO<sub>4</sub>; **d.** Li<sub>3</sub>N; **e.** Cr<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>; **f.** SnF<sub>2</sub>; **g.** NH<sub>4</sub>C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>; **h.** NH<sub>4</sub>HSO<sub>4</sub>; **i.** Co(NO<sub>3</sub>)<sub>3</sub>; **j.** Hg<sub>2</sub>Cl<sub>2</sub>; Mercury(I) exists as Hg<sub>2</sub><sup>2+</sup> ions. **k.** KClO<sub>3</sub>; **l.** NaH **67.** **a.** Na<sub>2</sub>O; **b.** Na<sub>2</sub>O<sub>2</sub>; **c.** KCN; **d.** Cu(NO<sub>3</sub>)<sub>2</sub>; **e.** SeBr<sub>4</sub>; **f.** HIO<sub>3</sub>; **g.** PbS<sub>2</sub>; **h.** CuCl; **i.** GaAs (from the positions in the periodic table, Ga<sup>3+</sup> and As<sup>3-</sup> are the predicted ions); **j.** CdSe; **k.** ZnS; **l.** HNO<sub>2</sub>; **m.** P<sub>2</sub>O<sub>5</sub> **69.** **a.** nitric acid, HNO<sub>3</sub>; **b.** perchloric acid, HClO<sub>4</sub>; **c.** acetic acid, HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>; **d.** sulfuric acid, H<sub>2</sub>SO<sub>4</sub>; **e.** phosphoric acid, H<sub>3</sub>PO<sub>4</sub> **71.** Yes, 1.0 g H would react with 37.0 g <sup>37</sup>Cl and 1.0 g H would react with 35.0 g <sup>35</sup>Cl. No, the mass ratio of H/Cl would always be 1 g H/37 g Cl for <sup>37</sup>Cl and 1 g H/35 g Cl for <sup>35</sup>Cl. As long as we had pure <sup>35</sup>Cl or pure <sup>37</sup>Cl, these ratios will always hold. If we have a mixture (such as the natural abundance of chlorine), the ratio will also be constant as long as the composition of the mixture of the two isotopes does not change. **73.** Only statement **a** is true. For statement **b**, X has 34 protons. For statement **c**, X has 45 neutrons. For statement **d**, X is selenium. **75.** **a.** lead(II) acetate; **b.** copper(II) sulfate; **c.** calcium oxide; **d.** magnesium sulfate; **e.** magnesium hydroxide; **f.** calcium sulfate; **g.** dinitrogen monoxide or nitrous oxide (common) **77.** X = Ra, 142 neutrons **79.** **a.** Ca<sub>3</sub>N<sub>2</sub>; calcium nitride; **b.** K<sub>2</sub>O; potassium oxide; **c.** RbF; rubidium fluoride; **d.** MgS; magnesium sulfide; **e.** BaI<sub>2</sub>; barium iodide; **f.** Al<sub>2</sub>Se<sub>3</sub>; aluminum selenide; **g.** Cs<sub>3</sub>P; cesium phosphide; **h.** InBr<sub>3</sub>; indium(III) bromide (In forms compounds with +1 and +3 ions. You would predict a +3 ion from the position of In in the periodic table.) **81.** 116 g S; 230. g O **83.** Cu, Ag, and Au **85.** C:H = 8:18 or 4:9 **87.** The ratio of the masses of R that combine with 1.00 g Q is 3:1, as expected by the law of multiple proportions. R<sub>3</sub>Q is the formula of the first compound. **89.** **a.** The compounds are isomers of each other. Isomers are compounds with the same formula but the atoms are attached differently, resulting in different properties. **b.** When wood burns,

most of the solid material is converted to gases, which escape. **c.** Atoms are not an indivisible particle. Atoms are composed of electrons, neutrons, and protons. **d.** The two hydride samples contain different isotopes of either hydrogen and/or lithium. Isotopes may have different masses but have similar chemical properties. **91.** tantalum(V) oxide; the formula would have the same subscripts, Ta<sub>2</sub>S<sub>5</sub>; 40 protons **93.** Ge<sup>4+</sup>; <sup>99</sup>Tc

## Chapter 3

**19.** From the relative abundances, there would be 9889 atoms of <sup>12</sup>C and 111 atoms of <sup>13</sup>C in the 10,000-atom sample. The average mass of carbon is independent of the sample size; it will always be 12.01 amu. The total mass would be  $1.201 \times 10^5$  amu. For one mol of carbon ( $6.022 \times 10^{23}$  atoms C), the average mass would still be 12.01 amu. There would be  $5.955 \times 10^{23}$  atoms of <sup>12</sup>C and  $6.68 \times 10^{21}$  atoms of <sup>13</sup>C. The total mass would be  $7.232 \times 10^{24}$  amu. The total mass in grams is 12.01 g/mol. **21.** Each person would have 100 trillion dollars. **23.** The mass percent of a compound is a constant no matter what amount of substance is present. Compounds always have constant composition. **25.** The information needed is mostly the coefficients in the balanced equation and the molar masses of the reactants and products. For percent yield, we would need the actual yield of the reaction and the amounts of reactants used.

$$\text{a. mass of CB produced} = 1.00 \times 10^4 \text{ molecules}$$

$$\text{A}_2\text{B}_2 \times \frac{1 \text{ mol A}_2\text{B}_2}{6.022 \times 10^{23} \text{ molecules A}_2\text{B}_2} \times \frac{2 \text{ mol CB}}{1 \text{ mol A}_2\text{B}_2} \times \frac{\text{molar mass of CB}}{\text{mol CB}}$$

$$\text{b. atoms of A produced} = 1.00 \times 10^4 \text{ molecules A}_2\text{B}_2 \times \frac{2 \text{ atoms A}}{1 \text{ molecule A}_2\text{B}_2}$$

$$\text{c. mol of C reacted} = 1.00 \times 10^4 \text{ molecules}$$

$$\text{A}_2\text{B}_2 \times \frac{1 \text{ mol A}_2\text{B}_2}{6.022 \times 10^{23} \text{ molecules A}_2\text{B}_2} \times \frac{2 \text{ mol C}}{1 \text{ mol A}_2\text{B}_2}$$

$$\text{d. \%yield} = \frac{\text{actual mass}}{\text{theoretical mass}} \times 100; \text{The theoretical mass of CB produced}$$

was calculated in part a. If the actual mass of CB produced is given, then the percent yield can be determined for the reaction using the percent yield equation.

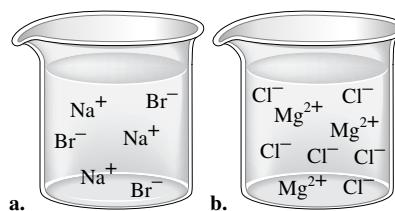
- 27.** 207.2 amu, Pb **29.** 185 amu **31.** There are three peaks in the mass spectrum, each 2 mass units apart. This is consistent with two isotopes, differing in mass by two mass units. **33.**  $4.64 \times 10^{-20}$  g Fe **35.**  $1.00 \times 10^{22}$  atoms C **37.** Al<sub>2</sub>O<sub>3</sub>, 101.96 g/mol; Na<sub>3</sub>AlF<sub>6</sub>, 209.95 g/mol **39.** **a.** 17.03 g/mol; **b.** 32.05 g/mol; **c.** 252.08 g/mol **41.** **a.** 0.0587 mol NH<sub>3</sub>; **b.** 0.0312 mol N<sub>2</sub>H<sub>4</sub>; **c.**  $3.97 \times 10^{-3}$  mol (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> **43.** **a.** 85.2 g NH<sub>3</sub>; **b.** 160. g N<sub>2</sub>H<sub>4</sub>; **c.** 1260 g (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> **45.** **a.** 70.1 g N; **b.** 140. g N; **c.** 140. g N **47.** **a.**  $3.54 \times 10^{22}$  molecules NH<sub>3</sub>; **b.**  $1.88 \times 10^{22}$  molecules N<sub>2</sub>H<sub>4</sub>; **c.**  $2.39 \times 10^{21}$  formula units (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> **49.** **a.**  $3.54 \times 10^{22}$  atoms N; **b.**  $3.76 \times 10^{22}$  atoms N; **c.**  $4.78 \times 10^{21}$  atoms N **51.** 176.12 g/mol;  $2.839 \times 10^{-3}$  mol;  $1.710 \times 10^{21}$  molecules **53.** **a.** 0.9393 mol; **b.**  $2.17 \times 10^{-4}$  mol; **c.**  $2.5 \times 10^{-8}$  mol **55.** **a.**  $4.01 \times 10^{22}$  atoms N; **b.**  $5.97 \times 10^{22}$  atoms N; **c.**  $3.67 \times 10^{22}$  atoms N; **d.**  $6.54 \times 10^{22}$  atoms N **57.** **a.** 294.30 g/mol; **b.**  $3.40 \times 10^{-2}$  mol; **c.** 459 g; **d.**  $1.0 \times 10^{19}$  molecules; **e.**  $4.9 \times 10^{21}$  atoms; **f.**  $4.9 \times 10^{-13}$  g; **g.**  $4.887 \times 10^{-22}$  g **59.** **a.** 50.00% C, 5.595% H, 44.41% O; **b.** 55.80% C, 7.025% H, 37.18% O; **c.** 67.90% C, 5.699% H, 26.40% N **61.** NO<sub>2</sub> = N<sub>2</sub>O<sub>4</sub> < NO < N<sub>2</sub>O **63.** 1360 g/mol **65.** **a.** 39.99% C, 6.713% H, 53.30% O; **b.** 40.00% C, 6.714% H, 53.29% O; **c.** 40.00% C, 6.714% H, 53.29% O (all the same except for rounding differences) **67.** **a.** NO<sub>2</sub>; **b.** CH<sub>2</sub>; **c.** P<sub>2</sub>O<sub>5</sub>; **d.** CH<sub>2</sub>O **69.** C<sub>8</sub>H<sub>11</sub>ON<sub>3</sub> **71.** compound I: HgO; compound II: Hg<sub>2</sub>O **73.** SN; S<sub>4</sub>N<sub>4</sub> **75.** C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>; C<sub>6</sub>H<sub>10</sub>O<sub>4</sub> **77.** C<sub>3</sub>H<sub>8</sub> **79.** C<sub>3</sub>H<sub>4</sub>, C<sub>9</sub>H<sub>12</sub> **81.** **a.** C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>(s) + 6O<sub>2</sub>(g) → 6CO<sub>2</sub>(g) + 6H<sub>2</sub>O(g); **b.** Fe<sub>2</sub>S<sub>3</sub>(s) + 6HCl(g) → 2FeCl<sub>3</sub>(s) + 3H<sub>2</sub>S(g); **c.** CS<sub>2</sub>(l) + 2NH<sub>3</sub>(g) → H<sub>2</sub>S(g) + NH<sub>4</sub>SCN(s) **83.** **a.** 3Ca(OH)<sub>2</sub>(aq) + 2H<sub>3</sub>PO<sub>4</sub>(aq) → 6H<sub>2</sub>O(l) + Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>(s); **b.** Al(OH)<sub>3</sub>(s) + 3HCl(aq) → AlCl<sub>3</sub>(aq) + 3H<sub>2</sub>O(l); **c.** 2AgNO<sub>3</sub>(aq) + H<sub>2</sub>SO<sub>4</sub>(aq) → Ag<sub>2</sub>SO<sub>4</sub>(s) + 2HNO<sub>3</sub>(aq) **85.** **a.** 2C<sub>6</sub>H<sub>6</sub>(l) + 15O<sub>2</sub>(g) → 12CO<sub>2</sub>(g) + 6H<sub>2</sub>O(g); **b.** 2C<sub>4</sub>H<sub>10</sub>(g) + 13O<sub>2</sub>(g) → 8CO<sub>2</sub>(g) + 10H<sub>2</sub>O(g); **c.** C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>(s) +

