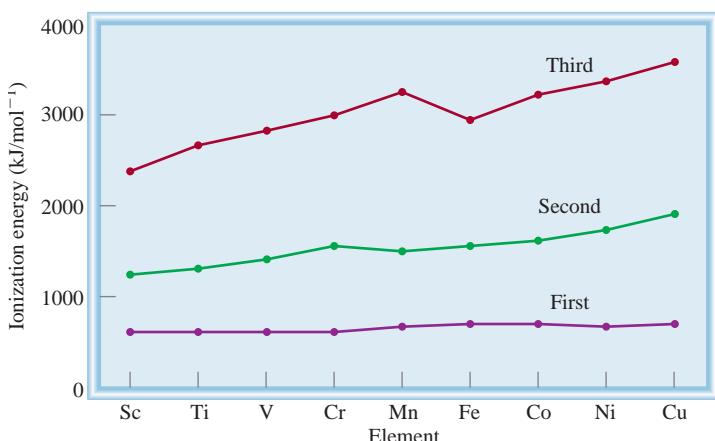


**Figure 15.3** Variation of the first, second, and third ionization energies for the first-row transition metals.



## Two Examples: The Chemistry of Iron and Copper

Figure 15.4 shows samples of the first-row transition metals. Here we will briefly survey the chemistry of two of these elements—iron and copper—paying particular attention to their occurrence, preparation, uses, and important compounds.

### Iron

After aluminum, iron is the most abundant metal in the Earth's crust (6.2 percent by mass). It is found in many ores; some of the economically important ones are *hematite* ( $\text{Fe}_2\text{O}_3$ ), *siderite* ( $\text{FeCO}_3$ ), and *magnetite* ( $\text{Fe}_3\text{O}_4$ ) (Figure 15.5). Pure iron is a gray metal and is not particularly hard. Its ion is essential in living systems because it reversibly binds oxygen to hemoglobin, the protein in blood that carries oxygen from the lungs to the rest of the tissues of the body.

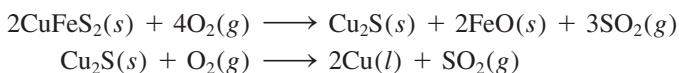
Iron reacts with hydrochloric acid to give hydrogen gas:



Concentrated sulfuric acid oxidizes the metal to  $\text{Fe}^{3+}$ , but concentrated nitric acid renders the metal “passive” by forming a thin layer of  $\text{Fe}_3\text{O}_4$  over the surface. One of the best-known reactions of iron is rust formation. The two oxidation states of iron are +2 and +3. Iron(II) compounds include  $\text{FeO}$  (black),  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (green),  $\text{FeCl}_2$  (yellow), and  $\text{FeS}$  (black). In the presence of oxygen,  $\text{Fe}^{2+}$  ions in solution are readily oxidized to  $\text{Fe}^{3+}$  ions. Iron(III) oxide is reddish brown, and iron(III) chloride is brownish black.

### Copper

Copper, a rarer element than iron ( $6.8 \times 10^{-3}$  percent of Earth's crust by mass), is found in nature in the uncombined state as well as in ores such as chalcopyrite ( $\text{CuFeS}_2$ ) (Figure 15.6). The reddish-brown metal is obtained by roasting the ore to give  $\text{Cu}_2\text{S}$  and then metallic copper:



Impure copper can be purified by electrolysis. After silver, which is too expensive for large-scale use, copper has the highest electrical conductivity. It is also a good thermal conductor. Copper is used in alloys, electrical cables, plumbing (pipes), and coins.



Scandium (Sc)



Titanium (Ti)



Vanadium (V)



Chromium (Cr)



Manganese (Mn)



Iron (Fe)



Cobalt (Co)



Nickel (Ni)



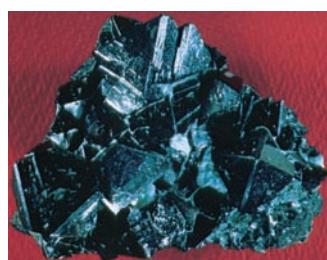
Copper (Cu)

**Figure 15.4** The first-row transition metals.

Copper reacts only with hot concentrated sulfuric acid and nitric acid. Its two important oxidation states are +1 and +2. The +1 state is less stable and disproportionate in solution:



All compounds of Cu(I) are diamagnetic and colorless except for  $\text{Cu}_2\text{O}$ , which is red. The Cu(II) compounds are all paramagnetic and colored. The hydrated  $\text{Cu}^{2+}$  ion is blue. Some important Cu(II) compounds are  $\text{CuO}$  (black),  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (blue), and  $\text{CuS}$  (black).

**Figure 15.5** The iron ore magnetite ( $\text{Fe}_3\text{O}_4$ ).**Figure 15.6** The copper ore chalcopyrite ( $\text{CuFeS}_2$ ).

## 15.2 | Transition Metals Can Form a Variety of Coordination Compounds

Transition metals have a strong tendency to form complex ions (see p. 648). A **coordination compound** typically consists of a complex ion and counter ion. (Some coordination compounds such as  $\text{Fe}(\text{CO})_5$  do not contain complex ions.) Much of what we now know about coordination compounds stems from the classic work of

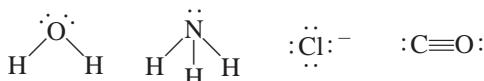
Recall that a complex ion contains a central metal ion bonded to one or more ions or molecules (see Section 11.7).

Alfred Werner,<sup>1</sup> who prepared and characterized many coordination compounds. In 1893, at the age of 26, Werner proposed what is now commonly referred to as *Werner's coordination theory*.

Nineteenth-century chemists were puzzled by a certain class of reactions that seemed to violate valence theory. For example, the valences of the elements in cobalt(III) chloride and in ammonia seem to be completely satisfied, and yet these two substances react to form a stable compound having the formula  $\text{CoCl}_3 \cdot 6\text{NH}_3$ . To explain this behavior, Werner postulated that most elements exhibit two types of valence: *primary valence* and *secondary valence*. In modern terminology, primary valence corresponds to the oxidation number and secondary valence to the coordination number of the element. In  $\text{CoCl}_3 \cdot 6\text{NH}_3$ , according to Werner, cobalt has a primary valence of +3 and a secondary valence of +6.

Today we use the formula  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  to indicate that the ammonia molecules and the cobalt atom form a complex ion; the chloride ions are not part of the complex but are held to it by ionic forces. Most, but not all, of the metals in coordination compounds are transition metals.

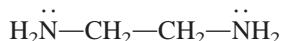
The molecules or ions that surround the metal in a complex ion are called **ligands** (Table 15.3). Every ligand has at least one unshared pair of valence electrons, as these following examples demonstrate:



Ligands, therefore, act as Lewis bases (see Section 3.4), donating one or more electron pairs to the metal. On the other hand, the transition metal atom (in either its neutral or positively charged state) acts as a Lewis acid, accepting (and sharing) pairs of electrons from the ligands. As a result, the metal-ligand bonds are usually coordinate covalent bonds (see Section 3.4).

The atom in a ligand that is bound directly to the metal atom is known as the **donor atom**. For example, nitrogen is the donor atom of the  $\text{NH}_3$  ligand in the  $[\text{Cu}(\text{NH}_3)_4]_2$  complex ion. The **coordination number** in coordination compounds is the number of donor atoms surrounding the central metal atom in a complex ion. For example, the coordination number of Ag in  $[\text{Ag}(\text{NH}_3)_2]^+$  is 2, of  $\text{Cu}^{2+}$  in  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  is 4, and of  $\text{Fe}^{3+}$  in  $[\text{Fe}(\text{CN})_6]^{3-}$  is 6. The most common coordination numbers are 4 and 6, but other coordination numbers, such as 2 or 5, are also known.

Depending on the number of donor atoms present, ligands are classified as *monodentate*, *bidentate*, or *polydentate* (see Table 15.3).  $\text{H}_2\text{O}$  and  $\text{NH}_3$  are monodentate ligands because they have only one donor atom each. Ethylenediamine (sometimes abbreviated “en”) is a bidentate ligand:

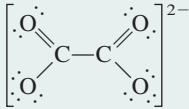


The two nitrogen atoms can coordinate with a metal atom as shown in Figure 15.7.

*Bidentate and polydentate ligands* are also called **chelating agents** because they can hold the metal atom like a claw (from the Greek *chele*, meaning “claw”). Ethylenediaminetetraacetate ion (EDTA) is a polydentate ligand used to treat metal poisoning (Figure 15.8). Six donor atoms enable EDTA to form a very stable, water-soluble complex ion with lead. In this form, lead is removed from the blood and tissues and excreted from the body. EDTA is also used to clean up spills of radioactive metals.

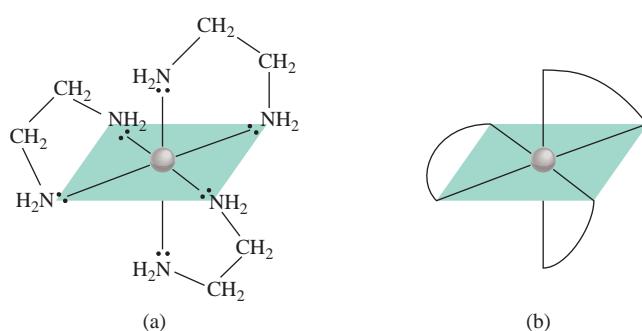
1. Alfred Werner (1866–1919). Swiss chemist. Werner started as an organic chemist but became interested in coordination chemistry. For his theory of coordination compounds, Werner was awarded the Nobel Prize in Chemistry in 1913.

**Table 15.3** Some Common Ligands

Name	Structure
<i>Monodentate ligands</i>	
Ammonia	$\begin{array}{c} \cdot\ddot{\text{N}}\cdot \\   \\ \text{H} \end{array}$
Carbon monoxide	$:\text{C}\equiv\text{O}:^{\cdot\cdot}$
Chloride ion	$:\ddot{\text{Cl}}:^-$
Cyanide ion	$[\cdot\ddot{\text{C}}\equiv\text{N}:]^-$
Thiocyanate ion	$[\cdot\ddot{\text{S}}-\text{C}\equiv\text{N}:]^-$
Water	$\begin{array}{c} \cdot\ddot{\text{O}}\cdot \\   \\ \text{H} \end{array}$
<i>Bidentate ligands</i>	
Ethylenediamine	$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ 
Oxalate ion	$[\cdot\ddot{\text{O}}\cdot=\text{C}-\text{C}(=\ddot{\text{O}}\cdot)\cdot\ddot{\text{O}}\cdot]^{2-}$
<i>Polydentate ligand</i>	
Ethylenediaminetetraacetate ion (EDTA)	$[\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_2-\text{C}(=\text{O})\text{O}^-)-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_2-\text{C}(=\text{O})\text{O}^-)-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})\text{O}^-]^{4-}$

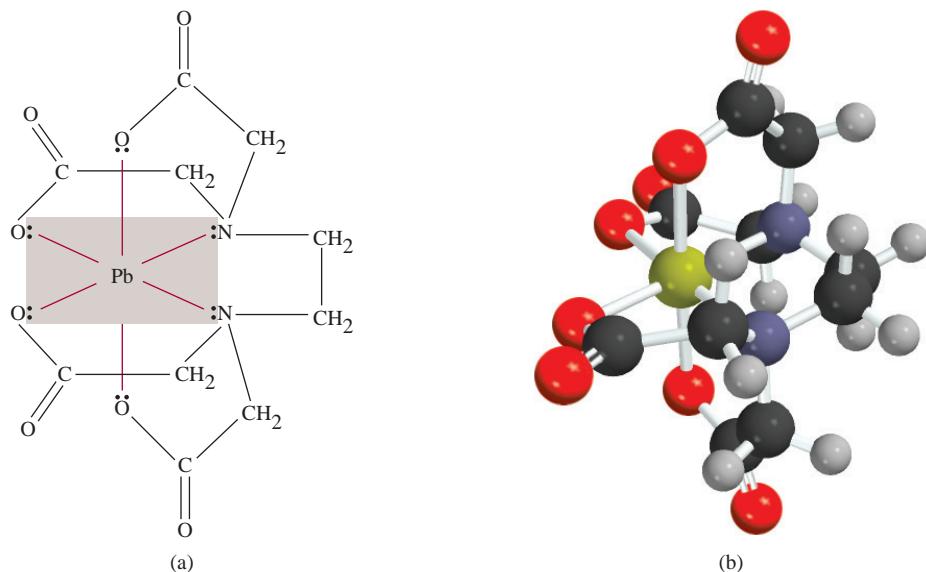
## Oxidation Numbers of Metals in Coordination Compounds

Another important property of coordination compounds is the oxidation number of the central metal atom. The net charge of a complex ion is the sum of the charges on the central metal atom and its surrounding ligands. In the  $[\text{PtCl}_6]^{2-}$  ion, for example, each chloride ion has an oxidation number of  $-1$ , so the oxidation number of Pt must be  $+4$ . If the ligands do not bear net charges, the oxidation number of the metal is



**Figure 15.7** (a) Structure of metal-ethylenediamine complex. Each ethylenediamine molecule provides two N donor atoms and is therefore a bidentate ligand. (b) Simplified structure of the same complex.

**Figure 15.8** (a) EDTA complex of lead. The complex bears a net charge of  $-2$  because each O donor atom has one negative charge and the lead ion carries two positive charges. Note the octahedral geometry around the  $\text{Pb}^{2+}$  ion. (b) Molecular model of the  $\text{Pb}^{2+}$ -EDTA complex. The yellow sphere is the  $\text{Pb}^{2+}$  ion.



equal to the charge of the complex ion. Thus, in  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  each  $\text{NH}_3$  is neutral, so the oxidation number of Cu is +2.

Example 15.1 shows how to determine the oxidation numbers of metals in coordination compounds.

### Example 15.1

Specify the oxidation number of the central metal atom in each of the following compounds: (a)  $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_2$ , (b)  $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_3$ , (c)  $[\text{Fe}(\text{CO})_5]$ , and (d)  $\text{K}_4[\text{Fe}(\text{CN})_6]$ .

**Strategy** The oxidation number of the metal atom is equal to its charge. First, we total the charges on the anions or the cations that electrically balance the complex ion. This gives us the net charge of the complex ion. Next, based on whether the ligands are charged or neutral, we can deduce the net charge of the metal and hence its oxidation number.

- Solution**
- Each of the two chloride ions carries a  $-1$  charge, so the charge on the complex ion is  $+2$ . The oxidation number of Ru must also be  $+2$  because both  $\text{NH}_3$  and  $\text{H}_2\text{O}$  are neutral species.
  - Each of the three nitrate ions has a charge of  $-1$ , so the complex cation must be  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ .  $\text{NH}_3$  is a neutral ligand, so the oxidation number of Cr is  $+3$ .
  - The complex is neutral (there are no anions or cations to electrically balance its charge) and the CO ligands are neutral, too, so the oxidation number of Fe is zero.
  - Each of the four potassium ions has a charge of  $+1$ , so the complex anion is  $[\text{Fe}(\text{CN})_6]^{4-}$ . Next, each cyanide ligand bears a charge of  $-1$ , so Fe must have an oxidation number of  $+2$ .

**Practice Exercise** Write the oxidation numbers of the transition metals in the following compounds: (a)  $[\text{CuBr}_4]\text{Cl}_2$ , (b)  $[\text{Cr}(\text{NH}_3)\text{SO}_4]\text{Br}$ , and (c)  $[\text{Pt}(\text{en})_2\text{Cl}_2](\text{NO}_3)_2$ .

**Table 15.4** Some Common Ligands in Coordination Compounds

Ligand	Name of Ligand in Coordination Compound
Bromide, Br <sup>-</sup>	Bromo
Chloride, Cl <sup>-</sup>	Chloro
Cyanide, CN <sup>-</sup>	Cyano
Hydroxide, OH <sup>-</sup>	Hydroxo
Oxide, O <sup>2-</sup>	Oxo
Carbonate, CO <sub>3</sub> <sup>2-</sup>	Carbonato
Nitrite, NO <sub>2</sub> <sup>-</sup>	Nitro
Oxalate, C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	Oxalato
Ammonia, NH <sub>3</sub>	Ammine
Carbon monoxide, CO	Carbonyl
Water, H <sub>2</sub> O	Aquo
Ethylenediamine	Ethylenediamine
Ethylenediaminetetraacetate	Ethylenediaminetetraacetato

### Naming Coordination Compounds

Having discussed the various types of ligands and the oxidation numbers of metals, it is now time to learn how to name coordination compounds. The rules for naming coordination compounds are as follows:

1. The cation is named before the anion, as in other ionic compounds. The rule holds regardless of whether the complex ion bears a net positive or a net negative charge. In K<sub>3</sub>[Fe(CN)<sub>6</sub>] and [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Cl, for example, we name the K<sup>+</sup> and [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup> cations first, respectively.
2. Within a complex ion, the ligands are named first, in alphabetical order, and the metal ion is named last.
3. The names of anionic ligands end with the letter *o*, whereas a neutral ligand is usually called by the name of the molecule. The exceptions are H<sub>2</sub>O (aqua), CO (carbonyl), and NH<sub>3</sub> (ammine). Table 15.4 lists the names of some common ligands.
4. When several ligands of a particular kind are present, we use the Greek prefixes *di-*, *tri-*, *tetra-*, *penta-*, and *hexa-* to name them. Thus, the ligands in the cation [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup> are “tetraamminedichloro.” (Note that prefixes are ignored when alphabetizing the ligands.) If the ligand itself contains a Greek prefix, we use the prefixes *bis* (2), *tris* (3), and *tetrakis* (4) to indicate the number of ligands present. For example, the ethylenediamine ligand already contains the prefix *di*, so if a complex contains two such ligands then the name is *bis(ethylenediamine)*.
5. The oxidation number of the metal is written in Roman numerals following the name of the metal. For example, the Roman numeral III is used to indicate the +3 oxidation state of chromium in [Cr(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup>, which is called tetraammine-dichlorochromium(III) ion.
6. If the complex is an anion, its name ends in *-ate*. For example, in K<sub>4</sub>[Fe(CN)<sub>6</sub>] the anion [Fe(CN)<sub>6</sub>]<sup>4-</sup> is called hexacyanoferrate(II) ion. The Roman numeral II indicates the oxidation state of iron. Table 15.5 gives the names of anions containing metal atoms.

**Table 15.5**

### Names of Anions Containing Metal Atoms

Metal	Name of Metal in Anionic Complex
Aluminum	Aluminate
Chromium	Chromate
Cobalt	Cobaltate
Copper	Cuprate
Gold	Aurate
Iron	Ferrate
Lead	Plumbate
Manganese	Managanate
Molybdenum	Molybdate
Nickel	Nickelate
Silver	Argentate
Tin	Stannate
Tungsten	Tungstate
Zinc	Zincate

Examples 15.2 and 15.3 show how to apply these rules to the naming of coordination compounds.

### Example 15.2

Write the systematic names of the following coordination compounds: (a)  $\text{Ni}(\text{CO})_4$ , (b)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ , (c)  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , and (d)  $[\text{Cr}(\text{en})_3]\text{Cl}_3$ .

**Strategy** Follow the preceding procedure for naming coordination compounds and refer to Tables 15.4 and 15.5 for the names of ligands and anions containing metal atoms, respectively.

- Solution**
- (a) The CO ligands are neutral, so the Ni atom bears no net charge. The compound is called tetracarbonylnickel(0), or more commonly, nickel tetracarbonyl.
  - (b) The chloride ion has a  $-1$  charge, so the complex ion has a  $+1$  charge, namely,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ . The ammonia molecule is neutral and each of the two chloride ions bears a  $-1$  charge. As a result, the oxidation number of Co must be  $+3$  (to give a net positive charge to the complex ion). The compound is called tetraamminedichlorocobalt(III) chloride.
  - (c) The complex ion is the anion, and it bears a  $-3$  charge because each of the potassium ions bear a  $+1$  charge. The oxidation number of Fe must be  $+3$  because each of the six cyanide ions in  $[\text{Fe}(\text{CN})_6]^{3-}$  bears a  $-1$  charge. The compound is potassium hexacyanoferrate(III)—commonly called potassium ferricyanide.
  - (d) Each of the three chloride ions bears a  $-1$  charge, so the cation is  $[\text{Cr}(\text{en})_3]^{3+}$ , where *en* is the abbreviation for the ethylenediamine ligand. The *en* ligands are neutral, so the oxidation number of Cr must be  $+3$ . Because there are three *en* groups present and the name of the ligand already contains the prefix *di* (rule 4), the compound is called *tris*(ethylenediamine)chromium(III) chloride.

**Practice Exercise** What are the systematic names for (a)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$ , (b)  $[\text{Pt}(\text{NH}_3)\text{Br}]\text{Cl}$ , (c)  $\text{K}_3[\text{CoF}_6]$ , and (d)  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}]\text{NO}_3$ ?

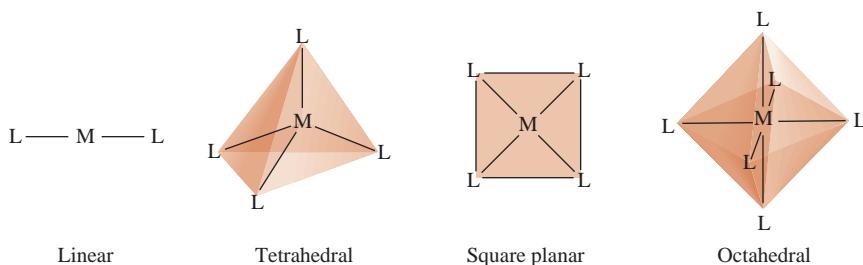
### Example 15.3

Write the formulas for the following compounds: (a) pentaamminechlorocobalt(III) chloride, (b) dichlorobis(ethylenediamine)platinum(IV) nitrate, and (c) sodium hexanitrocobaltate( III).

**Strategy** Follow the preceding procedure, and refer to Tables 15.4 and 15.5 for the names of ligands and anions containing metal atoms, respectively.

- Solution**
- (a) The complex cation contains five  $\text{NH}_3$  groups, a  $\text{Cl}^-$  ion, and a Co ion having a  $+3$  oxidation number. The net charge of the cation must be  $+2$ ,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ . Two chloride anions are needed to balance the positive charges. Therefore, the formula of the compound is  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ .
  - (b) There are two chloride ions ( $-1$  each), two *en* groups (neutral), and a Pt ion with an oxidation number of  $+4$ . The net charge on the cation must be  $+2$ ,  $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$ . Two nitrate ions are needed to balance the  $+2$  charge of the complex cation. Therefore, the formula of the compound is  $[\text{Pt}(\text{en})_2\text{Cl}_2](\text{NO}_3)_2$ .
  - (c) The complex anion contains six nitro groups ( $-1$  each) and a cobalt ion with an oxidation number of  $+3$ . The net charge on the complex anion must be  $-3$ ,  $[\text{Co}(\text{NO}_2)_6]^{3-}$ . Three sodium cations are needed to balance the  $-3$  charge of the complex anion. Therefore, the formula of the compound is  $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ .

—Continued



**Figure 15.9** Common geometries of complex ions. In each case, M is a metal and L is a monodentate ligand.

*Continued—*

**Practice Exercise** Write the formulas for the following compounds:

- (a) *tris(ethylenediamine)cobalt(III)* sulfate,
- (b) potassium hexacyanoferrate(III),
- (c) potassium tetracyanonickelate(II), and
- (d) calcium tetrabromodichloroplatinate(II).