- 120**  $12\text{O}_2(g) \rightarrow 12\text{CO}_2(g) + 11\text{H}_2\text{O}(g)$ ; **d.**  $4\text{Fe}(s) + 3\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s)$ ; **e.**  $4\text{FeO}(s) + \text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s)$  **87. a.**  $\text{SiO}_2(s) + 2\text{C}(s) \rightarrow \text{Si}(s) + 2\text{CO}(g)$ ; **b.**  $\text{SiCl}_4(l) + 2\text{Mg}(s) \rightarrow \text{Si}(s) + 2\text{MgCl}_2(s)$ ; **c.**  $\text{Na}_2\text{SiF}_6(s) + 4\text{Na}(s) \rightarrow \text{Si}(s) + 6\text{NaF}(s)$  **89.** 7.26 g Al; 21.5 g  $\text{Fe}_2\text{O}_3$ ; 13.7 g  $\text{Al}_2\text{O}_3$  **91.** 4.355 kg **93.** 32 kg **95. a.** 73.9 g; **b.**  $1.30 \times 10^2$  g **97.**  $2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$ ; NO is limiting. **99.** 0.301 g  $\text{H}_2\text{O}_2$ ;  $3.6 \times 10^{-2}$  g HCl in excess **101.**  $2.81 \times 10^6$  g HCN;  $5.63 \times 10^6$  g  $\text{H}_2\text{O}$  **103.** 1.96 g (theoretical yield); 76.5% **105.**  $1.20 \times 10^3$  kg = 1.20 metric tons **107. 6** **109. a.** stoichiometric mixture; **b.** O<sub>2</sub>; **c.** H<sub>2</sub>; **d.** H<sub>2</sub>; **e.** H<sub>2</sub>; **f.** stoichiometric mixture; **g.** H<sub>2</sub> **111.**  $9.25 \times 10^{22}$  H atoms **113.**  $4.30 \times 10^{-2}$  mol; 2.50 g **115. 5** **117.** 42.8% **119.** 81.1 g **121.** 86.2% **123.**  $\text{C}_{20}\text{H}_{30}\text{O}$  **125.**  $\text{C}_7\text{H}_5\text{N}_3\text{O}_6$  **127.** 38.7% **129.** 40.08% **131.**  $\text{N}_4\text{H}_6$  **133.**  $1.8 \times 10^6$  g Cu(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>;  $5.9 \times 10^5$  g NH<sub>3</sub> **135.** 207 amu, Pb **137.**  $\text{Al}_2\text{Se}_3$  **139.** 0.48 mol **141. a.** 113 Fe atoms; **b.** mass =  $9.071 \times 10^{-20}$  g; **c.** 540 Ru atoms **143.** M = Y, X = Cl, yttrium(III) chloride; 1.84 g

## Chapter 4

**9. a.** Polarity is a term applied to covalent compounds. Polar covalent compounds have an unequal sharing of electrons in bonds that results in an unequal charge distribution in the overall molecule. Polar molecules have a partial negative end and a partial positive end. These are not full charges like in ionic compounds, but are charges much less in magnitude. Water is a polar molecule and dissolves other polar solutes readily. The oxygen end of water (the partial negative end of the polar water molecule) aligns with the partial positive end of the polar solute while the hydrogens of water (the partial positive end of the polar water molecule) align with the partial negative end of the solute. These opposite charged attractions stabilize polar solutes in water. This process is called hydration. Nonpolar solutes do not have permanent partial negative and partial positive ends; nonpolar solutes are not stabilized in water and do not dissolve. **b.** KF is a soluble ionic compound so it is a strong electrolyte. KF(aq) actually exists as separate hydrated K<sup>+</sup> ions and hydrated F<sup>-</sup> ions in solution: C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> is a polar covalent molecule that is a nonelectrolyte. C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> is hydrated as described in part a. **c.** RbCl is a soluble ionic compound so it exists as separate hydrated Rb<sup>+</sup> ions and hydrated Cl<sup>-</sup> ions in solution. AgCl is an insoluble ionic compound so the ions stay together in solution and fall to the bottom of the container as a precipitate. **d.** HNO<sub>3</sub> is a strong acid and exists as separate hydrated H<sup>+</sup> ions and hydrated NO<sub>3</sub><sup>-</sup> ions in solution. CO is a polar covalent molecule and is hydrated as explained in part a. **11.** Bromides: NaBr, KBr, and HgBr (and others) would be soluble and AgBr, PbBr<sub>2</sub>, and Hg<sub>2</sub>Br<sub>2</sub> would be insoluble. Sulfates: Na<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (and others) would be soluble and BaSO<sub>4</sub>, CaSO<sub>4</sub>, and PbSO<sub>4</sub> (or Hg<sub>2</sub>SO<sub>4</sub>) would be insoluble. Hydroxides: NaOH, KOH, Ca(OH)<sub>2</sub> (and others) would be soluble and Al(OH)<sub>3</sub>, Fe(OH)<sub>3</sub>, and Cu(OH)<sub>2</sub> (and others) would be insoluble. Phosphates: Na<sub>3</sub>PO<sub>4</sub>, K<sub>3</sub>PO<sub>4</sub>, (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub> (and others) would be soluble and Ag<sub>3</sub>PO<sub>4</sub>, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, and FePO<sub>4</sub> (and others) would be insoluble. Lead: PbCl<sub>2</sub>, PbBr<sub>2</sub>, PbI<sub>2</sub>, Pb(OH)<sub>2</sub>, PbSO<sub>4</sub>, and PbS (and others) would be insoluble. Pb(NO<sub>3</sub>)<sub>2</sub> would be a soluble Pb<sup>2+</sup> salt. **13.** The Brønsted-Lowry definitions are best for our purposes. An acid is a proton donor and a base is a proton acceptor. A proton is an H<sup>+</sup> ion. Neutral hydrogen has 1 electron and 1 proton, so an H<sup>+</sup> ion is just a proton. An acid–base reaction is the transfer of an H<sup>+</sup> ion (a proton) from an acid to a base. **15. a.** The species reduced is the element that gains electrons. The reducing agent causes reduction to occur by itself being oxidized. The reducing agent is generally listed as the entire formula of the compound/ion that contains the element oxidized. **b.** The species oxidized is the element that loses electrons. The oxidizing agent causes oxidation to occur by itself being reduced. The oxidizing agent is generally listed as the entire formula of the compound/ion that contains the element reduced. **c.** For simple binary ionic compounds, the actual charge on the ions are the oxidation states. For covalent compounds, nonzero oxidation states are pretend charges the elements would have if they were held together by ionic bonds (assuming the bond is between two different nonmetals). Nonzero oxidation states for elements in covalent compounds are not actual charges. Oxidation states for covalent compounds are a bookkeeping method to keep track of electrons in a reaction.

**17.**



- c.** For answers c–i, we will describe what should be in each solution. For c, the drawing should have three times as many NO<sub>3</sub><sup>-</sup> anions as Al<sup>3+</sup> cations. **d.** The drawing should have twice as many NH<sub>4</sub><sup>+</sup> cations as SO<sub>4</sub><sup>2-</sup> anions. **e.** The drawing should have equal numbers of Na<sup>+</sup> cations and OH<sup>-</sup> anions. **f.** The drawing should have equal numbers of Fe<sup>2+</sup> cations and SO<sub>4</sub><sup>2-</sup> anions. **g.** The drawing should have equal numbers of K<sup>+</sup> cations and MnO<sub>4</sub><sup>-</sup> anions. **h.** The drawing should have equal numbers of H<sup>+</sup> cations and ClO<sub>4</sub><sup>-</sup> anions. **i.** The drawing should have equal numbers of NH<sub>4</sub><sup>+</sup> cations and C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup> anions. **19.**  $\text{CaCl}_2(s) \rightarrow \text{Ca}^{2+}(aq) + 2\text{Cl}^-(aq)$  **21. a.** 0.2677 M; **b.**  $1.255 \times 10^{-3}$  M; **c.**  $8.065 \times 10^{-3}$  M **23. a.**  $M_{\text{Ca}^{2+}} = 1.00$  M,  $M_{\text{NO}_3^-} = 2.00$  M; **b.**  $M_{\text{Na}^+} = 4.0$  M,  $M_{\text{SO}_4^{2-}} = 2.0$  M; **c.**  $M_{\text{NH}_4^+} = M_{\text{Cl}^-} = 0.187$  M; **d.**  $M_{\text{K}^+} = 0.0564$  M,  $M_{\text{PO}_4^{3-}} = 0.0188$  M **25.** 100.0 mL of 0.30 M AlCl<sub>3</sub> **27.** 4.00 g **29. a.** Place 20.0 g NaOH in a 2-L volumetric flask; add water to dissolve the NaOH and fill to the mark. **b.** Add 500. mL of the 1.00 M NaOH stock solution to a 2-L volumetric flask; fill to the mark with water. **c.** As in a, instead using 38.8 g K<sub>2</sub>CrO<sub>4</sub>. **d.** As in b, instead using 114 mL of 1.75 M K<sub>2</sub>CrO<sub>4</sub> stock solution. **31.**  $M_{\text{NH}_4^+} = 0.272$  M,  $M_{\text{SO}_4^{2-}} = 0.136$  M **33.**  $5.94 \times 10^{-8}$  M steroid **35.** Aluminum nitrate, magnesium chloride, and rubidium sulfate are soluble. **37. a.** no precipitate forms; **b.** Al(OH)<sub>3</sub>(s); **c.** CaSO<sub>4</sub>(s); **d.** NiS(s) **39. a.** No reaction occurs because all possible products are soluble salts. **b.**  $2\text{Al}(\text{NO}_3)_3(aq) + 3\text{Ba}(\text{OH})_2(aq) \rightarrow 2\text{Al}(\text{OH})_3(s) + 3\text{Ba}(\text{NO}_3)_2(aq); 2\text{Al}^{3+}(aq) + 6\text{NO}_3^-(aq) + 3\text{Ba}^{2+}(aq) + 6\text{OH}^-(aq) \rightarrow 2\text{Al}(\text{OH})_3(s) + 3\text{Ba}^{2+}(aq) + 6\text{NO}_3^-(aq); \text{Al}^{3+}(aq) + 3\text{OH}^-(aq) \rightarrow \text{Al}(\text{OH})_3(s); \text{c.}$   $\text{CaCl}_2(aq) + \text{Na}_2\text{SO}_4(aq) \rightarrow \text{CaSO}_4(s) + 2\text{NaCl}(aq); \text{Ca}^{2+}(aq) + 2\text{Cl}^-(aq) + 2\text{Na}^+(aq) + \text{SO}_4^{2-}(aq) \rightarrow \text{CaSO}_4(s) + 2\text{Na}^+(aq) + 2\text{Cl}^-(aq); \text{Ca}^{2+}(aq) + \text{SO}_4^{2-}(aq) \rightarrow \text{CaSO}_4(s); \text{d.}$   $\text{K}_2\text{S}(aq) + \text{Ni}(\text{NO}_3)_2(aq) \rightarrow 2\text{KNO}_3(aq) + \text{NiS}(s); 2\text{K}^+(aq) + \text{S}^{2-}(aq) + \text{Ni}^{2+}(aq) + 2\text{NO}_3^-(aq) \rightarrow 2\text{K}^+(aq) + 2\text{NO}_3^-(aq) + \text{NiS}(s); \text{Ni}^{2+}(aq) + \text{S}^{2-}(aq) \rightarrow \text{NiS}(s)$  **41. a.** CuSO<sub>4</sub>(aq) + Na<sub>2</sub>S(aq)  $\rightarrow \text{CuS}(s) + \text{Na}_2\text{SO}_4(aq); \text{Cu}^{2+}(aq) + \text{S}^{2-}(aq) \rightarrow \text{CuS}(s)$ ; the grey spheres are the Na<sup>+</sup> spectator ions and the blue-green spheres are the SO<sub>4</sub><sup>2-</sup> spectator ions; **b.** CoCl<sub>2</sub>(aq) + 2NaOH(aq)  $\rightarrow \text{Co}(\text{OH})_2(s) + 2\text{NaCl}(aq); \text{Co}^{2+}(aq) + 2\text{OH}^-(aq) \rightarrow \text{Co}(\text{OH})_2(s)$ ; the grey spheres are the Na<sup>+</sup> spectator ions and the green spheres are the Cl<sup>-</sup> spectator ions; **c.** AgNO<sub>3</sub>(aq) + KI(aq)  $\rightarrow \text{AgI}(s) + \text{KNO}_3(aq); \text{Ag}^+(aq) + \text{I}^-(aq) \rightarrow \text{AgI}(s)$ ; the red spheres are the K<sup>+</sup> spectator ions and the blue spheres are the NO<sub>3</sub><sup>-</sup> spectator ions **43. a.**  $\text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq) \rightarrow \text{BaSO}_4(s)$ ; **b.**  $\text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq) \rightarrow \text{PbCl}_2(s)$ ; **c.** No reaction; **d.** No reaction; **e.**  $\text{Cu}^{2+}(aq) + 2\text{OH}^-(aq) \rightarrow \text{Cu}(\text{OH})_2(s)$  **45. Ca**<sup>2+</sup>, Sr<sup>2+</sup>, or Ba<sup>2+</sup> could all be present. **47.** 0.607 g **49.** 0.520 g Al(OH)<sub>3</sub> **51.** 2.9 g AgCl; 0 M Ag<sup>+</sup>; 0.10 M NO<sub>3</sub><sup>-</sup>; 0.075 M Ca<sup>2+</sup>; 0.050 M Cl<sup>-</sup> **53.** 23 amu; Na **55. a.**  $2\text{HClO}_4(aq) + \text{Mg}(\text{OH})_2(s) \rightarrow \text{Mg}(\text{ClO}_4)_2(aq) + 2\text{H}_2\text{O}(l); 2\text{H}^+(aq) + 2\text{ClO}_4^-(aq) + \text{Mg}(\text{OH})_2(s) \rightarrow \text{Mg}^{2+}(aq) + 2\text{ClO}_4^-(aq) + 2\text{H}_2\text{O}(l); 2\text{H}^+(aq) + \text{Mg}(\text{OH})_2(s) \rightarrow \text{Mg}^{2+}(aq) + 2\text{H}_2\text{O}(l)$ ; **b.**  $\text{HCN}(aq) + \text{NaOH}(aq) \rightarrow \text{NaCN}(aq) + \text{H}_2\text{O}(l)$ ;  $\text{HCN}(aq) + \text{Na}^+(aq) + \text{OH}^-(aq) \rightarrow \text{Na}^+(aq) + \text{CN}^-(aq) + \text{H}_2\text{O}(l)$ ;  $\text{HCN}(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l) + \text{CN}^-(aq)$ ; **c.**  $\text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l); \text{H}^+(aq) + \text{Cl}^-(aq) + \text{Na}^+(aq) + \text{OH}^-(aq) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq) + \text{H}_2\text{O}(l); \text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l)$  **57. a.**  $\text{KOH}(aq) + \text{HNO}_3(aq) \rightarrow \text{H}_2\text{O}(l) + \text{KNO}_3(aq); \text{K}^+(aq) + \text{OH}^-(aq) + \text{H}^+(aq) + \text{NO}_3^-(aq) \rightarrow \text{H}_2\text{O}(l) + \text{K}^+(aq) + \text{NO}_3^-(aq); \text{OH}^-(aq) + \text{H}^+(aq) \rightarrow \text{H}_2\text{O}(l)$ ; **b.**  $\text{Ba}(\text{OH})_2(aq) + 2\text{HCl}(aq) \rightarrow 2\text{H}_2\text{O}(l) + \text{BaCl}_2(aq); \text{Ba}^{2+}(aq) + 2\text{OH}^-(aq) + 2\text{H}^+(aq) + 2\text{Cl}^-(aq) \rightarrow \text{Ba}^{2+}(aq) + 2\text{Cl}^-(aq) + 2\text{H}_2\text{O}(l); \text{OH}^-(aq) + \text{H}^+(aq) \rightarrow \text{H}_2\text{O}(l)$ ; **c.**  $3\text{HClO}_4(aq) + \text{Fe}(\text{OH})_3(s) \rightarrow 3\text{H}_2\text{O}(l) + \text{Fe}(\text{ClO}_4)_3(aq); 3\text{H}^+(aq) + 3\text{ClO}_4^-(aq) + \text{Fe}(\text{OH})_3(s) \rightarrow 3\text{H}_2\text{O}(l) + \text{Fe}^{3+}(aq) + 3\text{ClO}_4^-(aq); 3\text{H}^+(aq) + \text{Fe}(\text{OH})_3(s) \rightarrow 3\text{H}_2\text{O}(l) + \text{Fe}^{3+}(aq)$  **59. a.** 100. mL; **b.** 66.7 mL; **c.** 50.0 mL **61.**  $2.0 \times 10^{-2}$  M excess OH<sup>-</sup> **63.** 0.102 M **65.** 0.4178 g **67. a.** K, +1; O, -2; Mn, +7; **b.** Ni, +4; O, -2; **c.** Na, +1; Fe, +2; O,