## Structure of Coordination Compounds

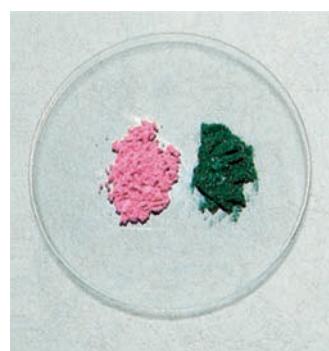
In studying the geometry of coordination compounds, there is often more than one way to arrange the ligands around the central atom. Compounds rearranged in this fashion have distinctly different physical and chemical properties. Figure 15.9 shows four different geometric arrangements for metal atoms with monodentate ligands.

In these diagrams the structure and coordination number of the metal atom relate to each other as follows:

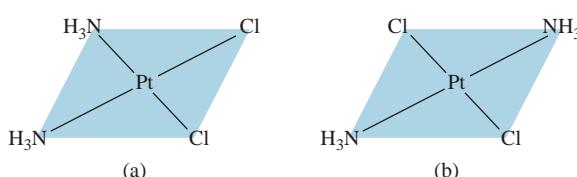
Coordination Number	Structure
2	Linear
4	Tetrahedral or square planar
6	Octahedral

The three-dimensional spatial arrangements in coordination compounds can lead to stereoisomerism. Recall from Section 4.4 that *stereoisomers* are compounds that are made up of the same types and numbers of atoms bonded together in the same sequence, but with different three-dimensional structures. The two types of stereoisomers are *geometric isomers* (isomers that cannot be interconverted without breaking a chemical bond) and *optical isomers* (isomers that are nonsuperimposable mirror images). Coordination compounds may exhibit one or both types of stereoisomerism. Many coordination compounds, however, do not have stereoisomers.

We use the terms *cis* and *trans* to distinguish one geometric isomer of a compound from the other (Section 4.4). *Cis* means that two particular atoms (or groups of atoms) are adjacent to each other, and *trans* means that the atoms (or groups of atoms) are on opposite sides in the structural formula. The *cis* and *trans* isomers of coordination compounds generally have quite different colors, melting points, dipole moments, and chemical reactivities. Figure 15.10 shows the *cis* and *trans* isomers of



*cis*-tetraamminedichlorocobalt(III) chloride (left) and *trans*-tetraamminedichlorocobalt(III) chloride (right).



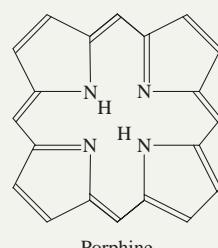
**Figure 15.10** The (a) *cis* and (b) *trans* isomers of diamminedichloroplatinum(II). Note that the two Cl atoms are adjacent to each other in the *cis* isomer and diagonal from each other in the *trans* isomer.

## Coordination Compounds in Living Systems

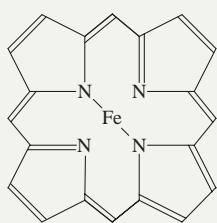
**C**oordination compounds play many important roles in animals and plants. They are essential in the storage and transport of oxygen, as electron transfer agents, as catalysts, and in photosynthesis. Here we focus on coordination compounds containing iron and magnesium.

Because of its central function as an oxygen carrier for metabolic processes, hemoglobin is probably the most studied of all the proteins. The molecule contains four long, folded protein chains called *subunits*. Hemoglobin carries oxygen in the blood from the lungs to the tissues, where it delivers the oxygen molecules to myoglobin. Myoglobin, which is made up of only one subunit, stores oxygen for metabolic processes in muscle.

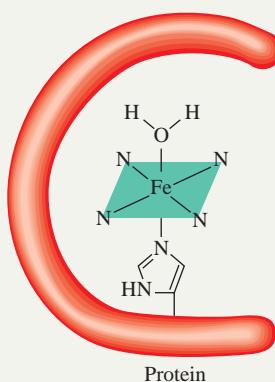
The porphine molecule forms an important part of the hemoglobin structure. Upon coordination to a metal, the  $H^+$  ions that are bonded to two of the four nitrogen atoms in porphine are displaced. Complexes derived from porphine are



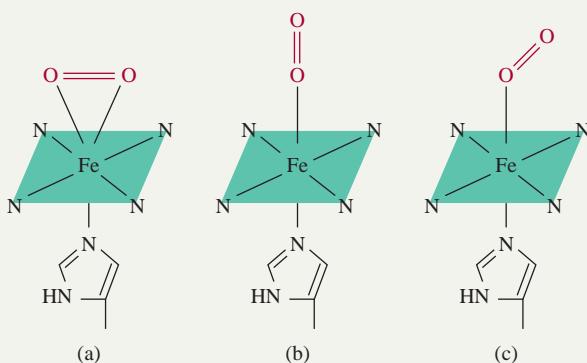
Porphine

 $Fe^{2+}$ -porphyrin

Simplified structures of the porphine molecule and the  $Fe^{2+}$ -porphyrin complex. The dashed lines represent coordinate covalent bonds.

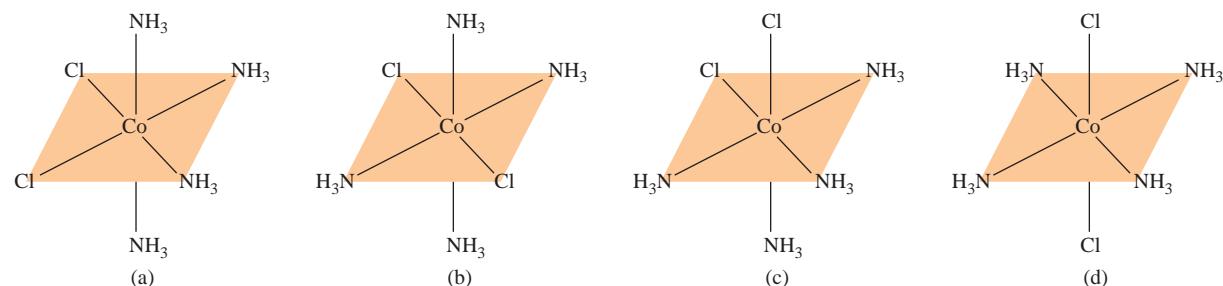


The heme group in hemoglobin. The  $Fe^{2+}$  ion is coordinated with the nitrogen atoms of the heme group. The ligand below the porphyrin is the histidine group, which is attached to the protein. The sixth ligand is a water molecule.



Three possible ways for molecular oxygen to bind to the heme group in hemoglobin. The structure shown in (a) would have a coordination number of 7, which is considered unlikely for  $Fe(II)$  complexes. Although the end-on arrangement in (b) seems the most reasonable, evidence points to the structure in (c) as the correct one.

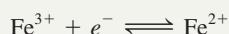
diamminedichloroplatinum(II). Although the types of bonds are the same in both isomers (two Pt—N and two Pt—Cl bonds), the spatial arrangements are different. Another example is tetraamminedichlorocobalt(III) ion, shown in Figure 15.11.



**Figure 15.11** The (a) *cis* and (b) *trans* isomers of the tetraamminedichlorocobalt(III) ion. The structure shown in (c) can be generated by rotating that in (a), and the structure shown in (d) can be generated by rotating that in (b). The ion has only two geometric isomers, (a) [or (c)] and (b) [or (d)].

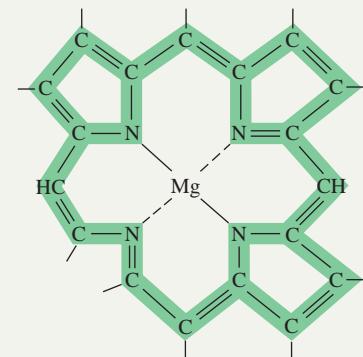
called *porphyrins*, and the iron-porphyrin combination is called the *heme* group. The iron in the heme group has an oxidation number of +2; it is coordinated to the four nitrogen atoms in the porphine group and also to a nitrogen donor atom in a ligand that is attached to the protein. The sixth ligand is a water molecule, which binds to the  $\text{Fe}^{2+}$  ion on the other side of the ring to complete the octahedral complex. This hemoglobin molecule is called *deoxyhemoglobin* and imparts a bluish tinge to venous blood. The water ligand can be replaced readily by molecular oxygen to form the red oxyhemoglobin found in arterial blood. Each of the four subunits contains a heme group, so each hemoglobin molecule can bind up to four  $\text{O}_2$  molecules. Most modern experimental evidence suggests that the bond between O and Fe in oxyhemoglobin is bent relative to the heme group.

The porphyrin group is a very effective chelating agent that occurs in a number of biological systems. The iron-heme complex is present in another class of proteins, called the *cytochromes*. The iron forms an octahedral complex in these proteins, but because both a histidine and a methionine group are firmly bound to the metal ion, these two amino acids cannot be displaced by oxygen or other ligands. Instead, the cytochromes act as electron carriers, which are essential to metabolic processes. In cytochromes, iron undergoes rapid reversible redox reactions:

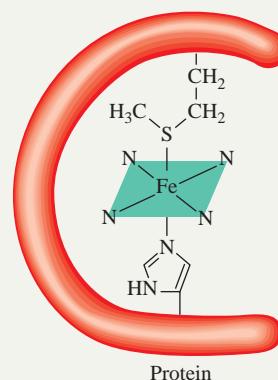


which are coupled to the oxidation of organic molecules such as the carbohydrates.

The chlorophyll molecule, which is necessary for plant photosynthesis, also contains a porphyrin ring, but in this case the metal ion is  $\text{Mg}^{2+}$  rather than  $\text{Fe}^{2+}$ .

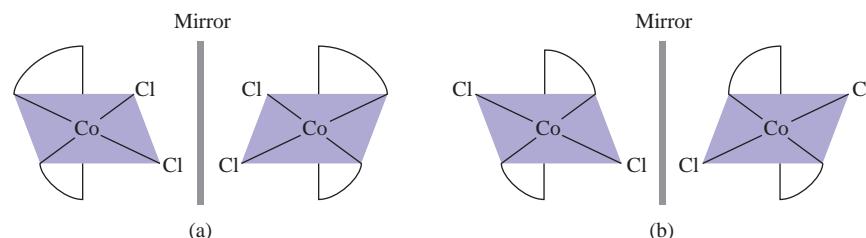


The porphyrin structure in chlorophyll. The dotted lines indicate the coordinate covalent bonds. The electron-delocalized portion of the molecule is shown in color.



The heme group in cytochrome c. The ligands above and below the porphyrin are a methionine group and a histidine group of the protein, respectively.

As an example of optical isomerism (see Section 4.4) in coordination compounds, Figure 15.12 shows the *cis* and *trans* isomers of dichlorobis(ethylenediamine)cobalt(III) ion and their mirror images. The *trans* isomer and its mirror image are superimposable, but the *cis* isomer and its mirror image are not. The *cis* isomer and its mirror image are, therefore, optical isomers. Unlike geometric isomers, optical isomers have identical physical and chemical properties, except for the way in which they interact with polarized light and in the way they react with other chiral molecules.



**Figure 15.12** The (a) *cis* and (b) *trans* isomers of the dichlorobis(ethylenediamine)cobalt(III) ion and their mirror images. If you could rotate the mirror image in (b) 90° clockwise about the vertical position and place the ion over the *trans* isomer, you would find that the two are superimposable. No matter how you rotated the *cis* isomer and its mirror image, however, you could not superimpose one on the other.

### 15.3 | Bonding in Coordination Compounds Can Be Described by Crystal Field Theory

A satisfactory theory of bonding in coordination compounds must account for their color and magnetism as well as their stereochemistry and bond strength. So far, no single theory can do all that. Instead, several different approaches have been applied to transition metal complexes. We will discuss only one of them here—crystal field theory—because it accounts for both the color and magnetic properties of many coordination compounds.