## A44 Answers to Selected Exercises

-2; H, +1 **d.** H, +1; O, -2; N, -3; P, +5; **e.** P, +3; O, -2; **f.** O, -2; Fe, + $\frac{8}{3}$ ; **g.** O, -2; F, -1; Xe, -6; **h.** S, +4; F, -1; **i.** C, +2; O, -2; **j.** C, 0; H, +1; O, -2 **69. a.** -3; **b.** -3; **c.** -2; **d.** +2; **e.** +1; **f.** +4; **g.** +3; **h.** +5; **i.** 0

71. Redox?	Oxidizing Agent	Reducing Agent	Substance Oxidized	Substance Reduced
a. Yes	Ag <sup>+</sup>	Cu	Cu	Ag <sup>+</sup>
b. No	—	—	—	—
c. No	—	—	—	—
d. Yes	SiCl <sub>4</sub>	Mg	Mg	SiCl <sub>4</sub> (Si)
e. No	—	—	—	—

In b, c, and e, no oxidation numbers change from reactants to products.

**73. a.** Zn + 2HCl → Zn<sup>2+</sup> + H<sub>2</sub> + 2Cl<sup>-</sup>; **b.** 2H<sup>+</sup> + 3I<sup>-</sup> + ClO<sup>-</sup> → I<sub>3</sub><sup>-</sup> + Cl<sup>-</sup> + H<sub>2</sub>O; **c.** 7H<sub>2</sub>O + 4H<sup>+</sup> + 3As<sub>2</sub>O<sub>3</sub> + 4NO<sub>3</sub><sup>-</sup> → 4NO + 6H<sub>3</sub>AsO<sub>4</sub>; **d.** 16H<sup>+</sup> + 2MnO<sub>4</sub><sup>-</sup> + 10Br<sup>-</sup> → 5Br<sub>2</sub> + 2Mn<sup>2+</sup> + 8H<sub>2</sub>O; **e.** 8H<sup>+</sup> + 3CH<sub>3</sub>OH + Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> → 2Cr<sup>3+</sup> + 3CH<sub>2</sub>O + 7H<sub>2</sub>O **75. a.** 2H<sub>2</sub>O + Al + MnO<sub>4</sub><sup>-</sup> → Al(OH)<sub>4</sub><sup>-</sup> + MnO<sub>2</sub>; **b.** 2OH<sup>-</sup> + Cl<sub>2</sub> → Cl<sup>-</sup> + ClO<sup>-</sup> + H<sub>2</sub>O; **c.** OH<sup>-</sup> + H<sub>2</sub>O + NO<sub>2</sub><sup>-</sup> + 2Al → NH<sub>3</sub> + 2AlO<sub>2</sub><sup>-</sup> **77.** 4NaCl + 2H<sub>2</sub>SO<sub>4</sub> + MnO<sub>2</sub> → 2Na<sub>2</sub>SO<sub>4</sub> + MnCl<sub>2</sub> + Cl<sub>2</sub> + 2H<sub>2</sub>O **79.** Only statement b is true. **a.** A non-electrolyte solute can make a concentrated solution. **c.** Weak acids like acetic acid, HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, are weak electrolytes. **d.** Some ionic compounds do not dissolve in water (are insoluble). These compounds are not strong electrolytes (nor any type of electrolyte). The electrolyte designation refers to solutes that are soluble in water. **81. a.** AgNO<sub>3</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, and Hg<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> would form precipitates with the Cl<sup>-</sup> ion; Ag<sup>+(aq)</sup> + Cl<sup>-(aq)</sup> → AgCl(s); Pb<sup>2+(aq)</sup> + 2Cl<sup>-(aq)</sup> → PbCl<sub>2</sub>(s); Hg<sub>2</sub><sup>2+(aq)</sup> + 2Cl<sup>-(aq)</sup> → Hg<sub>2</sub>Cl<sub>2</sub>(s); **b.** Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, and Na<sub>3</sub>PO<sub>4</sub> would form precipitates with the Ca<sup>2+</sup> ion; Ca<sup>2+(aq)</sup> + SO<sub>4</sub><sup>2-</sup>(aq) → CaSO<sub>4</sub>(s); Ca<sup>2+(aq)</sup> + CO<sub>3</sub><sup>2-</sup>(aq) → CaCO<sub>3</sub>(s); 3Ca<sup>2+(aq)</sup> + 2PO<sub>4</sub><sup>3-</sup>(aq) → Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>(s); **c.** NaOH, Na<sub>2</sub>S, and Na<sub>2</sub>CO<sub>3</sub> would form precipitates with the Fe<sup>3+</sup> ion; Fe<sup>3+(aq)</sup> + 3OH<sup>-</sup>(aq) → Fe(OH)<sub>3</sub>(s); 2Fe<sup>3+(aq)</sup> + 3S<sup>2-</sup>(aq) → Fe<sub>2</sub>S<sub>3</sub>(s); 2Fe<sup>3+(aq)</sup> + 3CO<sub>3</sub><sup>2-</sup>(aq) → Fe<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>(s); **d.** BaCl<sub>2</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, and Ca(NO<sub>3</sub>)<sub>2</sub> would form precipitates with the SO<sub>4</sub><sup>2-</sup> ion; Ba<sup>2+(aq)</sup> + SO<sub>4</sub><sup>2-(aq)</sup> → BaSO<sub>4</sub>(s); Pb<sup>2+(aq)</sup> + SO<sub>4</sub><sup>2-(aq)</sup> → PbSO<sub>4</sub>(s); Ca<sup>2+(aq)</sup> + SO<sub>4</sub><sup>2-(aq)</sup> → CaSO<sub>4</sub>(s); **e.** Na<sub>2</sub>SO<sub>4</sub>, NaCl, and NaI would form precipitates with the Hg<sub>2</sub><sup>2+</sup> ion; Hg<sub>2</sub><sup>2+(aq)</sup> + SO<sub>4</sub><sup>2-(aq)</sup> → Hg<sub>2</sub>SO<sub>4</sub>(s); Hg<sub>2</sub><sup>2+(aq)</sup> + 2Cl<sup>-(aq)</sup> → Hg<sub>2</sub>Cl<sub>2</sub>(s); Hg<sub>2</sub><sup>2+(aq)</sup> + 2I<sup>-</sup>(aq) → Hg<sub>2</sub>I<sub>2</sub>(s); **f.** NaBr, Na<sub>2</sub>CrO<sub>4</sub>, and Na<sub>3</sub>PO<sub>4</sub> would form precipitates with the Ag<sup>+</sup> ion; Ag<sup>+(aq)</sup> + Br<sup>-(aq)</sup> → AgBr(s); 2Ag<sup>+(aq)</sup> + CrO<sub>4</sub><sup>2-</sup>(aq) → Ag<sub>2</sub>CrO<sub>4</sub>(s); 3Ag<sup>+(aq)</sup> + PO<sub>4</sub><sup>3-</sup>(aq) → Ag<sub>3</sub>PO<sub>4</sub>(s) **83. Ba** **85.** 39.49 mg/tablet; 67.00% **87. 2.00 M** **89. a.** 0.8393 M; **b.** 5.010% **91. C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>** **93. Ca(OH)<sub>2</sub>**, Sr(OH)<sub>2</sub>, and Ba(OH)<sub>2</sub> are possibilities for the base. **95.** 2H<sup>+(aq)</sup> + Mn(s) + 2HNO<sub>3</sub>(aq) → Mn<sup>2+</sup>(aq) + 2NO<sub>2</sub>(g) + 2H<sub>2</sub>O(l); 3H<sub>2</sub>O(l) + 2Mn<sup>2+</sup>(aq) + 5IO<sub>4</sub><sup>-</sup>(aq) → 2MnO<sub>4</sub><sup>-</sup>(aq) + 5IO<sub>3</sub><sup>-</sup>(aq) + 6H<sup>+(aq)</sup> **97. a.** 24.8% Co, 29.7% Cl, 5.09% H, 40.4% O; **b.** CoCl<sub>2</sub> · 6H<sub>2</sub>O; **c.** CoCl<sub>2</sub> · 6H<sub>2</sub>O(aq) + 2AgNO<sub>3</sub>(aq) → 2AgCl(s) + Co(NO<sub>3</sub>)<sub>2</sub>(aq) + 6H<sub>2</sub>O(l), CoCl<sub>2</sub> · 6H<sub>2</sub>O(aq) + 2NaOH(aq) → Co(OH)<sub>2</sub>(s) + 2NaCl(aq) + 6H<sub>2</sub>O(l), 4Co(OH)<sub>2</sub>(s) + O<sub>2</sub>(g) → 2Co<sub>2</sub>O<sub>3</sub>(s) + 4H<sub>2</sub>O(l) **99. a.** 7.000 M K<sup>+</sup>; **b.** 0.750 M CrO<sub>4</sub><sup>2-</sup> **101.** 0.123 g SO<sub>4</sub><sup>2-</sup>, 60.0% SO<sub>4</sub><sup>2-</sup>; 61% K<sub>2</sub>SO<sub>4</sub> and 39% Na<sub>2</sub>SO<sub>4</sub> **103.** 4.90 M **105. Y**, 2.06 mL/min; Z, 4.20 mL/min **107.** 57.6 mL **109. a.** MgO(s) + 2HCl(aq) → MgCl<sub>2</sub>(aq) + H<sub>2</sub>O(l), Mg(OH)<sub>2</sub>(s) + 2HCl(aq) → MgCl<sub>2</sub>(aq) + 2H<sub>2</sub>O(l), Al(OH)<sub>3</sub>(s) + 3HCl(aq) → AlCl<sub>3</sub>(aq) + 3H<sub>2</sub>O(l); **b.** MgO **111.** Citric acid has three acidic hydrogens per citric acid molecule. **113.** 0.07849 ± 0.00016 M or 0.0785 ± 0.0002 M **115.** 3(NH<sub>4</sub>)<sub>2</sub>CrO<sub>4</sub>(aq) + 2Cr(NO<sub>3</sub>)<sub>3</sub>(aq) → 6NH<sub>4</sub>NO<sub>2</sub>(aq) + Cr<sub>2</sub>(CrO<sub>4</sub>)<sub>3</sub>(s); 7.34 g **117. X = Se**; H<sub>2</sub>Se is hydroseleinic acid; 0.252 g

## Chapter 5

**17.** higher than; 13.6 times taller; When the pressure of the column of liquid standing on the surface of the liquid is equal to the pressure exerted by air on the rest of the surface of the liquid, then the height of the column of liquid is a measure of atmospheric pressure. Because water is 13.6 times less dense than

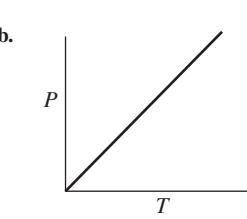
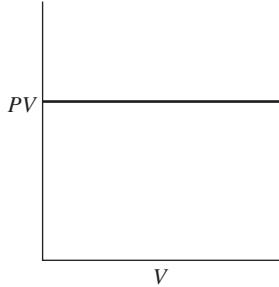
mercury, the column of water must be 13.6 times longer than that of mercury to match the force exerted by the columns of liquid standing on the surface.

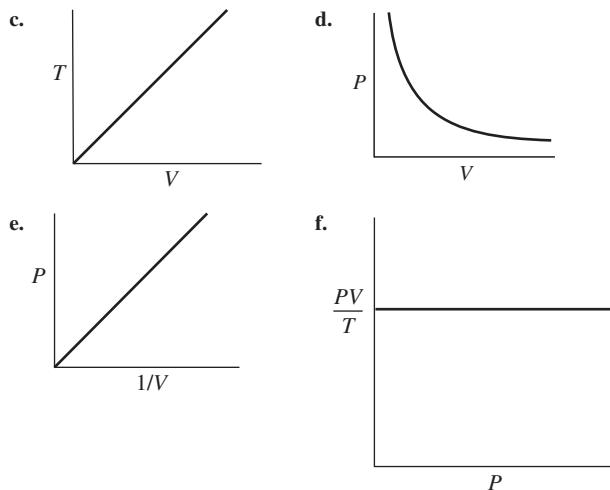
**19.** The *P* versus *1/V* plot is incorrect. The plot should be linear with positive slope and a *y*-intercept of zero.  $PV = k$  so  $P = k(1/V)$ , which is in the form of the straight-line equation  $y = mx + b$ . **21.**  $d = (\text{molar mass}) P/RT$ ; Because *d* is directly proportional to the molar mass of the gas. Helium, which has the smallest molar mass of all the noble gases, will have the smallest density. **23.** No; At any nonzero Kelvin temperature, there is a distribution of kinetic energies. Similarly, there is a distribution of velocities at any nonzero Kelvin temperature. **25.** 2NH<sub>3</sub>(g) → N<sub>2</sub>(g) + 3H<sub>2</sub>(g); At constant *P* and *T*, volume is directly proportional to the moles of gas present. In the reaction, the moles of gas doubles as reactants are converted to products, so the volume of the container should double. At constant *V* and *T*, *P* is directly proportional to the moles of gas present. As the moles of gas doubles, the pressure will double. The partial pressure of N<sub>2</sub> will be 1/2 the initial pressure of NH<sub>3</sub> and the partial pressure of H<sub>2</sub> will be 3/2 the initial pressure of NH<sub>3</sub>. The partial pressure of H<sub>2</sub> will be three times the partial pressure of N<sub>2</sub>. **27 a.**  $3.6 \times 10^3$  mm Hg; **b.**  $3.6 \times 10^3$  torr; **c.**  $4.9 \times 10^5$  Pa; **d.** 71 psi **29.** 65 torr,  $8.7 \times 10^3$  Pa,  $8.6 \times 10^{-2}$  atm **31. a.** 642 torr, 0.845 atm; 8.56 × 10<sup>4</sup> Pa; **b.** 975 torr; 1.28 atm;  $1.30 \times 10^5$  Pa; **c.** 517 torr; 850. torr **33.** The balloon will burst. **35.** 0.89 mol **37. a.** 14.0 L; **b.**  $4.72 \times 10^{-2}$  mol; **c.** 678 K; **d.** 133 atm **39.**  $4.44 \times 10^3$  g He;  $2.24 \times 10^3$  g H<sub>2</sub> **41.** a. 69.6 K; **b.** 32.3 atm **43.** 1.27 mol **45.**  $P_B = 2P_A$  **47.**  $5.1 \times 10^4$  torr **49.** The volume of the balloon increases from 1.00 L to 2.82 L, so the change in volume is 1.82 L. **51.** 3.21 g Al **53.** 135 g NaN<sub>3</sub> **55.**  $1.5 \times 10^7$  g Fe,  $2.6 \times 10^7$  g 98% H<sub>2</sub>SO<sub>4</sub> **57.** 2.47 mol H<sub>2</sub>O **59. a.** 2CH<sub>4</sub>(g) + 2NH<sub>3</sub>(g) + 3O<sub>2</sub>(g) → 2HCN(g) + 6H<sub>2</sub>O(g); **b.** 13.3 L **61.** Cl<sub>2</sub> **63.** 12.6 g/L **65.** 1.1 atm,  $P_{CO_2} = 1.1$  atm,  $P_{\text{TOTAL}} = 2.1$  atm **67.**  $P_{H_2} = 317$  torr,  $P_{N_2} = 50.7$  torr,  $P_{\text{TOTAL}} = 368$  torr **69. a.**  $\chi_{CH_4} = 0.412$ ,  $\chi_{O_2} = 0.588$ ; **b.** 0.161 mol; **c.** 1.06 g CH<sub>4</sub>, 3.03 g O<sub>2</sub> **71.** 0.990 atm; 0.625 g **73.** 18.0% **75.**  $P_{\text{tot}} = 6.0$  atm;  $P_{N_2} = 1.5$  atm;  $P_{H_2} = 4.5$  atm **77.** Both CH<sub>4</sub>(g) and N<sub>2</sub>(g) have the same average kinetic energy at the various temperatures. 273 K,  $5.65 \times 10^{-21}$  J/molecule; 546 K,  $1.13 \times 10^{-20}$  J/molecule **79.** CH<sub>4</sub>: 652 m/s (273 K); 921 m/s (546 K); N<sub>2</sub>: 493 m/s (273 K); 697 m/s (546 K)

Average KE	Average Velocity	Wall-Collision Frequency
a. Increase	Increase	Increase
b. Decrease	Decrease	Decrease
c. Same	Same	Increase
d. Same	Same	Increase

**83. a.** All the same; **b.** Flask C **85.** CF<sub>2</sub>Cl<sub>2</sub> **87.** The relative rates of effusion of <sup>12</sup>C<sup>16</sup>O, <sup>12</sup>C<sup>17</sup>O, and <sup>12</sup>C<sup>18</sup>O are 1.04, 1.02, and 1.00. Advantage: CO<sub>2</sub> isn't as toxic as CO. Disadvantages: Can get a mixture of oxygen isotopes in CO<sub>2</sub>, so some species would effuse at about the same rate. **89. a.** 12.24 atm; **b.** 12.13 atm; **c.** The ideal gas law is high by 0.91%. **91.**  $5.2 \times 10^{-6}$  atm;  $1.3 \times 10^{14}$  atoms He/cm<sup>3</sup> **93.** 2NO<sub>2</sub>(g) + H<sub>2</sub>O(l) → HNO<sub>3</sub>(aq) + HNO<sub>2</sub>(aq); SO<sub>3</sub>(g) + H<sub>2</sub>O(l) → H<sub>2</sub>SO<sub>4</sub>(aq)

**95. a.**





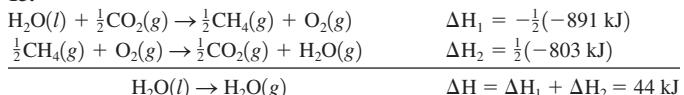
**97.** 0.772 atm · L; In Sample Exercise 5.3, 1.0 mol of gas was present at 0°C. The moles of gas and/or the temperature must have been different for Boyle's data. **99.** MnCl<sub>4</sub> **101.** 1490 **103.** 24 torr **105.** 4.1 × 10<sup>6</sup> L air; 7.42 × 10<sup>5</sup> L H<sub>2</sub> **107.** 490 atm **109.** 13.3% N **111.** C<sub>12</sub>H<sub>21</sub>NO; C<sub>24</sub>H<sub>42</sub>N<sub>2</sub>O<sub>2</sub> **113.** C<sub>3</sub>H<sub>8</sub> should have the largest *b* constant. Since CO<sub>2</sub> has the largest *a* constant, CO<sub>2</sub> will have the strongest intermolecular attractions. **115.** 13.4% CaO, 86.6% BaO **117.** C<sub>2</sub>H<sub>6</sub> **119. a.** 8.7 × 10<sup>3</sup> L air/min; **b.** χ<sub>CO</sub> = 0.0017, χ<sub>CO<sub>2</sub></sub> = 0.032, χ<sub>O<sub>2</sub></sub> = 0.13, χ<sub>N<sub>2</sub></sub> = 0.77, χ<sub>H<sub>2</sub>O</sub> = 0.067 **121. a.** 1.01 × 10<sup>4</sup> g; **b.** 6.65 × 10<sup>4</sup> g; **c.** 8.7 × 10<sup>3</sup> g **123. a.** Due to air's larger average molar mass, a given volume of air at a given set of conditions has a higher density than helium. We need to heat the air to greater than 25°C to lower the air density (by driving air out of the hot-air balloon) until the density is the same as that for helium (at 25°C and 1.00 atm). **b.** 2150 K **125. a.** 0.19 torr; **b.** 6.6 × 10<sup>15</sup> molecules CO/cm<sup>3</sup> **127.** 0.023 mol **129.** 4.8 g/L; UF<sub>3</sub> will effuse 1.02 times faster.

## Chapter 6

**9.** Path-dependent functions for a trip from Chicago to Denver are those quantities that depend on the route taken. One can fly directly from Chicago to Denver or one could fly from Chicago to Atlanta to Los Angeles and then to Denver. Some path-dependent quantities are miles traveled, fuel consumption of the airplane, time traveling, airplane snacks eaten, etc. State functions are path-independent; they only depend on the initial and final states. Some state functions for an airplane trip from Chicago to Denver would be longitude change, latitude change, elevation change, and overall time zone change.

**11.** Both *q* and *w* are negative.

**13.**



**15.** Fossil fuels contain carbon; the incomplete combustion of fossil fuels produces CO(g) instead of CO<sub>2</sub>(g). This occurs when the amount of oxygen reacting is not sufficient to convert all of the carbon in fossil fuels to CO<sub>2</sub>. Carbon monoxide is a poisonous gas to humans. **17.** 150 J **19.** 1.0 kg object with velocity of 2.0 m/s. **21. a.** 41 kJ; **b.** 35 kJ; **c.** 47 kJ; **d.** part a only **23.** 375 J heat transferred to the system **25.** −13.2 kJ **27.** 11.0 L **29.** *q* = 30.9 kJ, *w* = −12.4 kJ,  $\Delta E$  = 18.5 kJ **31.** This is an endothermic reaction, so heat must be absorbed to convert reactants into products. The high-temperature environment of internal combustion engines provides the heat. **33. a.** endothermic; **b.** exothermic; **c.** exothermic; **d.** endothermic **35. a.** −1650 kJ; **b.** −826 kJ; **c.** −7.39 kJ; **d.** −34.4 kJ **37.** 4400 g C<sub>3</sub>H<sub>8</sub> **39.** When a liquid is converted into a gas, there is an increase in volume.