We begin the discussion of crystal field theory with the most straightforward case, namely, complex ions with octahedral geometry. We then apply it to tetrahedral and square-planar complexes.

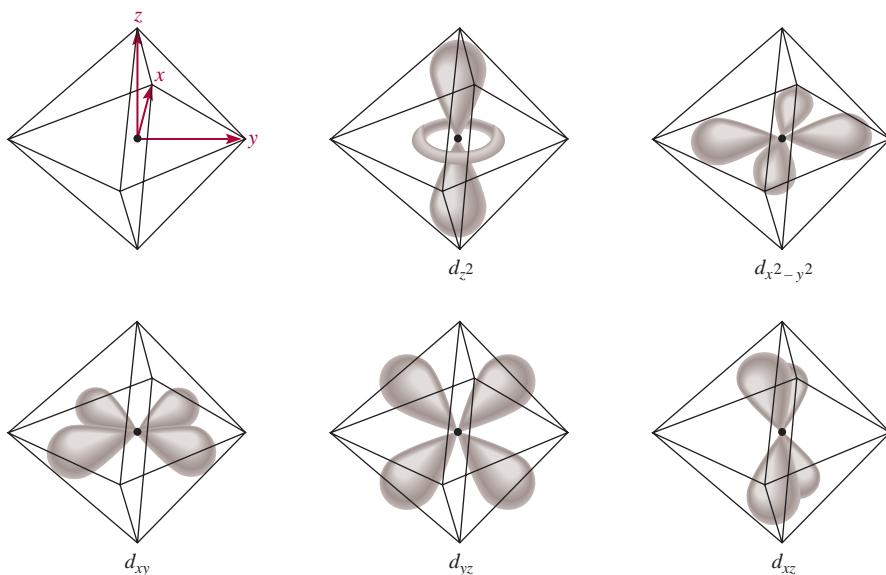
#### Crystal Field Splitting in Octahedral Complexes

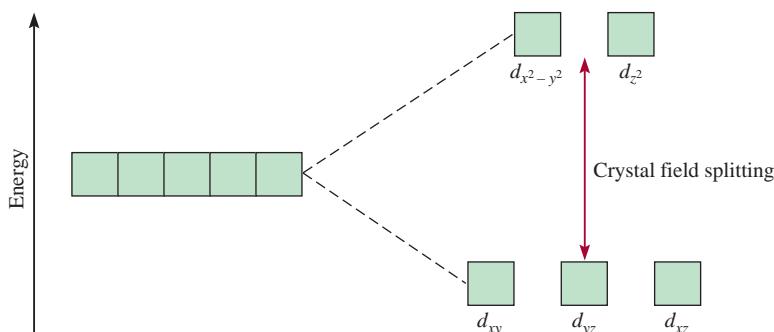
The name “crystal field” is associated with the theory used to explain the properties of solid, crystalline substances. The same theory is used to study coordination compounds.

**Crystal field theory** explains the bonding in complex ions purely in terms of electrostatic forces. In a complex ion, two types of electrostatic interaction come into play. One is the attraction between the positive metal ion and the negatively charged ligand or the partially negatively charged end of a polar ligand. This is the force that binds the ligands to the metal. The second type of interaction is electrostatic repulsion between the lone pairs on the ligands and the electrons in the *d* orbitals of the metals.

As we saw in Chapter 3, *d* orbitals have different orientations, but in the absence of external disturbance, they all have the same energy. In an octahedral complex, a central metal atom is surrounded by six lone pairs of electrons (on the six ligands), so all five *d* orbitals experience electrostatic repulsion. The magnitude of this repulsion depends on the orientation of the particular *d* orbital. Figure 15.13 shows, for example, that the lobes of the  $d_{x^2-y^2}$  orbital point toward the corners of the octahedron along the *x* and *y* axes, where the lone-pair electrons are positioned. Thus, an electron residing in this orbital would experience a greater repulsion from the ligands than an electron would in, say, the  $d_{xy}$  orbital. For this reason, the energy of the  $d_{x^2-y^2}$  orbital is increased relative to the  $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$  orbitals. The energy of the  $d_{z^2}$  orbital is also greater, because its lobes are pointed at the ligands along the *z* axis.

**Figure 15.13** The five *d* orbitals in an octahedral environment. The metal atom (or ion) is at the center of the octahedron, and the six lone pairs on the donor atoms of the ligands are at the corners.





**Figure 15.14** Crystal field splitting between  $d$  orbitals in an octahedral complex.

As a result of these metal-ligand interactions, the five  $d$  orbitals in an octahedral complex are split between two sets of energy levels: a higher level with two orbitals ( $d_{x^2-y^2}$  and  $d_{z^2}$ ) having the same energy and a lower level with three equal energy orbitals ( $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$ ), as shown in Figure 15.14. The **crystal field splitting** ( $\Delta$ ) is the energy difference between the two sets of  $d$  orbitals in a metal atom when ligands are present. The magnitude of  $\Delta$ , which depends on the metal and the nature of the ligands, has a direct effect on the color and magnetic properties of complex ions.

## Color

In Chapter 1, we learned that white light, such as sunlight, is a combination of all colors. A substance appears black if it absorbs all the visible light that strikes it. It appears white or colorless if it absorbs no visible light. An object appears green if it absorbs all light but reflects the green component. An object also looks green if it reflects all colors except red, the *complementary* color of green (Figure 15.15).

What is true for reflected light also applies to transmitted light (that is, the light that passes through a medium, such as a solution). Consider the hydrated cupric ion ( $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ), for example. It absorbs light in the orange region of the spectrum, so an aqueous solution of  $\text{CuSO}_4$  appears blue to us. Recall from Chapter 1 that when the energy of a photon is equal to the difference between the ground state and an excited state, absorption occurs as the photon strikes the atom (or ion or compound) and an electron is promoted to a higher level. This concept makes it possible to calculate the energy change involved in the electron transition. The energy of a photon, given by Equation 1.3, is:

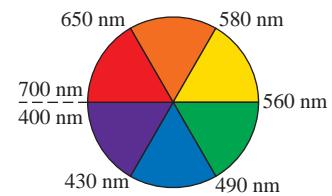
$$\Delta E = hv$$

where  $h$  represents Planck's constant ( $6.626 \times 10^{-34} \text{ J s}$ ) and  $v$  is the frequency of the radiation, which is  $5.00 \times 10^{14} \text{ s}^{-1}$  for the wavelength of orange light (600 nm). Here  $E = \Delta$ , the crystal field splitting, so we have

$$\begin{aligned}\Delta &= hv \\ &= (6.626 \times 10^{-34} \text{ J s})(5.00 \times 10^{14} \text{ s}^{-1}) \\ &= 3.32 \times 10^{-19} \text{ J}\end{aligned}$$

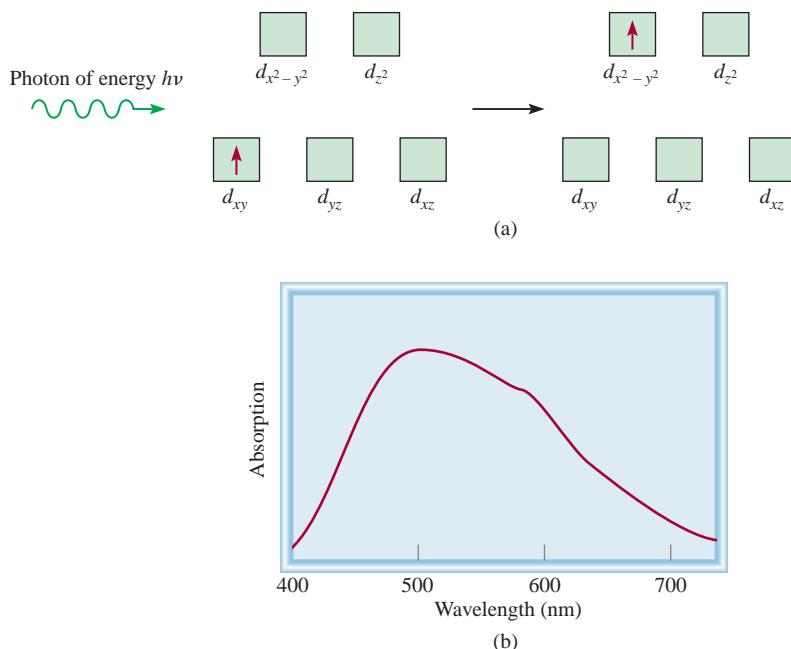
(This is the energy absorbed by *one* ion.) If the wavelength of the photon absorbed by an ion lies outside the visible region, then the transmitted light looks the same (to us) as the incident light—white—and the ion appears colorless.

The best way to measure crystal field splitting is to use spectroscopy to determine the wavelength at which light is absorbed. The  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  ion provides a



**Figure 15.15** A color wheel showing appropriate wavelengths. Complementary colors, such as red and green, are on opposite sides of the wheel.

**Figure 15.16** (a) The process of photon absorption, and (b) a graph of the absorption spectrum of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ . The energy of the incoming photon is equal to the crystal field splitting. The maximum absorption peak in the visible region occurs at 498 nm.



straightforward example because  $\text{Ti}^{3+}$  has only one  $3d$  electron (Figure 15.16). The  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  ion absorbs light in the visible region of the spectrum (Figure 15.17).

The wavelength corresponding to maximum absorption in Figure 15.16(b) is 498 nm. Thus, the crystal field splitting can be calculated as follows. We start by writing

$$\Delta = h\nu \quad (15.1)$$

Also

$$\nu = \frac{c}{\lambda}$$

where  $c$  is the speed of light and  $\lambda$  is the wavelength. Therefore,

$$\begin{aligned} \Delta &= \frac{hc}{\nu} = \frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \text{ m s}^{-1})}{(498 \text{ nm})(1 \times 10^{-9} \text{ m nm}^{-1})} \\ &= 3.99 \times 10^{-19} \text{ J} \end{aligned}$$

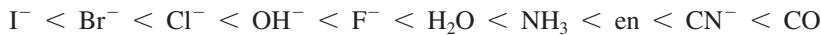
**Figure 15.17** The colors of some of the first-row transition metal ions in solution. From left to right:  $\text{Ti}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cu}^{2+}$ . The  $\text{Sc}^{3+}$  and  $\text{V}^{5+}$  ions are colorless.



This is the energy required to excite *one*  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  ion. To express this energy difference in the more convenient units of kilojoules per mole, we write

$$\begin{aligned}\Delta &= (3.99 \times 10^{-19} \text{ J ion}^{-1})(6.022 \times 10^{23} \text{ ions mol}^{-1}) \\ &= 2.40 \times 10^5 \text{ J mol}^{-1} \\ &= 240 \text{ kJ mol}^{-1}\end{aligned}$$

Aided by spectroscopic data for a number of complexes, all having the same metal ion but different ligands, chemists have calculated the crystal field splitting for each ligand and established a **spectrochemical series**, which is *a list of ligands arranged in increasing order of their abilities to split the d-orbital energy levels*:



These ligands are arranged in the order of increasing value of  $\Delta$ . CO and CN<sup>-</sup>, which cause a large splitting of the *d*-orbital energy levels, are called *strong-field ligands*. The halide ions and hydroxide ion, which split the *d* orbitals to a lesser extent, are called *weak-field ligands*.

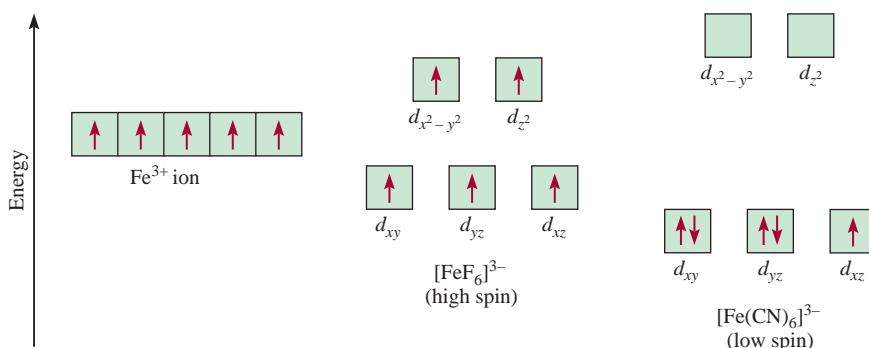
The order of the spectrochemical series is the same no matter which metal atom (or ion) is present.

## Magnetic Properties

The magnitude of the crystal field splitting also determines the magnetic properties of a complex ion. The  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  ion, having only one *d* electron, is always paramagnetic. For an ion with several *d* electrons, however, the situation is not as clear cut. Consider, for example, the octahedral complexes  $[\text{FeF}_6]^{3-}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  (Figure 15.18).

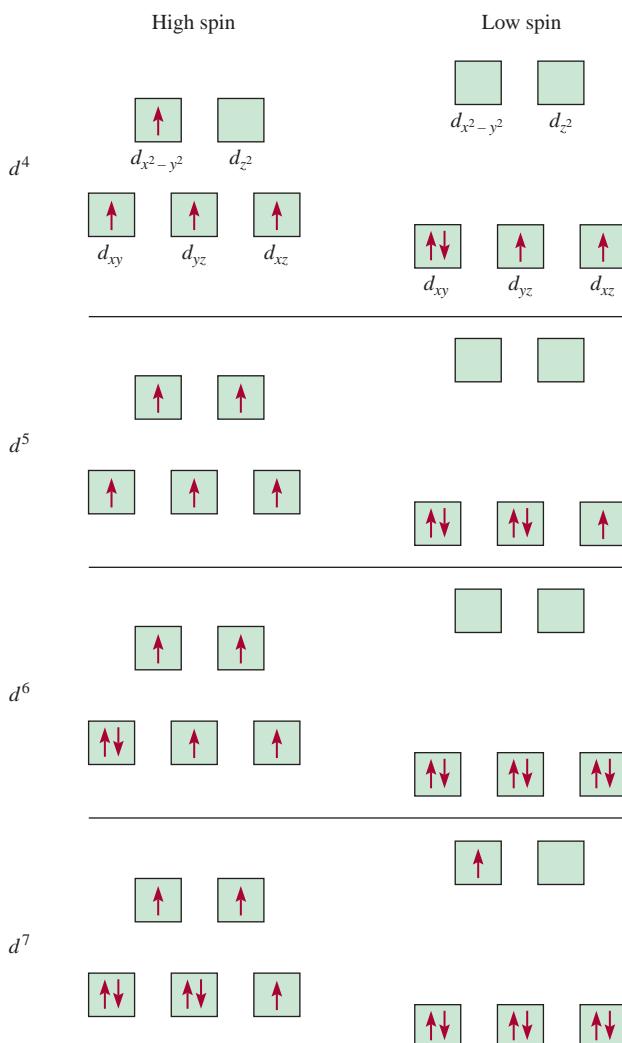
Both contain Fe<sup>+3</sup>, the electron configuration of which is [Ar]3d<sup>5</sup>, but there are two possible ways to distribute the five *d* electrons among the *d* orbitals. According to Hund's rule (see Section 2.2), maximum stability is reached when the electrons are placed in five separate orbitals with parallel spins. This arrangement can be achieved only if two of the five electrons are promoted to the higher-energy  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals. No such energy input is needed if all five electrons enter the  $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$  orbitals. According to the Pauli exclusion principle (Section 2.1), four of these electrons must pair up, leaving only one unpaired electron in this arrangement.

Figure 15.19 shows the distribution of electrons among the *d* orbitals that results in low-spin and high-spin complexes. The actual arrangement of the electrons is determined by the amount of stability gained by having maximum parallel spins versus the investment in energy required to promote electrons to higher *d* orbitals. Because F<sup>-</sup> is a weak-field ligand, the five *d* electrons enter five separate *d* orbitals with parallel spins to create a high-spin complex (see Figure 15.19). The cyanide ion is a strong-field



**Figure 15.18** Energy-level diagrams for the  $\text{Fe}^{3+}$  ion and for the  $[\text{FeF}_6]^{3-}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  complex ions.

**Figure 15.19** Orbital diagrams for the high-spin and low-spin octahedral complexes corresponding to the electron configurations  $d^4$ ,  $d^5$ ,  $d^6$ , and  $d^7$ . No such distinctions can be made for  $d^1$ ,  $d^2$ ,  $d^3$ ,  $d^8$ ,  $d^9$ , and  $d^{10}$ .



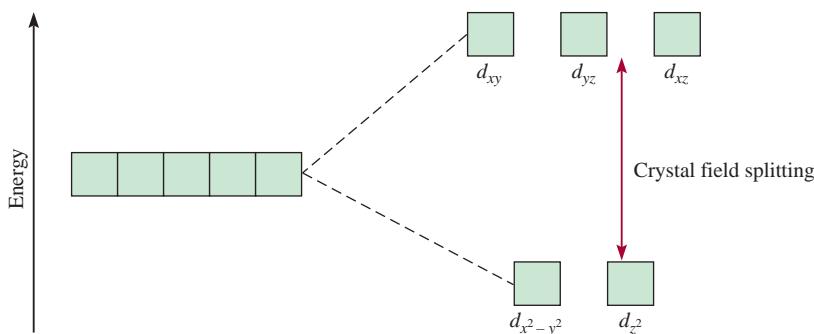
ligand, on the other hand, so the energy needed to promote two of the five  $d$  electrons to higher  $d$  orbitals is too much, and therefore a low-spin complex is formed.

The actual number of unpaired electrons (or spins) in a complex ion can be found by using a technique called *electron spin resonance spectroscopy* (ESR), and in general, experimental findings support predictions based on crystal field splitting. However, a distinction between low- and high-spin complexes can be made only if the metal ion contains more than three and fewer than eight  $d$  electrons, as shown in Figure 15.19.

The magnetic properties of a complex ion depend upon the number of unpaired electrons present.

### Tetrahedral and Square-Planar Complexes

So far we have concentrated on octahedral complexes. The splitting of the  $d$  orbital energy levels in tetrahedral and square-planar complexes can also be accounted for satisfactorily by the crystal field theory. In fact, the splitting pattern for a tetrahedral ion is just the reverse of that for octahedral complexes. In this case, the  $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$  orbitals are more closely directed at the ligands and therefore have more energy than the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals (Figure 15.20). Most tetrahedral complexes are high spin. Presumably, the tetrahedral arrangement reduces the magnitude of the metal-ligand



**Figure 15.20** Crystal field splitting between  $d$  orbitals in a tetrahedral complex.

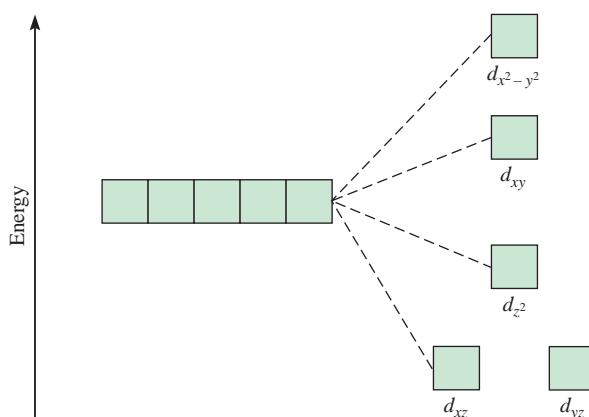
interactions, resulting in a smaller  $\Delta$  value. This is a reasonable assumption because the number of ligands is smaller in a tetrahedral complex.

As Figure 15.21 shows, the splitting pattern for square-planar complexes is the most complicated. The  $d_{x^2-y^2}$  orbital possesses the highest energy (as in the octahedral case), and the  $d_{xy}$  orbital the next highest. However, the relative placement of the  $d_z^2$  and the  $d_{xz}$  and  $d_{yz}$  orbitals cannot be determined simply by inspection and must be calculated.

### Ligand Field Theory

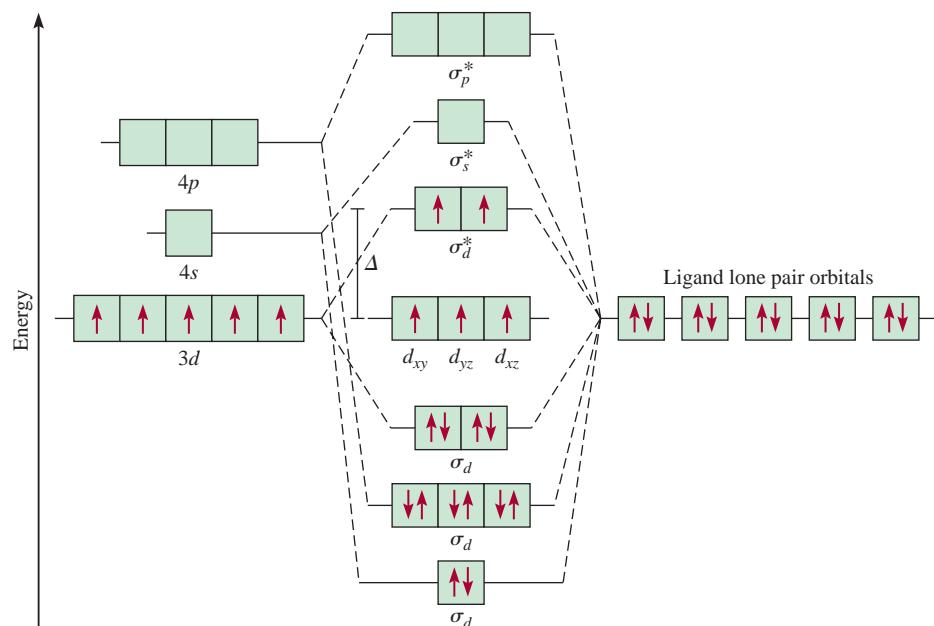
Crystal field theory, although quite successful at explaining the spectral and magnetic properties of many coordination compounds, ignores the covalent character of metal-ligand bonds because it is based solely on electrostatic interactions. Thus, it would be unable to predict the fact that a neutral ligand, such as CO or ethylenediamine, can have a larger crystal field splitting than an ionic ligand, such as  $\text{Cl}^-$  or  $\text{F}^-$ . In order to take into account the covalent character of metal-ligand bonds, a molecular orbital approach (see Sections 3.5 and 4.5) to the electronic structure of coordination compounds, known as **ligand field theory**, has been developed.

Ligand field theory is based on the idea that atomic orbitals that are close in energy will mix more effectively in molecular orbitals than those that are far apart. Consider, for example, the octahedral complex ion  $\text{FeF}_6^{3-}$ . From Figure 15.13, we saw that the  $d_{x^2-y^2}$  and  $d_z^2$  atomic orbitals are oriented toward the ligands. As such, the  $3d_{x^2-y^2}$  and  $3d_z^2$  orbitals on the metal center will mix with the ligand lone-pair orbitals to form two bonding and two antibonding  $\sigma$  molecular orbitals. The remaining  $3d$  orbitals— $3d_{xy}$ ,  $3d_{yz}$ , and  $3d_{xz}$ —are oriented in between the ligands and, because of



**Figure 15.21** Energy-level diagram for a square-planar complex. Because there are more than two energy levels, we cannot define crystal field splitting as we can for the octahedral and tetrahedral complexes.