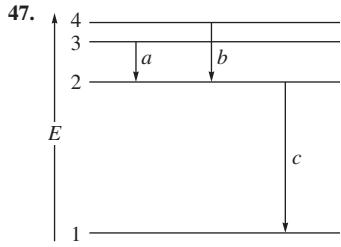
The 2.5 kJ/mol quantity can be considered as the work done by the vaporization process in pushing back the atmosphere. **41.** H<sub>2</sub>O(l); 2.30 × 10<sup>3</sup> J; Hg(l); 140°C **43.** Al(s) **45.** 311 K **47.** 23.7°C **49.** 0.25 J/g · °C **51.** −66 kJ/mol **53.** 39.2°C **55. a.** 31.5 kJ/C; **b.** −1.10 × 10<sup>3</sup> kJ/mol **57.** −220.8 kJ **59.** 1268 kJ; No, because this reaction is very endothermic, it would not be a practical way of making ammonia due to the high energy costs. **61.** −233 kJ **63.** −713 kJ **65.** The enthalpy change for the formation of one mole of a compound from its elements, with all substances in their standard states. Na(s) +  $\frac{1}{2}\text{Cl}_2(g) \rightarrow \text{NaCl}(s)$ ; H<sub>2</sub>(g) +  $\frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l)$ ; 6C(graphite)(s) + 6H<sub>2</sub>(g) + 3O<sub>2</sub>(g) → C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>(s); Pb(s) + S(s) + 2O<sub>2</sub>(g) → PbSO<sub>4</sub>(s) **67. a.** −940. kJ; **b.** −265 kJ; **c.** −176 kJ **69. a.** −908 kJ, −112 kJ, −140. kJ; **b.** 12NH<sub>3</sub>(g) + 21O<sub>2</sub>(g) → 8HNO<sub>3</sub>(aq) + 4NO(g) + 14H<sub>2</sub>O(g), exothermic **71.** −2677 kJ **73.** −169 kJ/mol **75.** −29.67 kJ/g **77.** For C<sub>3</sub>H<sub>8</sub>(g), −50.37 kJ/g vs. −47.7 kJ/g for octane. Because of the low boiling point of propane, there are extra safety hazards associated with using the necessary high-pressure compressed gas tanks. **79.** 1.05 × 10<sup>5</sup> L **81. a.** 2SO<sub>2</sub>(g) + O<sub>2</sub>(g) → 2SO<sub>3</sub>(g); *w* > 0; **b.** COCl<sub>2</sub>(g) → CO(g) + Cl<sub>2</sub>(g); *w* < 0; **c.** N<sub>2</sub>(g) + O<sub>2</sub>(g) → 2NO(g); *w* = 0; Compare the sum of the coefficients of all the product gases in the balanced equation to the sum of the coefficients of all the reactant gases. When a balanced reaction has more mol of product gases than mol of reactant gases, then the reaction will expand in volume ( $\Delta V$  is positive) and the system does work on the surroundings (*w* < 0). When a balanced reaction has a decrease in the mol of gas from reactants to products, then the reaction will contract in volume ( $\Delta V$  is negative) and the surroundings does compression work on the system (*w* > 0). When there is no change in the mol of gas from reactants to products, then  $\Delta V$  = 0 and *w* = 0. **83.** 25 J **85.** −4.2 kJ heat released **87.** The calculated  $\Delta H$  value will be less positive (smaller) than it should be. **89.** 25.91°C **91. a.** 632 kJ; **b.** C<sub>2</sub>H<sub>2</sub>(g) **93. a.** −361 kJ; **b.** −199 kJ; **c.** −227 kJ; **d.** −112 kJ **95. a.** C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>(s) + 12O<sub>2</sub>(g) → 12CO<sub>2</sub>(g) + 11H<sub>2</sub>O(l); **b.** −5630 kJ; **c.** −5630 kJ **97.** 37 m<sup>2</sup> **99.** 1 × 10<sup>4</sup> steps **101.** 56.9 kJ **103.** 1.74 kJ **105.** 3.3 cm

## Chapter 7

**15.** The equations relating the terms are  $\nu\lambda = c$ ,  $E = h\nu$ , and  $E = hc/\lambda$ . From the equations, wavelength and frequency are inversely related, photon energy and frequency are directly related, and photon energy and wavelength are inversely related. The unit of 1 Joule (J) = 1 kg m<sup>2</sup>/s<sup>2</sup>. This is why you must change mass units to kg when using the deBroglie equation. **17.** Sample Exercise 7.3 calculates the deBroglie wavelength of a ball and of an electron. The ball has a wavelength on the order of 10<sup>−34</sup> m. This is incredibly short and, as far as the wave-particle duality is concerned, the wave properties of large objects are insignificant. The electron, with its tiny mass, also has a short wavelength; on the order of 10<sup>−10</sup> m. However, this wavelength is significant as it is on the same order as the spacing between atoms in a typical crystal. For very tiny objects like electrons, the wave properties are important. The wave properties must be considered, along with the particle properties, when hypothesizing about the electron motion in an atom. **19.** For the radial probability distribution, the space around the hydrogen nucleus is cut up into a series of thin spherical shells. When the total probability of finding the electron in each spherical shell is plotted versus the distance from the nucleus, we get the radial probability distribution graph. The plot shows a steady increase with distance from the nucleus, maximizes at a certain distance from the nucleus, then shows a steady decrease. Even though it is likely to find an electron near the nucleus, the volume of the spherical shell close to the nucleus is tiny, resulting in a low radial probability. The maximum radial probability distribution occurs at a distance of  $5.29 \times 10^{-2}$  nm from the nucleus; the electron is most likely to be found in the volume of the shell centered at this distance from the nucleus. The  $5.29 \times 10^{-2}$  nm distance is the exact radius of innermost (*n* = 1) orbit in the Bohr model. **21.** If one more electron is added to a half-filled subshell, electron-electron repulsions will increase because two electrons must now occupy the same atomic orbital. This may slightly decrease the stability of the atom. Hence, half-filled subshells minimize electron-electron

## A46 Answers to Selected Exercises

repulsions. **23.** The valence electrons are strongly attracted to the nucleus for elements with large ionization energies. One would expect these species to readily accept another electron and have very exothermic electron affinities. The noble gases are an exception; they have a large ionization energy but an endothermic electron affinity. Noble gases have a stable arrangement of electrons. Adding an electron disrupts this stable arrangement, resulting in unfavorable electron affinities. **25.** For hydrogen, all orbitals with the same value of  $n$  have the same energy. For polyatomic atoms/ions, the energy of the orbitals also depends on  $\ell$ . Because there are more nondegenerate energy levels for polyatomic atoms/ions as compared with hydrogen, there are many more possible electronic transitions resulting in more complicated line spectra. **27.** Yes, the maximum number of unpaired electrons in any configuration corresponds to a minimum in electron-electron repulsions. **29.** Ionization energy applies to the removal of the electron from the atom in the gas phase. The work function applies to the removal of an electron from the solid. **31.**  $4.5 \times 10^{14} \text{ s}^{-1}$  **33.**  $3.0 \times 10^{10} \text{ s}^{-1}$ ,  $2.0 \times 10^{-23} \text{ J/photon}$ ,  $12 \text{ J/mol}$  **35.** Wave a has the longer wavelength ( $4.0 \times 10^{-4} \text{ m}$ ). Wave b has the higher frequency ( $1.5 \times 10^{12} \text{ s}^{-1}$ ) and larger photon energy ( $9.9 \times 10^{-22} \text{ J}$ ). Since both of these waves represent electromagnetic radiation, they both should travel at the same speed,  $c$ , the speed of light. Both waves represent infrared radiation. **37.**  $1.50 \times 10^{23}$  atoms **39.**  $427.7 \text{ nm}$  **41.** **a.**  $2.4 \times 10^{-11} \text{ m}$ ; **b.**  $3.4 \times 10^{-34} \text{ m}$  **43.**  $1.6 \times 10^{-27} \text{ kg}$  **45.** **a.**  $656.7 \text{ nm}$  (visible); **b.**  $486.4 \text{ nm}$  (visible); **c.**  $121.6 \text{ nm}$  (ultraviolet)



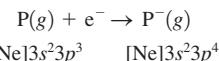
**49.**  $n = 1 \rightarrow n = 5$ ,  $\lambda = 95.00 \text{ nm}$ ;  $n = 2 \rightarrow n = 6$ ,  $\lambda = 410.4 \text{ nm}$ ; visible light has sufficient energy for the  $n = 2 \rightarrow n = 6$  transition but does not have sufficient energy for the  $n = 1 \rightarrow n = 5$  transition. **51.**  $n = 1$ ,  $91.20 \text{ nm}$ ;  $n = 2$ ,  $364.8 \text{ nm}$  **53.**  $n = 2$  **55.** **a.**  $5.79 \times 10^{-4} \text{ m}$ ; **b.**  $3.64 \times 10^{-33} \text{ m}$ ; **c.** The diameter of an H atom is roughly  $1.0 \times 10^{-8} \text{ cm}$ . The uncertainty in position is much larger than the size of the atom. **d.** The uncertainty is insignificant compared to the size of a baseball. **57.**  $n = 1, 2, 3, \dots$ ;  $\ell = 0, 1, 2, \dots (n - 1)$ ;  $m_\ell = -\ell, \dots, -2, -1, 0, 1, 2, \dots, +\ell$ . **59.** **b.** For  $\ell = 3$ ,  $m_\ell$  can range from  $-3$  to  $+3$ ; thus  $+4$  is not allowed. **c.**  $n$  cannot equal zero. **d.**  $\ell$  cannot be a negative number. **61.**  $\psi^2$  gives the probability of finding the electron at that point. **63.** 3; 1; 5; 25; 16 **65.** **a.** 32; **b.** 8; **c.** 25; **d.** 10; **e.** 6

<b>67. a.</b>					
1s	2s	2p	3s	3s	
<b>b.</b>					
1s	2s	2p	3s	3p	
<b>c.</b>					
1s	2s	2p	3s	3p	
<b>d.</b>					
4s	3d				
<b>e.</b>					
4s	3d				

**69.** Si:  $1s^2 2s^2 2p^6 3s^2 3p^2$  or  $[\text{Ne}]3s^2 3p^2$ ; Ga:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$  or  $[\text{Ar}]4s^2 3d^1 4p^1$ ; As:  $[\text{Ar}]4s^2 3d^1 4p^3$ ; Ge:  $[\text{Ar}]4s^2 3d^1 4p^2$ ; Al:  $[\text{Ne}]3s^2 3p^1$ ; Cd:  $[\text{Kr}]5s^2 4d^{10}$ ; S:  $[\text{Ne}]3s^2 3p^4$ ; Se:  $[\text{Ar}]4s^2 3d^1 4p^4$  **71.** Sc:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$ ; Fe:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$ ; P:  $1s^2 2s^2 2p^6 3s^2 3p^3$ ; Cs:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^1$  (Actual:  $[\text{Xe}]6s^2 4f^7$ ); Pt:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^8$  (Actual:  $[\text{Xe}]6s^1 4f^{14} 5d^9$ ); Xe:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$ ; Br:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$ ; **73.** **a.** I:  $[\text{Kr}]5s^2 4d^{10} 5p^5$ ; **b.** element 120:  $[\text{Rn}]7s^2 5f^{14} 6d^{10} 7p^8$ ; **c.** Rn:  $[\text{Xe}]6s^2 4f^{14} 6d^{10} 6p^6$ ; **d.** Cr:  $[\text{Ar}]4s^3 3d^5$  **75.** **a.** 18; **b.** 30; **c.** 10; **d.** 40

B: $1s^2 2s^2 2p^1$				N: $1s^2 2s^2 2p^3$			
$n$	$\ell$	$m_\ell$	$m_s$	$n$	$\ell$	$m_\ell$	$m_s$
1s	1	0	$+\frac{1}{2}$	1s	1	0	$+\frac{1}{2}$
1s	1	0	$-\frac{1}{2}$	1s	1	0	$-\frac{1}{2}$
2s	2	0	$+\frac{1}{2}$	2s	2	0	$+\frac{1}{2}$
2s	2	0	$-\frac{1}{2}$	2s	2	0	$-\frac{1}{2}$
2p	2	1	$+\frac{1}{2}$	2p	2	1	$+\frac{1}{2}$
				2p	2	1	$+\frac{1}{2}$
				2p	2	1	$+\frac{1}{2}$

For boron, there are six possibilities for the  $2p$  electron. For nitrogen, all the  $2p$  electrons could have  $m_s = -\frac{1}{2}$ . **79.** none; an excited state; energy released **81.** C, O, Si, S, Ti, Ni, Ge, Se **83.** Li (1 unpaired electron), N (3 unpaired electrons), Ni (2 unpaired electrons), and Te (2 unpaired electrons) are all expected to be paramagnetic because they have unpaired electrons. **85.** **a.** S < Se < Te; **b.** Br < Ni < K; **c.** F < Si < Ba **87.** **a.** Te < Se < S; **b.** K < Ni < Br; **c.** Ba < Si < F **89.** **a.** He; **b.** Cl; **c.** element 117; **d.** Si; **e.**  $\text{Na}^+$  **91.** **a.**  $[\text{Rn}]7s^2 5f^{14} 6d^4$ ; **b.** W; **c.**  $\text{SgO}_3$  and  $\text{SgO}_4^{2-}$  probably would form (similar to Cr). **93.** Se is an exception to the general ionization trend. There are extra electron-electron repulsions in Se because two electrons are in the same  $4p$  orbital, resulting in a lower ionization energy than expected. **95.** **a.** C, Br; **b.** N, Ar; **c.** C, Br **97.** Al (-44), Si (-120), P (-74), S (-200.4), Cl (-348.7); Based on the increasing nuclear charge, we would expect the electron affinity (EA) values to become more exothermic as we go from left to right in the period. Phosphorus is out of line. The reaction for the EA of P is



The additional electron in  $\text{P}^-$  will have to go into an orbital that already has one electron. There will be greater repulsions between the paired electrons in  $\text{P}^-$ , causing the EA of P to be less favorable than predicted based solely on attractions to the nucleus. **99.** **a.** I < Br < F < Cl; **b.** N < O < F **101.** **a.**  $\text{Se}^{3+}(g) \rightarrow \text{Se}^{4+}(g) + e^-$ ; **b.**  $\text{S}^-(g) + e^- \rightarrow \text{S}^{2-}(g)$ ; **c.**  $\text{Fe}^{3+}(g) + e^- \rightarrow \text{Fe}^{2+}(g)$ ; **d.**  $\text{Mg}(g) \rightarrow \text{Mg}^+(g) + e^-$  **103.** potassium peroxide,  $\text{K}_2\text{O}_2$ ;  $\text{K}^{2+}$  unstable **105.**  $6.582 \times 10^{14} \text{ s}^{-1}$ ;  $4.361 \times 10^{-19} \text{ J}$  **107.** Yes; the ionization energy general trend decreases down a group and the atomic radius trend increases down a group. The data in Table 7.8 confirm both of these general trends. **109.** **a.**  $6\text{Li}(s) + \text{N}_2(g) \rightarrow 2\text{Li}_3\text{N}(s)$ ; **b.**  $2\text{Rb}(s) + \text{S}(s) \rightarrow \text{Rb}_2\text{S}(s)$  **111.** 386 nm **113.** 200 s **115.**  $\lambda = 4.104 \times 10^{-5} \text{ cm}$  so violet light is emitted. **117.** **a.** true for H only; **b.** true for all atoms; **c.** true for all atoms **119.** When the  $p$  and  $d$  orbital functions are evaluated at various points in space, the results sometimes have positive values and sometimes have negative values. The term *phase* is often associated with the + and - signs. For example, a sine wave has alternating positive and negative phases. This is analogous to the positive and negative values (phases) in the  $p$  and  $d$  orbitals. **121.** The element with the smallest first ionization energy ( $I_1$ ) is Al (the green plot), the next highest  $I_1$  belongs to Mg (the blue plot), and Si has the largest  $I_1$  (the red plot). Mg is the element with the huge jump between  $I_2$  and  $I_3$ ; it has two valence electrons so the third electron removed is an inner-core electron. Inner-core electrons are always much more difficult to remove as compared to valence electrons because they are closer to the nucleus, on average, as

compared to the valence electrons. **123.** Valence electrons are easier to remove than inner-core electrons. The large difference in energy between  $I_2$  and  $I_3$  indicates that this element has two valence electrons. The element is most likely an alkaline earth metal because alkaline earth metals have two valence electrons. **125.** **a.** 146 kJ; **b.** 407 kJ; **c.** 1117 kJ; **d.** 1524 kJ **127.** **a.** line A,  $n = 6$  to  $n = 3$ ; line B,  $n = 5$  to  $n = 3$ ; **b.** 121.6 nm **129.** For  $r = a_0$  and  $\theta = 0^\circ$ ,  $\psi^2 = 2.46 \times 10^{28}$ . For  $r = a_0$  and  $\theta = 90^\circ$ ,  $\psi^2 = 0$ . As expected, the  $xy$  plane is a node for the  $2p_z$  atomic orbital.

**131. a.**

1				2			
3				4			
5	6	7	8	9	10	11	12
13	14	15	16	17	18	19	20

**b.** 2, 4, 12, and 20; **c.** There are many possibilities. One example of each formula is  $XY = 1 + 11$ ,  $XY_2 = 6 + 11$ ,  $X_2Y = 1 + 10$ ,  $XY_3 = 7 + 11$ , and  $X_2Y_3 = 7 + 10$ ; **d.** 6; **e.** 0; **f.** 18 **133.** The ratios for Mg, Si, P, Cl, and Ar are about the same. However, the ratios for Na, Al, and S are higher. For Na, the second IE is extremely high because the electron is taken from  $n = 2$  (the first electron is taken from  $n = 3$ ). For Al, the first electron requires a bit less energy than expected by the trend due to the fact it is a  $3p$  electron. For S, the first electron requires a bit less energy than expected by the trend due to electrons being paired in one of the  $p$  orbitals. **135. a.** As we remove succeeding electrons, the electron being removed is closer to the nucleus and there are fewer electrons left repelling it. The remaining electrons are more strongly attracted to the nucleus and it takes more energy to remove these electrons. **b.** For  $I_4$ , we begin removing an electron with  $n = 2$ . For  $I_3$ , we removed an electron with  $n = 3$ . In going from  $n = 3$  to  $n = 2$  there is a big jump in ionization energy because the  $n = 2$  electrons (inner core) are much closer to the nucleus on the average than the  $n = 3$  electrons (valence electrons). Since the  $n = 2$  electrons are closer to the nucleus, they are held more tightly and require a much larger amount of energy to remove them. **c.**  $Al^{4+}$ ; the electron affinity for  $Al^{4+}$  is  $\Delta H$  for the reaction



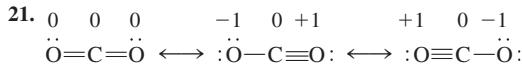
**d.** The greater the number of electrons, the greater the size. So



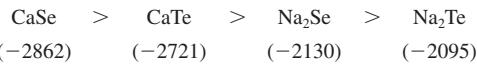
**137.** Solving for the molar mass of the element gives 40.2 g/mol; this is calcium. **139. a.**  $Fr = [Rn]7s^1$ ,  $Fr^+ = [Rn]$ ; **b.**  $7.7 \times 10^{22}$  Fr atoms; **c.**  $2.27790 \times 10^{-22} \text{ g}$

## Chapter 8

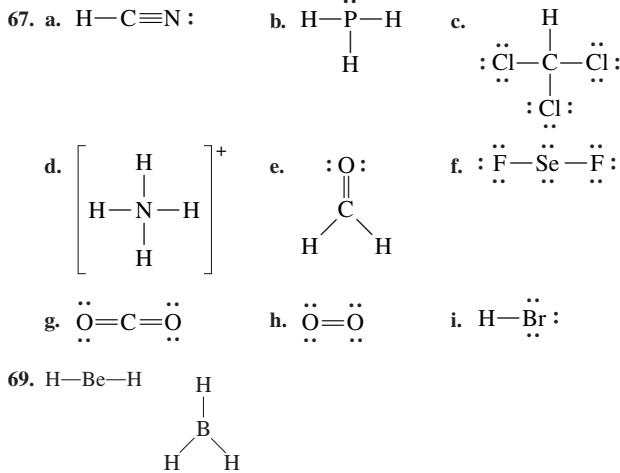
**13.**  $(NH_4)_2SO_4$  and  $Ca_3(PO_4)_2$  are compounds with both ionic and covalent bonds. **15.** Electronegativity increases left to right across the periodic table and decreases from top to bottom. Hydrogen has an electronegativity value between B and C in the second row, and identical to P in the third row. Going further down the periodic table, H has an electronegativity value between As and Se (row 4) and identical to Te (row 5). It is important to know where hydrogen fits into the electronegativity trend, especially for rows 2 and 3. If you know where H fits into the trend, then you can predict bond dipole directions for nonmetals bonded to hydrogen. **17.** For ions, concentrate on the number of protons and the number of electrons present. The species whose nucleus holds the electrons most tightly will be smallest. For example, compare the size of an anion to the neutral atom. The anion has more electrons held by the same number of protons in the nucleus. These electrons will not be held as tightly, resulting in a bigger size for the anion as compared to the neutral atom. For isoelectronic ions, the same number of electrons are held by different numbers of protons in the various ions. The ion with the most protons holds the electrons tightest and has smallest size. **19.** Fossil fuels contain a lot of carbon and hydrogen atoms. Combustion of fossil fuels (reaction with  $O_2$ ) produces  $CO_2$  and  $H_2O$ . Both these compounds have very strong bonds. Because strong bonds are formed, combustion reactions are very exothermic.



The formal charges are shown above the atoms in the three Lewis structures. The best Lewis structure for  $CO_2$ , from a formal charge standpoint, is the first structure with each oxygen double bonded to carbon. This structure has a formal charge of zero on all atoms (which is preferred). The other two resonance structures have nonzero formal charges on the oxygens, making them less reasonable. For  $CO_2$ , we usually ignore the last two resonance structures and think of the first structure as the true Lewis structure for  $CO_2$ . **23. a.**  $C < N < O$ ; **b.**  $Se < S < Cl$ ; **c.**  $Sn < Ge < Si$ ; **d.**  $Tl < Ge < S$  **25. a.**  $Ge-F$ ; **b.**  $P-Cl$ ; **c.**  $S-F$ ; **d.**  $Ti-Cl$  **27.** Order of electronegativity from Fig. 8.3: **a.**  $C(2.5) < N(3.0) < O(3.5)$ , same; **b.**  $Se(2.4) < S(2.5) < Cl(3.0)$ , same; **c.**  $Si = Ge = Sn(1.8)$ , different; **d.**  $Tl(1.8) = Ge(1.8) < S(2.5)$ , different. Most polar bonds using actual electronegativity values: **a.**  $Si-F$  and  $Ge-F$  equal polarity ( $Ge-F$  predicted); **b.**  $P-Cl$  (same as predicted); **c.**  $S-F$  (same as predicted); **d.**  $Ti-Cl$  (same as predicted) **29.** Incorrect: **b.**, **d.**, **e.**; **b.**  $\delta^-Cl-\delta^+I$ ; **d.** nonpolar bond so no dipole moment; **e.**  $\delta^-O-\delta^+P$  **31.**  $F-H > O-H > N-H > C-H > P-H$  **33.**  $Fr^+$ :  $[Xe]6s^24f^{14}5d^{10}6p^6$ ;  $Be^{2+}$ :  $ls^2$ ;  $P^{3-}$  and  $Cl^-$ :  $[Ne]3s^23p^6$ ;  $Se^{2-}$ :  $[Ar]4s^23d^104p^6$  **35. a.**  $Sc^{3+}$ ; **b.**  $Te^{2-}$ ; **c.**  $Ce^{4+}$ ,  $Ti^{4+}$ ; **d.**  $Ba^{2+}$  **37.**  $Sb^{3-}$ ,  $Te^{2-}$ ,  $I^-$ ,  $Cs^+$ ,  $Ba^{2+}$ , and  $La^{3+}$  are some possibilities.  $La^{3+} < Ba^{2+} < Cs^+ < I^- < Te^{2-} < Sb^{3-}$  **39. a.**  $Cu > Cu^+ > Cu^{2+}$ ; **b.**  $Pt^{2+} > Pd^{2+} > Ni^{2+}$ ; **c.**  $O^{2-} > O^- > O$ ; **d.**  $La^{3+} > Eu^{3+} > Gd^{3+} > Yb^{3+}$ ; **e.**  $Te^{2-} > I^- > Cs^+ > Ba^{2+} > La^{3+}$  **41. a.**  $Al_2S_3$ , aluminum sulfide; **b.**  $K_3N_1$ , Potassium nitride; **c.**  $MgCl_2$ , Magnesium chloride; **d.**  $CsBr$ , Cesium bromide **43. a.**  $NaCl$ ,  $Na^+$  smaller than  $K^+$ ; **b.**  $LiF$ ,  $F^-$  smaller than  $Cl^-$ ; **c.**  $MgO$ ,  $O^{2-}$  greater charge than  $OH^-$ ; **d.**  $Fe(OH)_3$ ,  $Fe^{3+}$  greater charge than  $Fe^{2+}$ ; **e.**  $Na_2O$ ,  $O^{2-}$  greater charge than  $Cl^-$ ; **f.**  $MgO$ ,  $Mg^{2+}$  smaller than  $Ba^{2+}$ , and  $O^{2-}$  smaller than  $S^{2-}$  **45.**  $-437 \text{ kJ/mol}$  **47.** The lattice energy for  $Mg^{2+}O^{2-}$  will be much more exothermic than for  $Mg^+O^-$ . **49.**  $181 \text{ kJ/mol}$  **51.**  $Ca^{2+}$  has greater charge than  $Na^+$ , and  $Se^{2-}$  is smaller than  $Te^{2-}$ . Charge differences affect lattice energy values more than size differences, and we expect the trend from most exothermic to least exothermic to be:

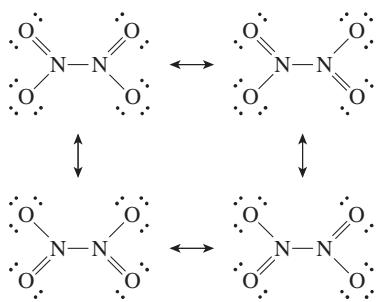
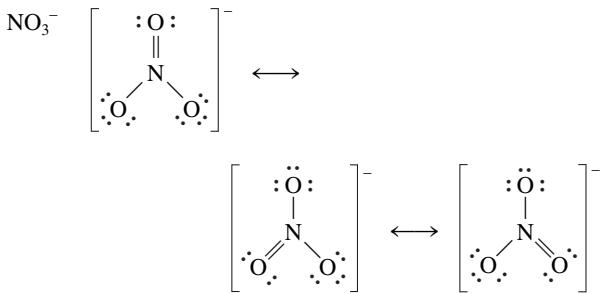
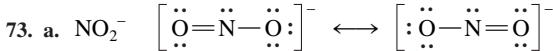
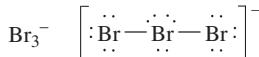
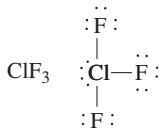
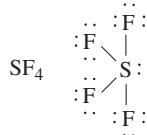
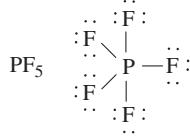


**53. a.**  $-183 \text{ kJ}$ ; **b.**  $-109 \text{ kJ}$  **55.**  $-42 \text{ kJ}$  **57.**  $-1276 \text{ kJ}$  **59.**  $-295 \text{ kJ}$  **61.**  $485 \text{ kJ/mol}$  **63. a.** Using standard enthalpies of formation,  $\Delta H^\circ = -184 \text{ kJ}$  vs.  $-183 \text{ kJ}$  from bond energies; **b.** Using standard enthalpies of formation,  $\Delta H = -92 \text{ kJ}$  vs.  $-109 \text{ kJ}$  from bond energies. Bond energies give a reasonably good estimate for  $\Delta H$ , especially when all reactants and products are gases. **65. a.** Using  $SF_4$  data:  $D_{SF} = 342.5 \text{ kJ/mol}$ . Using  $SF_6$  data:  $D_{SF} = 327.0 \text{ kJ/mol}$ . **b.** The S—F bond energy in the table is 327 kJ/mol. The value in the table was based on the S—F bond in  $SF_6$ . **c.**  $S(g)$  and  $F(g)$  are not the most stable forms of the elements at  $25^\circ\text{C}$ . The most stable forms are  $S_8(s)$  and  $F_2(g)$ ;  $\Delta H_f^\circ = 0$  for these two species.