**Figure 15.22** Molecular-orbital energy-level diagram for the octahedral complex  $\text{FeF}_6^{3-}$ . The  $\sigma_d^*$  molecular orbitals are essentially pure  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals of the central metal ion. In this complex, the crystal field splitting ( $\Delta$ ) between the three nonbonding orbitals ( $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$ ) and the two  $\sigma_d^*$  orbitals is small ( $F^-$  is a weak-field ligand) so Hund's rule applies, and these five orbitals each contain one electron with all the spins parallel.



minimal overlap, they will not mix with the ligand lone-pair orbitals, that is, they will be nonbonding orbitals. The 4s orbital on the metal center is spherical in shape and will overlap with all of the lone-pair ligand orbitals to form a pair of bonding and antibonding  $\sigma$  molecular orbitals. The remaining three 4p orbitals on the metal center will overlap individually with the lone-pair ligand orbitals along the  $x$ ,  $y$ , and  $z$  axes. So we have the six 4s, 4p,  $3d_{x^2-y^2}$ , and  $3d_{z^2}$  orbitals of the metal center mixing with the ligand lone-pair orbitals to form six bonding and six antibonding  $\sigma$  molecular orbitals oriented along the six vertices of an octahedron, with three nonbonding orbitals corresponding to the  $3d_{xy}$ ,  $3d_{yz}$ , and  $3d_{xz}$  orbitals.

The MO energy-level diagram for  $\text{FeF}_6^{3-}$  is shown in Figure 15.22. The arrangement of the highest occupied molecular orbitals ( $3d_{xy}$ ,  $3d_{yz}$ ,  $3d_{xz}$ , and the two  $\sigma_d^*$  orbitals) is identical to that predicted by crystal field theory with the  $3d_{x^2-y^2}$  and  $3d_{z^2}$  orbitals replaced with the two  $\sigma_d^*$  molecular orbitals. However, the MO-based ligand field theory is more complete as it provides an understanding of the dependence of the crystal field splitting on the ligand type. In this octahedral complex, the  $3d_{xy}$ ,  $3d_{yz}$ , and  $3d_{xz}$  orbitals are not oriented along the metal-ligand bond axes, but instead are oriented in between the ligands. As such, they will interact most strongly with the orbitals of the ligand ( $p$  or  $\pi$ ) that are perpendicular to the metal-ligand bond. In the case of monatomic ionic ligands, such as  $\text{OH}^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ , the electrostatic repulsion from the full  $p$  orbitals on these ligands raises the energy of the  $3d_{xy}$ ,  $3d_{yz}$ , and  $3d_{xz}$  orbitals resulting in a reduction of the crystal field splitting ( $\Delta$ )—thus, these species are weak-field ligands. This repulsion is stronger if the  $p$  electrons are less tightly bound to the ligand, that is, if the ligand is less electronegative, thus explaining why  $\text{I}^-$  has a lower crystal field splitting than  $\text{F}^-$  in the spectrochemical series. On the other hand, ligands with unoccupied antibonding  $\pi^*$  orbitals, such as CO or  $\text{CN}^-$ , tend to lower the energy of the  $3d_{xy}$ ,  $3d_{yz}$ , and  $3d_{xz}$  orbitals, leading to an increase in the crystal field splitting. Such species are strong-field ligands. The lowering of the  $3d_{xy}$ ,  $3d_{yz}$ , and  $3d_{xz}$  orbital energies in this fashion is called **back bonding** and is due to mixing with the unoccupied  $\pi^*$  orbitals on the ligand, which are oriented away from the ligand double (or triple bond) and toward the  $3d_{xy}$ ,  $3d_{yz}$ , and  $3d_{xz}$  orbitals of the metal center (see Figure 3.18). Neutral ligands, such as  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , neither have a strong repulsion from  $p$  orbitals nor back

bonding of the  $\pi$  orbitals and so are generally intermediate between weak- and strong-field ligands in the spectrochemical series.

## 15.4 | The Reactions of Coordination Compounds Have a Wide Number of Useful Applications

Complex ions undergo ligand exchange (or substitution) reactions in solution. The rates of these reactions vary widely, depending on the nature of the metal ion and the ligands.

In studying ligand exchange reactions, it is often useful to distinguish between the stability of a complex ion and its tendency to react, which we call *kinetic lability*. Stability in this context is a thermodynamic property, which is measured in terms of the species' formation constant  $K_f$ . For example, the complex ion tetracyanonickelate(II) is stable because it has a large formation constant ( $K_f \approx 1 \times 10^{30}$ ):

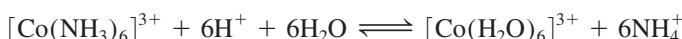


By using cyanide ions labeled with the radioactive isotope carbon-14, chemists have shown that  $[\text{Ni}(\text{CN})_4]^{2-}$  undergoes ligand exchange very rapidly in solution. The following equilibrium is established almost as soon as the species are mixed:



where the asterisk denotes a C-14 atom. Complexes like the tetracyanonickelate(II) ion are ***labile complexes*** because they *undergo rapid ligand exchange reactions*. Thus, a thermodynamically stable species (that is, one that has a large formation constant) is not necessarily unreactive.

A complex that is thermodynamically *unstable* in acidic solution is  $[\text{Co}(\text{NH}_3)_6]^{3+}$ . The equilibrium constant for the following reaction is about  $1 \times 10^{20}$ :



When equilibrium is reached, the concentration of the  $[\text{Co}(\text{NH}_3)_6]^{3+}$  ion is very low. It takes several days to achieve equilibrium, however, because the  $[\text{Co}(\text{NH}_3)_6]^{3+}$  ion is an ***inert complex***—a complex ion that undergoes very slow exchange reactions (on the order of hours or even days). Thus, a thermodynamically unstable species is not necessarily chemically reactive. The rate of reaction is determined by the energy of activation, which is high in this case.

Most complex ions containing  $\text{Co}^{3+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Pt}^{2+}$  are kinetically inert. Because they exchange ligands very slowly, they are easy to study in solution. As a result, our knowledge of the bonding, structure, and isomerism of coordination compounds has come largely from studies of these compounds with these ligands.

### Applications of Coordination Compounds

Coordination compounds are found in living systems and have many uses in the home, in industry, and in medicine. We describe a few examples here and in the insert on page 784.

#### Metallurgy

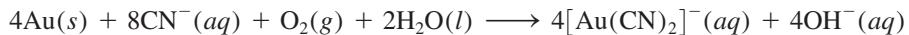
Coordination compounds can be used to extract and purify metals, such as gold and silver. Although gold and silver are usually found in the uncombined state in nature, in other metal ores they may be present in relatively small concentrations and are more difficult to extract. In a typical process, the crushed ore is treated with an aqueous

At equilibrium, there is a distribution of  $^*\text{CN}^-$  ions in the complex ion.

**Figure 15.23** A cyanide pond for extracting gold from metal ore.



cyanide solution in the presence of air to dissolve the gold by forming the soluble complex ion  $[\text{Au}(\text{CN})_2]^-$ :



The complex ion  $[\text{Au}(\text{CN})_2]^-$  (along with some cation, such as  $\text{Na}^+$ ) is separated from other insoluble materials by filtration and treated with an electropositive metal such as zinc to recover the gold:

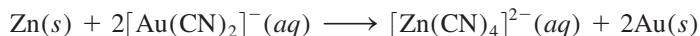


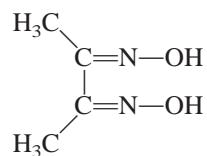
Figure 15.23 shows an aerial view of a “cyanide pond” used for the extraction of gold.

### ***Therapeutic Chelating Agents***

Recall from Section 15.2 that the chelating agent EDTA is used in the treatment of lead poisoning. Certain platinum-containing compounds can effectively inhibit the growth of cancerous cells. A specific case is discussed in the insert on p. 795.

### ***Chemical Analysis***

Although EDTA has a great affinity for a large number of metal ions (especially +2 and +3 ions), other chelates are more selective in their binding. For example, dimethylglyoxime,



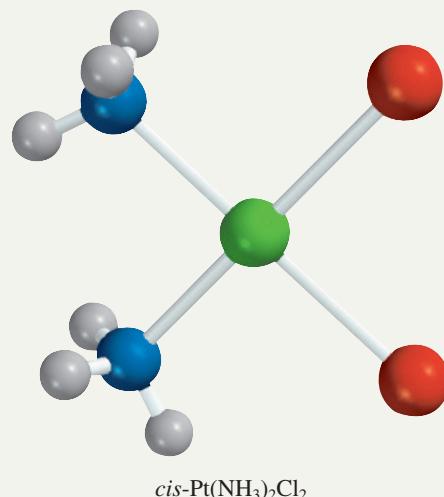
forms an insoluble brick-red solid with  $\text{Ni}^{2+}$  and an insoluble bright-yellow solid with  $\text{Pd}^{2+}$ . These characteristic colors are used in qualitative analysis to identify nickel and palladium. Furthermore, the quantities of ions present can be determined by gravimetric

## Cisplatin—An Anticancer Drug

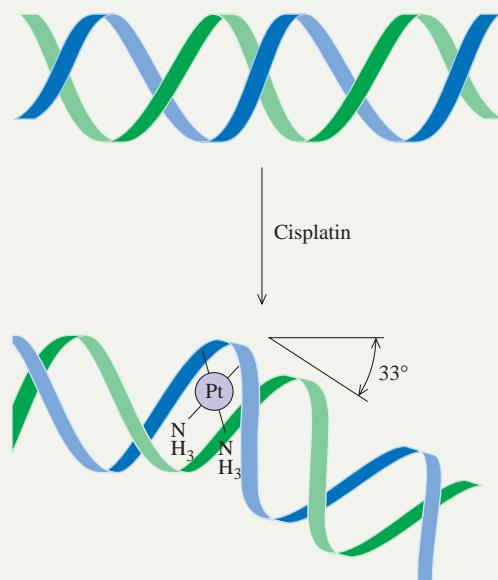
Luck often plays a role in major scientific breakthroughs, but it takes an alert and well-trained person to recognize the significance of an accidental discovery and to take full advantage of it. Such was the case when, in 1964, the bio-physicist Barnett Rosenberg and his research group at Michigan State University were studying the effect of an electric field on the growth of bacteria. They suspended a bacterial culture between two platinum electrodes and passed an electric current through it. To their surprise, they found that after an hour or so the bacteria cells ceased dividing. It did not take long for the group to determine that a platinum-containing substance extracted from the bacterial culture inhibited cell division.

Rosenberg reasoned that the platinum compound might be useful as an anticancer agent because cancer involves uncontrolled division of the affected cells, so he set out to identify the substance. Given the presence of ammonia and chloride ions in solution during electrolysis, Rosenberg synthesized a number of platinum compounds containing ammonia and chlorine. The one that proved most effective at inhibiting cell division was *cis*-diamminedichloroplatinum(II) [ $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ ], also called cisplatin.

Cisplatin works by chelating DNA (deoxyribonucleic acid), the molecule that contains the genetic code. During

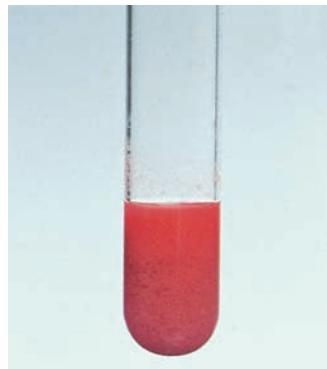


cell division, the double-stranded DNA splits into two single strands, which must be accurately copied in order for the new cells to be identical to their parent cell. X-ray studies show that cisplatin binds to DNA by forming cross-links in which the two chlorides on cisplatin are replaced by nitrogen atoms in the adjacent guanine bases on the *same* strand of the DNA. (Guanine is one of the four bases in DNA. See Figure 16.27.) Consequently, the double-stranded structure assumes a bent configuration at the binding site. Scientists believe that this structural distortion is a key factor in inhibiting replication. The damaged cell is then destroyed by the immune system of the body. Because the binding of cisplatin to DNA requires both Cl atoms to be on the same side of the complex, the *trans* isomer of the compound is totally ineffective as an anticancer drug. Unfortunately, cisplatin can cause serious side effects, including severe kidney damage. Therefore, ongoing research efforts are directed toward finding related complexes that destroy cancer cells with less harm to healthy tissue.