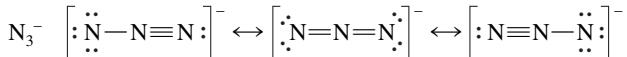
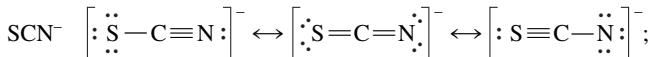
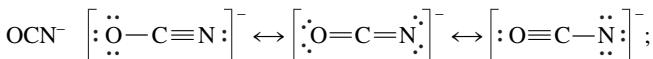


## A48 Answers to Selected Exercises

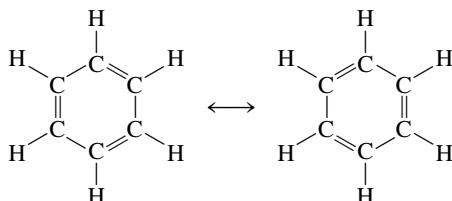
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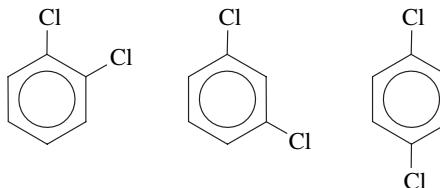
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75.



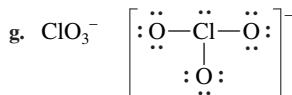
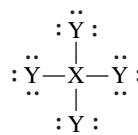
77. With resonance all carbon–carbon bonds are equivalent (we indicate this with a circle in the ring), giving three different structures:



Localized double bonds give four unique structures.

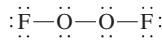
79.  $\text{N}_2$  (triple bond) <  $\text{N}_2\text{F}_2$  (double bond) <  $\text{N}_2\text{F}_4$  (single bond)

81. a.–f. and h. all have similar Lewis structures:



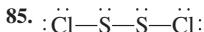
Formal charges: a. +1; b. +2; c. +3; d. +1; e. +2; f. +4; g. +2; h. +1

83.

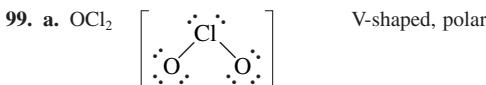


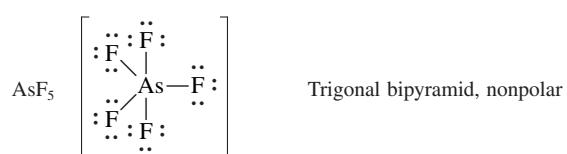
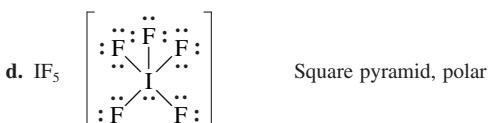
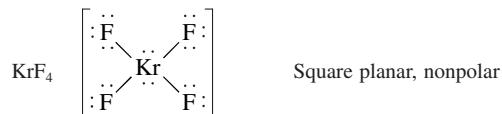
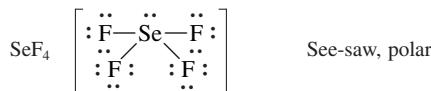
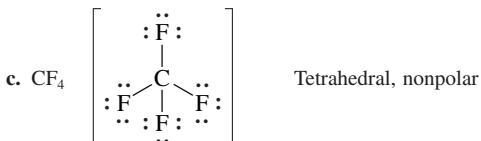
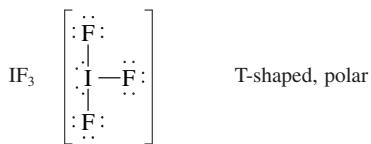
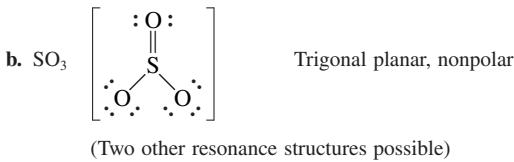
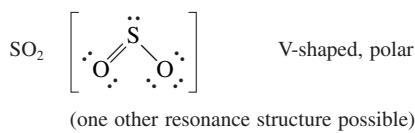
Formal charge: 0 0 0 0  
Oxidation number: -1 +1 +1 -1

Oxidation numbers are more useful. We are forced to assign +1 as the oxidation number for oxygen. Oxygen is very electronegative and +1 is not a stable oxidation state for this element.



87. [67] a. linear,  $180^\circ$ ; b. trigonal pyramidal,  $<109.5^\circ$ ; c. tetrahedral,  $109.5^\circ$ ; d. tetrahedral,  $109.5^\circ$ ; e. trigonal planar,  $120^\circ$ ; f. V-shaped,  $<109.5^\circ$ ; g. linear,  $180^\circ$ ; h. and i. linear, no bond angle in diatomic molecules; [73] a.  $\text{NO}_2^-$ : V-shaped,  $\sim 120^\circ$ ; b.  $\text{NO}_3^-$ : trigonal planar,  $120^\circ$ ; c.  $\text{N}_2\text{O}_4$ : trigonal planar about both N atoms,  $120^\circ$ ; d. all are linear,  $180^\circ$  89.  $\text{Br}_3^-$ : linear;  $\text{ClF}_3$ : T-shaped;  $\text{SF}_4$ : see-saw 91. a. trigonal planar,  $120^\circ$ ; b. V-shaped,  $\sim 120^\circ$  93. a. linear,  $180^\circ$ ; b. T-shaped,  $\sim 90^\circ$ ; c. see-saw,  $\sim 90^\circ$  and  $\sim 120^\circ$ ; d. trigonal bipyramidal,  $90^\circ$  and  $120^\circ$  95.  $\text{SeO}_2$  (bond dipoles do not cancel each other out in  $\text{SeO}_2$ ) 97.  $\text{ICl}_3$  and  $\text{TeF}_4$  (bond dipoles do not cancel each other out in  $\text{ICl}_3$  and  $\text{TeF}_4$ )





101. Element E is a halogen (F, Cl, Br, or I); trigonal pyramid;  $<109.5^\circ$

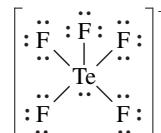
103. The polar bonds are symmetrically arranged about the central atoms, and all the individual bond dipoles cancel to give no net dipole moment for each molecule, i.e., the molecules are nonpolar. 105. a. radius:  $\text{N}^+ < \text{N}^- < \text{N}$ ; I.E.  $\text{N}^- < \text{N} < \text{N}^+$ ; b. radius:  $\text{Cl}^+ < \text{Cl}^- < \text{Se} < \text{Se}^-$ ; I.E.  $\text{Se}^- < \text{Se} < \text{Cl} < \text{Cl}^+$ ; c. radius:  $\text{Sr}^{2+} < \text{Rb}^+ < \text{Br}^-$ ; I.E.  $\text{Br}^- < \text{Rb}^+ < \text{Sr}^{2+}$ ; 107. a. 1549 kJ; b. 1390. kJ c. 1312 kJ; d. 1599 kJ

109. a.  $\text{NaBr}$ : In  $\text{NaBr}_2$ , the sodium ion would have a +2 charge assuming each bromine has a -1 charge. Sodium doesn't form stable  $\text{Na}^{2+}$  compounds.

b.  $\text{ClO}_4^-$ :  $\text{ClO}_4$  has 31 valence electrons so it is impossible to satisfy the octet rule for all atoms in  $\text{ClO}_4$ . The extra electron from the -1 charge in  $\text{ClO}_4^-$  allows for complete octets for all atoms. c.  $\text{XeO}_4$ : We can't draw a Lewis

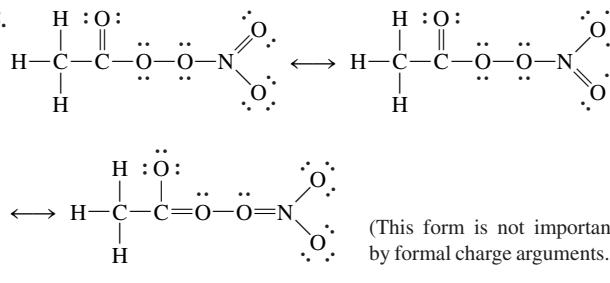
structure that obeys the octet rule for  $\text{SO}_4$  (30 electrons), unlike  $\text{XeO}_4$  (32 electrons). d.  $\text{SeF}_4$ : Both compounds require the central atom to expand its octet. O is too small and doesn't have low-energy  $d$  orbitals to expand its octet (which is true for all row 2 elements). 111. a. Both have one or more  $180^\circ$  bond angles; both are made up entirely of Xe and Cl; both have the individual bond dipoles arranged so they cancel each other (both are nonpolar); both have lone pairs on the central Xe atom; both have a central Xe atom that has more than 8 electrons around it. b. All have lone pairs on the central atom; all have a net dipole moment (all are polar). 113. Yes, each structure has the same number of effective pairs around the central atom. (We count a multiple bond as a single group of electrons.)

115.

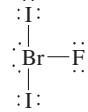
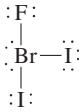


The lone pair of electrons around Te exerts a stronger repulsion than the bonding pairs. The stronger repulsion pushes the four square planner F atoms away from the lone pair, reducing the bond angles between the axial F atom and the square planar F atoms. 117. 17 kJ/mol 119. See Fig. 8.11 to see the data supporting  $\text{MgO}$  as an ionic compound. Note that the lattice energy is large enough to overcome all of the other processes (removing 2 electrons from Mg, and so on). The bond energy for  $\text{O}_2$  (247 kJ/mol) and electron affinity (737 kJ/mol) are the same when making CO. However, the energy needed to ionize carbon to form a  $\text{C}^{2+}$  ion must be too large. Figure 7.30 shows that the first ionization energy for carbon is about 400 kJ/mol greater than the first IE for magnesium. If all other numbers were equal, the overall energy change would be  $\sim 200$  kJ/mol (see Fig. 8.11). It is not unreasonable to assume that the second ionization energy for carbon is more than 200 kJ/mol greater than the second ionization energy of magnesium. 121. As the halogen atoms get larger, it becomes more difficult to fit three halogen atoms around the small nitrogen atom, and the  $\text{NX}_3$  molecule becomes less stable. 123. reaction i: -2636 kJ; reaction ii: -3471 kJ; reaction iii: -3543 kJ; Reaction iii yields the most energy per kg (-8085 kJ/kg)

125.



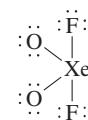
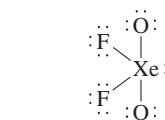
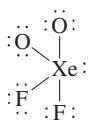
127. a. Two possible structures exist; each has a T-shaped molecular structure:



$90^\circ$  bond angle between I atoms

$180^\circ$  bond angle between I atoms

b. Three possible structures exist; each has a see-saw molecular structure.



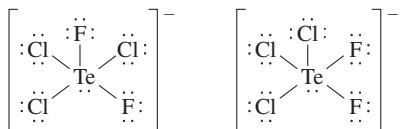
$90^\circ$  bond angle between O atoms

$180^\circ$  bond angle between O atoms

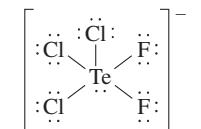
$120^\circ$  bond angle between O atoms

## A50 Answers to Selected Exercises

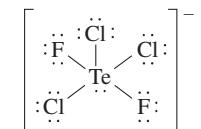
c. Three possible structures exist; each has a square pyramid molecular structure.



One F atom is 180° from lone pair.



Both F atoms are 90° from lone pair and 90° from each other.