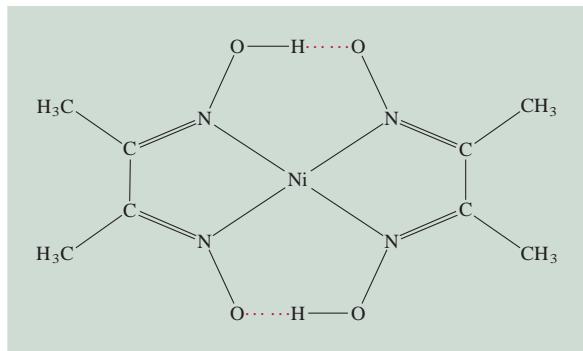


Cisplatin destroys the cancer cells' ability to reproduce by changing the configuration of their DNA. It binds to two sites on a strand of DNA, causing it to bend about  $33^\circ$  away from the rest of the strand.

**Figure 15.24** Structure of nickel dimethylglyoxime. Note that the overall structure is stabilized by hydrogen bonds.



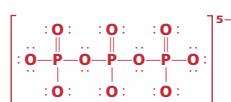
An aqueous suspension of bis(dimethylglyoximato)nickel(II)



analysis as follows: To a solution containing  $\text{Ni}^{2+}$  ions, we add an excess of dimethylglyoxime reagent, and a brick-red precipitate forms. The precipitate is then filtered, dried, and weighed. Knowing the formula of the complex (Figure 15.24), we can readily calculate the amount of nickel present in the original solution.

### Detergents

The cleansing action of soap in hard water is hampered by the reaction of the  $\text{Ca}^{2+}$  ions in the water with the soap molecules to form insoluble salts or curds. In the late 1940s, the detergent industry introduced a “builder,” usually sodium tripolyphosphate, to circumvent this problem. The tripolyphosphate ion is an effective chelating agent that forms stable, soluble complexes with  $\text{Ca}^{2+}$  ions. Sodium tripolyphosphate revolutionized the detergent industry. However, because phosphates are plant nutrients, phosphate-containing wastewater discharged into rivers and lakes caused algae to grow, depleting the waters of oxygen. As a result, most or all aquatic life eventually died. This process, called *eutrophication*, led many states to ban phosphate detergents beginning in the 1970s, thus forcing manufacturers to reformulate their products to eliminate phosphates.



Tripolyphosphate ion

## Summary of Facts and Concepts

### Section 15.1

- Transition metals usually have incompletely filled *d* subshells and a pronounced tendency to form complexes. Compounds that contain complex ions are called coordination compounds.
- The first-row transition metals (scandium to copper) are the most common of all the transition metals; their chemistry is characteristic, in many ways, of the entire group.

### Section 15.2

- Complex ions consist of a metal ion surrounded by ligands. The donor atoms in the ligands each contribute an electron pair to the central metal ion in a complex.
- Coordination compounds may display geometric and/or optical isomerism.

### Section 15.3

- Crystal field theory explains bonding in complexes in terms of electrostatic interactions. According to crystal field theory, the *d* orbitals are split into two higher-

energy and three lower-energy orbitals in an octahedral complex. The energy difference between these two sets of *d* orbitals is the basis of crystal field splitting.

- Strong-field ligands cause a large crystal field splitting, and weak-field ligands cause a small splitting. Electron spins tend to be parallel with weak-field ligands and paired with strong-field ligands, where a greater investment of energy is required to promote electrons into the high-lying *d* orbitals.
- Ligand field theory corrects some of the defects of crystal field theory by going beyond electrostatic interactions to include the effects of covalent metal-ligand bonding through the use of molecular orbital theory.

### Section 15.4

- Complex ions undergo ligand exchange reactions in solution.
- Coordination compounds find application in many different areas, for example, as antidotes for metal poisoning and in chemical analysis.

## Key Words

back bonding, p. 792	coordination number, p. 778	donor atom, p. 778	ligand, p. 778
chelating agent, p. 778	crystal field splitting, p. 787	inert complex, p. 793	ligand field theory, p. 791
coordination compound, p. 777	crystal field theory, p. 786	labile complex, p. 793	spectrochemical series, p. 789

## Problems

### Transition Metals Have Electron Configurations with Incomplete *d* or *f* Shells

- 15.1 Why is zinc not considered a transition metal?
- 15.2 Explain why atomic radii decrease very gradually from scandium to copper.
- 15.3 Without referring to the text, write the ground-state electron configurations of the first-row transition metals. Explain any irregularities.
- 15.4 Write the electron configurations of the following ions: V<sup>5+</sup>, Cr<sup>3+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, Cu<sup>2+</sup>, Sc<sup>3+</sup>, and Ti<sup>4+</sup>.
- 15.5 Why do transitional metals have more oxidation states than other elements?
- 15.6 Why does chromium seem to be less reactive than its standard reduction potential suggests?

### Transition Metals Can Form a Variety of Coordination Compounds

- 15.7 Complete the following statements for the complex ion [Co(en)<sub>2</sub>(H<sub>2</sub>O)CN]<sup>2+</sup>. (a) Among the ligands, en is the abbreviation for \_\_\_\_\_. (b) The oxidation number of Co is \_\_\_\_\_. (c) The coordination number of Co is \_\_\_\_\_. (d) \_\_\_\_\_ is a bidentate ligand.
- 15.8 Complete the following statements for the complex ion [Cr(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>-</sup>. (a) The oxidation number of Cr is \_\_\_\_\_. (b) The coordination number of Cr is \_\_\_\_\_. (c) \_\_\_\_\_ is a bidentate ligand.
- 15.9 Calculate the oxidation numbers of the metals in the following species: (a) K<sub>3</sub>[Fe(CN)<sub>6</sub>], (b) K<sub>3</sub>[Cr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>], and (c) [Ni(CN)<sub>4</sub>]<sub>2</sub>.
- 15.10 Give the oxidation numbers of the metals in the following species: (a) Na<sub>2</sub>MoO<sub>4</sub>, (b) MgWO<sub>4</sub>, and (c) Fe(CO)<sub>5</sub>.
- 15.11 What are the systematic names for the following ions and compounds: (a) [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>], (b) [Co(en)<sub>2</sub>Br<sub>2</sub>], (c) Cr(NH<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>, and (d) [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub>?
- 15.12 What are the systematic names for the following ions and compounds: (a) [cis-Co(en)<sub>2</sub>Cl<sub>2</sub>], (b) [Pt(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>3</sub>, and (c) [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub>?
- 15.13 Write the formulas for each of the following ions and compounds: (a) tetrahydroxozincate(II), (b) pentaquaquochlorochromium(III) chloride, (c) tetrabromocuprate(II), and (d) ethylenediaminetetraacetatoferate(II).
- 15.14 Write the formulas for each of the following ions and compounds: (a) bis(ethylenediamine)dichlorochromium(III), (b) pentacarbonyliron(0), (c) potassium

tetracyanocuprate(II), and (d) tetraammineaquochlorocobalt(III) chloride.

- 15.15 The complex ion [Ni(CN)<sub>2</sub>Br<sub>2</sub>]<sup>2-</sup> has a square-planar geometry. Draw the structures of the geometric isomers of this complex.
- 15.16 How many geometric isomers are possible for each of the following species: (a) [Co(NH<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub>]<sup>-</sup> and (b) [Co(NH<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>]<sup>-</sup>?
- 15.17 Draw structures of all the geometric and optical isomers of each of the following cobalt complexes: (a) [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>, (b) [Co(NH<sub>3</sub>)<sub>5</sub>Cl]<sup>2+</sup>, and (c) [Co(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>3-</sup>
- 15.18 Draw structures of all the geometric and optical isomers of each of the following cobalt complexes: (a) [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup> and (b) [Co(en)<sub>3</sub>]<sup>3+</sup>.

### Bonding in Coordination Compounds Can Be Described by Crystal Field Theory

- 15.19 The [Ni(CN)<sub>4</sub>]<sup>2-</sup> ion, which has square-planar geometry, is diamagnetic, whereas the [NiCl<sub>4</sub>]<sup>2-</sup> ion, which has tetrahedral geometry, is paramagnetic. Show the crystal field splitting diagrams for those two complexes.
- 15.20 Transition metal complexes containing CN<sup>-</sup> ligands are often yellow, whereas those containing H<sub>2</sub>O ligands are often green or blue. Explain.
- 15.21 Predict the number of unpaired electrons in the following complex ions: (a) [Cr(CN)<sub>6</sub>]<sup>4-</sup> and (b) [Cr(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>.
- 15.22 The absorption maximum for the complex ion [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> occurs at 470 nm. (a) Predict the color of the complex, and (b) calculate the crystal field splitting in kJ mol<sup>-1</sup>.
- 15.23 From each of the following pairs, choose the complex that absorbs light at a longer wavelength: (a) [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup>, [Co(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>; (b) [FeF<sub>6</sub>]<sup>3-</sup>, [Fe(CN)<sub>6</sub>]<sup>3-</sup>; and (c) [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>, [CuCl<sub>4</sub>]<sup>2-</sup>.
- 15.24 A solution made by dissolving 0.875 g of Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>3</sub> in 25.0 g of water freezes at -0.56°C. Calculate the number of moles of ions produced when 1 mole of Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>3</sub> is dissolved in water and suggest a structure for the complex ion present in this compound.

### The Reactions of Coordination Compounds Have a Wide Number of Useful Applications

- 15.25 Oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) is sometimes used to clean rust stains from sinks and bathtubs. Explain the chemistry behind this cleaning action.

- 15.26 The  $[\text{Fe}(\text{CN})_6]^{3-}$  complex is more labile than the  $[\text{Fe}(\text{CN})_6]^{4-}$  complex. Suggest an experiment that would prove that  $[\text{Fe}(\text{CN})_6]^{3-}$  is a labile complex.
- 15.27 Aqueous copper(II) sulfate solution is blue in color, but a green precipitate forms when aqueous potassium fluoride is added. When aqueous potassium chloride is added instead, a bright-green solution forms. Explain what is happening in these two cases.
- 15.28 When aqueous potassium cyanide is added to a solution of copper(II) sulfate, a white precipitate, soluble in an excess of potassium cyanide, forms. No precipitate forms when hydrogen sulfide is bubbled through the solution at this point. Explain.
- 15.29 A concentrated aqueous copper(II) chloride solution is bright green, but the solution turns light blue, when diluted with water. Explain.
- 15.30 In a dilute nitric acid solution,  $\text{Fe}^{3+}$  reacts with thiocyanate ion ( $\text{SCN}^-$ ) to form a dark-red complex:  

$$[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + \text{SCN}^- \rightleftharpoons \text{H}_2\text{O} + [\text{Fe}(\text{H}_2\text{O})_5\text{NCS}]^{2+}$$
 The equilibrium concentration of  $[\text{Fe}(\text{H}_2\text{O})_5\text{NCS}]^{2+}$  may be determined by the strength of the dark color of the solution (measured by a spectrometer). In one such experiment, 1.0 mL of 0.20 M  $\text{Fe}(\text{NO}_3)_3$  was mixed with 1.0 mL of  $1.0 \times 10^{-3}$  M KSCN and 8.0 mL of dilute  $\text{HNO}_3$ . The color of the solution quantitatively indicated that the  $[\text{Fe}(\text{H}_2\text{O})_5\text{NCS}]^{2+}$  concentration was  $7.3 \times 10^5$  M. Calculate the formation constant for  $[\text{Fe}(\text{H}_2\text{O})_5\text{NCS}]^{2+}$ .