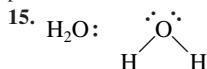


Both F atoms are 90° from lone pair and 180° from each other.

**129.**  $\Delta H = 0$  **131.** X is iodine; square pyramid **133.** Cr < As < P < Cl

### Chapter 9

**7.** In hybrid orbital theory, some or all of the valence atomic orbitals of the central atom in a molecule are mixed together to form hybrid orbitals; these hybrid orbitals point to where the bonded atoms and lone pairs are oriented. The  $\sigma$  bonds are formed from the hybrid orbitals overlapping head to head with an appropriate orbital on the bonded atom. The  $\pi$  bonds in hybrid orbital theory are formed from unhybridized  $p$  atomic orbitals. The  $p$  orbitals overlap side to side to form the  $\pi$  bond where the  $\pi$  electrons occupy the space above and below a line joining the atoms ( $\pi$  the internuclear axis). Assuming the  $z$ -axis is the internuclear axis, then the  $p_z$  atomic orbital will always be hybridized whether the hybridization is  $sp$ ,  $sp^2$ ,  $sp^3$ ,  $dsp^2$  or  $d^2sp^3$ . For  $sp$  hybridization, the  $p_x$  and  $p_y$  atomic orbitals are unhybridized; they are used to form two  $\pi$  bonds to the bonded atom(s). For  $sp^2$  hybridization, either the  $p_x$  or  $p_y$  atomic orbital is hybridized (along with the  $s$  and  $p_z$  orbitals); the other  $p$  orbital is used to form a  $\pi$  bond to a bonded atom. For  $sp^3$  hybridization, the  $s$  and all of the  $p$  orbitals are hybridized; no unhybridized  $p$  atomic orbitals are present, so typical  $\pi$  bonds do not form with  $sp^3$  hybridization. For  $dsp^3$  and  $d^2sp^3$  hybridization, we just mix in one or two  $d$  orbitals into the hybridization process. Which specific  $d$  orbitals are used is not important to our discussion. **9.** We use  $d$  orbitals when we have to; i.e., we use  $d$  orbitals when the central atom on a molecule has more than eight electrons around it. The  $d$  orbitals are necessary to accommodate the electrons over eight. Row 2 elements never have more than eight electrons around them so they never hybridize  $d$  orbitals. We rationalize this by saying there are no  $d$  orbitals close in energy to the valence  $2s$  and  $2p$  orbitals ( $2d$  orbitals are forbidden energy levels). However, for row 3 and heavier elements, there are  $3d$ ,  $4d$ ,  $5d$ , etc. orbitals which will be close in energy to the valence  $s$  and  $p$  orbitals. It is row 3 and heavier nonmetals that hybridize  $d$  orbitals when they have to. For sulfur, the valence electrons are in  $3s$  and  $3p$  orbitals. Therefore,  $3d$  orbitals are closest in energy and are available for hybridization. Arsenic would hybridize  $4d$  orbitals to go with the valence  $4s$  and  $4p$  orbitals while iodine would hybridize  $5d$  orbitals since the valence electrons are in  $n = 5$ . **11.** Bonding and antibonding molecular orbitals are both solutions to the quantum mechanical treatment of the molecule. Bonding orbitals form when in phase orbitals combine to give constructive interference. This results in enhanced electron probability located between the two nuclei. The end result is that a bonding MO is lower in energy than the atomic orbitals of which it is composed. Antibonding orbitals form when out-of-phase orbitals combine. The mismatched phases produce destructive interference leading to a node in the electron probability between the two nuclei. With electron distribution pushed to the outside, the energy of an antibonding orbital is higher than the energy of the atomic orbitals of which it is composed. **13.** The localized electron model does not deal effectively with molecules containing unpaired electrons. We can draw all of the possible resonance structures for NO, but still not have a good feel for whether the bond in NO is weaker or stronger than the bond in  $\text{NO}^-$ . MO theory can handle odd electron species without any modifications. In addition, hybrid orbital theory does not predict that  $\text{NO}^-$  is paramagnetic. The MO theory correctly makes this prediction.



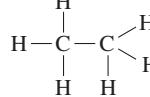
$\text{H}_2\text{O}$  has a tetrahedral arrangement of the electron pairs about the O atom that requires  $sp^3$  hybridization. Two of the  $sp^3$  hybrid orbitals are used to form bonds to the two hydrogen atoms, and the other two  $sp^3$  hybrid orbitals hold the two lone pairs on oxygen.

**17.**  $\text{H}_2\text{CO}$ :



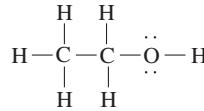
The central carbon atom has a trigonal planar arrangement of the electron pairs that requires  $sp^2$  hybridization. Two of the  $sp^2$  hybrid orbitals are used to form the two bonds to hydrogen. The other  $sp^2$  hybrid orbital forms the  $\sigma$  bond to oxygen. The unchanged (unhybridized)  $p$  orbital on carbon is used to form the  $\pi$  bond between carbon and oxygen.

**19.** Ethane:

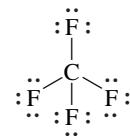


The carbon atoms are  $sp^3$  hybridized. The six C—H bonds are formed from the  $sp^3$  hybrid orbitals on C with the 1s atomic orbitals from the hydrogen atoms. The carbon–carbon bond is formed from an  $sp^3$  hybrid orbital on each C atom.

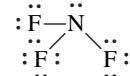
Ethanol:



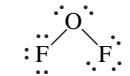
The two C atoms and the O atom are all  $sp^3$  hybridized. All bonds are formed from these  $sp^3$  hybrid orbitals. The C—H and O—H bonds form from  $sp^3$  hybrid orbitals and the 1s atomic orbitals from the hydrogen atom. The C—C and C—O bonds are formed from  $sp^3$  hybrid orbitals on each atom. **21.** [67] **a.**  $sp$ ; **b.**  $sp^3$ ; **c.**  $sp^3$ ; **d.**  $sp^3$ ; **e.**  $sp^2$ ; **f.**  $sp^3$ ; **g.**  $sp$ ; **h.** each O is  $sp^2$  hybridized; **i.** Br is  $sp^3$  hybridized [73] **a.**  $\text{NO}_2^-$ ,  $sp^2$ ; **b.**  $\text{NO}_3^-$ ,  $sp^2$ ; **c.**  $\text{N}_2\text{O}_4$ : both N atoms are  $sp^2$  hybridized; **d.** All are  $sp$  hybridized. **23.** All exhibit  $dsp^3$  hybridization. **25.** The molecules in Exercise 91 all exhibit  $sp^2$  hybridization about the central atom; the molecules in Exercise 92 all exhibit  $sp^3$  hybridization about the central atom. **27.** **a.** tetrahedral,  $109.5^\circ$ ,  $sp^3$ , nonpolar



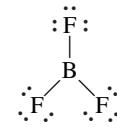
**b.** trigonal pyramid,  $<109.5^\circ$ ,  $sp^3$ , polar



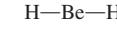
**c.** V-shaped,  $<109.5^\circ$ ,  $sp^3$ , polar

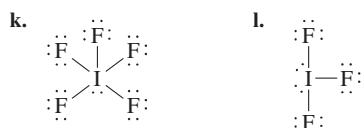
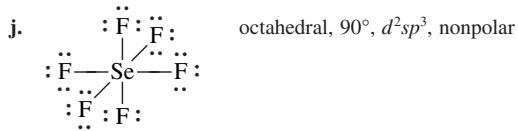
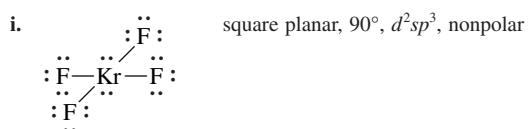
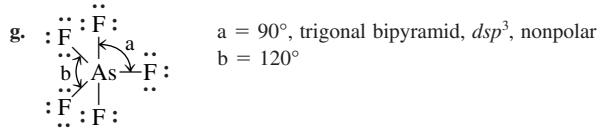
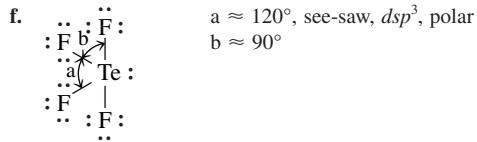


**d.** trigonal planar,  $120^\circ$ ,  $sp^2$ , nonpolar

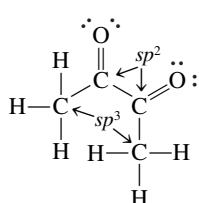


**e.** linear,  $180^\circ$ ,  $sp$ , nonpolar

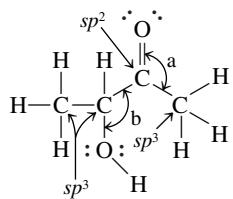




29. The  $\pi$  bond forces all six atoms into the same plane. 31. Biacetyl

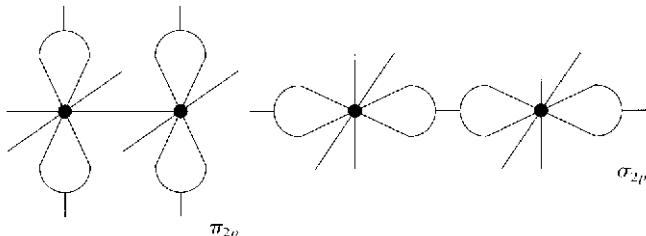


All CCO angles are  $120^\circ$ . The six atoms are not in the same plane.  $11\sigma$  and  $2\pi$  Acetoin

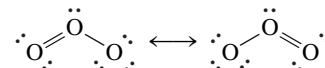


angle a =  $120^\circ$ , angle b =  $109.5^\circ$ , 13  $\sigma$  and 1  $\pi$  bond 33. To complete the Lewis structure, add lone pairs to complete octets for each atom. a. 6; b. 4; c. The center N in  $-N=N=N$  group; d. 33  $\sigma$ ; e. 5  $\pi$ ; f.  $180^\circ$ ; g.  $<109.5^\circ$ ; h.  $sp^3$  35. a.  $H_2^+$ ,  $H_2$ ,  $H_2^-$ ; b.  $He_2^{2+}$  and  $He_2^+$  37. a.  $(\sigma_{2s})^2$ ; B.O. = 1; diamagnetic (0 unpaired electrons); b.  $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4$ ; B.O. = 2; diamagnetic (0 unpaired electrons); c.  $(\sigma_{3s})^2(\sigma_{3s}^*)^2(\sigma_{3p})^2(\pi_{3p})^4(\pi_{3p}^*)^2$ ; B.O. = 2; paramagnetic (2 unpaired electrons) 39. When  $O_2$  loses an electron, it comes from a pi antibonding orbital, which strengthens the bond from a bond order of 2 to a bond order of 2.5. When  $N_2$  loses an electron,

it comes a pi bonding orbital, which changes the bond order from 3 to 2.5 (the bond weakens). 41.  $N_2^-$  and  $N_2^+$  43. a.  $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$ ; B.O. = 3; diamagnetic; b.  $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^1$ ; B.O. = 2.5; paramagnetic; c.  $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4$ ; B.O. = 2; diamagnetic; bond length:  $CO < CO^+ < CO^{2+}$ ; bond energy:  $CO^{2+} < CO^+ < CO$  45.  $H_2$ ;  $B_2$ ;  $C_2^{2-}$  47.

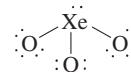


49. a. The electrons would be closer to F on the average. The F atom is more electronegative than the H atom, and the 2p orbital of F is lower in energy than the 1s orbital of H; b. The bonding MO would have more fluorine 2p character because it is closer in energy to the fluorine 2p orbital; c. The antibonding MO would place more electron density closer to H and would have a greater contribution from the higher-energy hydrogen 1s atomic orbital. 51.  $O_3$  and  $NO_2^-$  have identical Lewis structures, so we need to discuss only one of them. The Lewis structure for  $O_3$  is

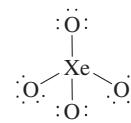


Localized electron model: The central oxygen atom is  $sp^2$  hybridized, which is used to form the two  $\sigma$  bonds and hold the lone pair of electrons. An unchanged (unhybridized)  $p$  atomic orbital forms the  $\pi$  bond with the neighboring oxygen atoms. The  $\pi$  bond resonates between the two positions. Molecular orbital model: There are two localized  $\sigma$  bonds and a  $\pi$  bond that is delocalized over the entire surface of the molecule. The delocalized  $\pi$  bond results from overlap of a  $p$  atomic orbital on each oxygen atom in  $O_3$ .

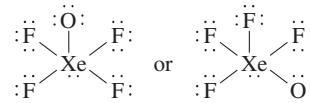
53. a. Trigonal pyramid;  $sp^3$



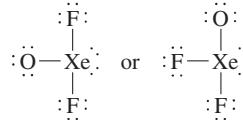
b. Tetrahedral;  $sp^3$



c. Square pyramid;  $d^2sp^3$



d. T-shaped;  $dsp^3$



e. Trigonal bipyramidal;  $dsp^3$