### Additional Problems

- 15.31 As we read across the first-row transition metals from left to right, the +2 oxidation state becomes more stable in comparison with the +3 state. Why?
- 15.32 Which is a stronger oxidizing agent in aqueous solution,  $\text{Mn}^{3+}$  or  $\text{Cr}^{3+}$ ? Explain your choice.
- 15.33 Carbon monoxide binds to Fe in hemoglobin some 200 times more strongly than oxygen. This is why CO is so toxic. The metal-to-ligand sigma bond is formed by donating a lone pair from the donor atom to an empty  $sp^3d^2$  orbital on Fe. (a) On the basis of electronegativities, would you expect the C or O atom to form the bond to Fe? (b) Draw a diagram illustrating the overlap of the orbitals involved in the bonding.
- 15.34 What are the oxidation states of Fe and Ti in the ore ilmenite ( $\text{FeTiO}_3$ )? (Hint: Look up the ionization energies of Fe and Ti in Table 15.1; the fourth ionization energy of Ti is 4180 kJ mol<sup>-1</sup>.)
- 15.35 A student has prepared a cobalt complex that has one of the following three structures:  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ ,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ , or  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ . Explain how the student could distinguish between these possibilities by performing an electrical conductance experiment. At the student's disposal are three

strong electrolytes— $\text{NaCl}$ ,  $\text{MgCl}_2$ , and  $\text{FeCl}_3$ —which may be used for comparison purposes.

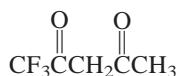
- 15.36 Chemical analysis shows that hemoglobin contains 0.34 percent of Fe by mass. What is the minimum possible molar mass of hemoglobin? The actual molar mass of hemoglobin is about 65,000 g. How do you account for the discrepancy between your minimum value and the actual value?
- 15.37 Explain the following facts: (a) Copper and iron have several oxidation states, whereas zinc has only one. (b) Copper and iron form colored ions, whereas zinc does not.
- 15.38 A student in 1895 prepared three coordination compounds containing chromium that had the following properties:

Formula	Color	$\text{Cl}^-$ Ions in Solution per Formula Unit
$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	Violet	3
$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	Light green	2
$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	Dark green	1

Write modern formulas for these compounds and suggest a method for confirming the number of  $\text{Cl}^-$  ions present in solution in each case. (Hint: Some of the compounds may exist as hydrates.)

- 15.39 The formation constant for the reaction
- $$\text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]$$
- is
- $1.5 \times 10^7$
- and that for the reaction
- $$\text{Ag} + 2\text{CN}^- \rightleftharpoons [\text{Ag}(\text{CN})_2]$$
- is
- $1.0 \times 10^{21}$
- at 25°C. Calculate the equilibrium constant and
- $\Delta G^\circ$
- at 25°C for the reaction
- $$[\text{Ag}(\text{NH}_3)_2] + 2\text{CN}^- \rightleftharpoons [\text{Ag}(\text{CN})_2] + 2\text{NH}_3$$
- 15.40 From the standard reduction potentials listed in Table 13.1 for  $\text{Zn}/\text{Zn}^{2+}$  and  $\text{Cu}/\text{Cu}^{2+}$ , calculate  $\Delta G^\circ$  and the equilibrium constant for the following reaction:
- $$\text{Zn}(s) + 2\text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Cu}^+(\text{aq})$$
- 15.41 Using the standard reduction potentials listed in Table 13.1 and the *Handbook of Chemistry and Physics*, show that the following reaction is favorable under standard-state conditions:
- $$2\text{Ag}(s) + \text{Pt}^{2+}(\text{aq}) \longrightarrow 2\text{Ag}^+(\text{aq}) + \text{Pt}(s)$$
- What is the equilibrium constant of this reaction at 25°C?
- 15.42 The  $\text{Co}^{2+}$ -porphyrin complex is more stable than the  $\text{Fe}^{2+}$ -porphyrin complex. Why, then, is iron the metal ion in hemoglobin (and other heme-containing proteins)?

- 15.43 Oxyhemoglobin is bright red, whereas deoxyhemoglobin is purple. Show that the difference in color can be accounted for qualitatively on the basis of high-spin and low-spin complexes. (*Hint:* O<sub>2</sub> is a strong-field ligand; see the inset on p. 784.)
- 15.44 Hydrated Mn<sup>2+</sup> ions are practically colorless (see Figure 15.17) even though they possess five 3d electrons. Explain. (*Hint:* Electronic transitions in which there is a change in the number of unpaired electrons do not occur readily.)
- 15.45 Which of the following hydrated cations are colorless: Fe<sup>2+</sup>(aq), Zn<sup>2+</sup>(aq), Cu<sup>+(aq)</sup>, Cu<sup>2+</sup>(aq), V<sup>5+</sup>(aq), Ca<sup>2+</sup>(aq), Co<sup>2+</sup>(aq), Sc<sup>2+</sup>(aq), or Pb<sup>2+</sup>(aq)? Explain your choice.
- 15.46 Aqueous solutions of CoCl<sub>2</sub> are generally either light pink or blue. Low concentrations and low temperatures favor the pink form, whereas high concentrations and high temperatures favor the blue form. Adding hydrochloric acid to a pink solution of CoCl<sub>2</sub> causes the solution to turn blue; the pink color is restored by the addition of HgCl<sub>2</sub>. Account for these observations.
- 15.47 Suggest a method that would allow you to distinguish between *cis*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and *trans*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>.
- 15.48 You are given two solutions containing FeCl<sub>2</sub> and FeCl<sub>3</sub> at the same concentration. One solution is light yellow, and the other one is brown. Identify these solutions based only on color.
- 15.49 The label of a certain brand of mayonnaise lists EDTA as a food preservative. How does EDTA prevent the spoilage of mayonnaise?
- 15.50 The compound 1,1,1-trifluoroacetylacetone (tfa) is a bidentate ligand:



It forms a tetrahedral complex with Be<sup>2+</sup> and a square-planar complex with Cu<sup>2+</sup>. Draw structures of these complex ions, and identify the type of isomerism exhibited by them.

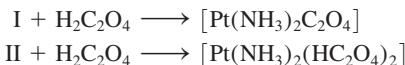
- 15.51 How many geometric isomers can the following square planar complex have?



## Answers to Practice Exercises

- 15.1** (a) +2, (b) +3, (c) +4 **15.2** (a) tetraaquodichlorochromium(III) chloride; (b) triaminebromoplatinum(II) chloride; (c) potassium hexafluorocobaltate(III); and (d) tetraammine-

- 15.52 [Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] is found to exist in two geometric isomers designated I and II, which react with oxalic acid as follows:



Comment on the structures of I and II.

- 15.53 Commercial silver-plating operations frequently use a solution containing the complex Ag(CN)<sub>2</sub><sup>-</sup> ion. Because the formation constant ( $K_f$ ) is quite large, this procedure ensures that the free Ag<sup>+</sup> concentration in solution is low for uniform electrodeposition. In one process, a chemist added 9.0 L of 5.0 M NaCN to 90.0 L of 0.20 M AgNO<sub>3</sub>. Calculate the concentration of free Ag<sup>+</sup> ions at equilibrium. See Table 11.5 for  $K_f$  values.
- 15.54 Draw qualitative diagrams for the crystal field splittings in (a) a linear complex ion ML<sub>2</sub>, (b) a trigonal-planar complex ion ML<sub>3</sub>, and (c) a trigonal-bipyramidal complex ion ML<sub>5</sub>.
- 15.55 (a) The free Cu(I) ion is unstable in solution and has a tendency to disproportionate:



Use the information in Table 13.1 to calculate the equilibrium constant for the reaction. (b) Based on your result in (a), explain why most Cu(I) compounds are insoluble.

- 15.56 Consider the following two ligand exchange reactions:
- $$\begin{array}{l} [\text{Co}(\text{H}_2\text{O})_6]^{3+} + 6\text{NH}_3 \rightleftharpoons [\text{Co}(\text{NH}_3)_6]^{3+} + 6\text{H}_2\text{O} \\ [\text{Co}(\text{H}_2\text{O})_6]^{3+} + 3\text{en} \rightleftharpoons [\text{Co}(\text{en})_6]^{3+} + 6\text{H}_2\text{O} \end{array}$$
- (a) Which of the reactions should have the larger  $\Delta S^\circ$ ?
- (b) Given that the Co—N bond strength is approximately the same in both complexes, which reaction will have a larger equilibrium constant? Explain your choices.
- 15.57 Copper is known to exist in a +3 oxidation state, which is believed to be involved in some biological electron transfer reactions. (a) Would you expect this oxidation state of copper to be stable? Explain. (b) Name the compound K<sub>3</sub>CuF<sub>6</sub>, and predict the geometry of the complex ion and its magnetic properties. (c) Most of the known Cu(III) compounds have square-planar geometry. Are these compounds diamagnetic or paramagnetic?

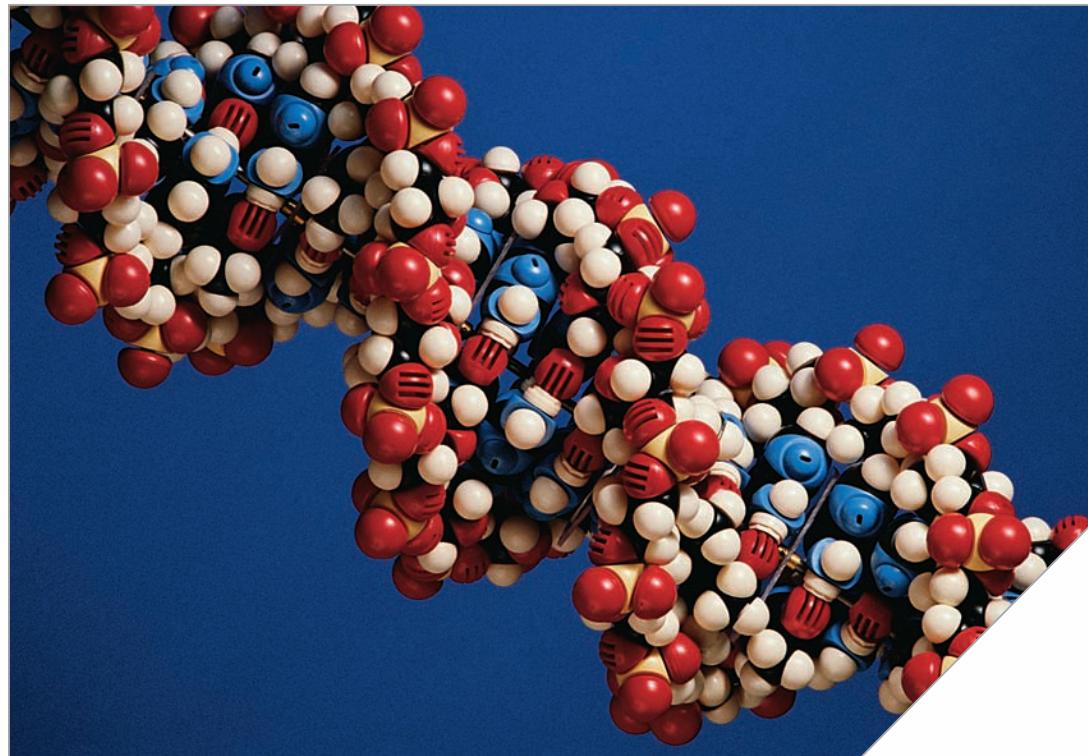
- chloronitrocobalt(III) nitrate **15.3** (a) [Co(en)<sub>3</sub>]<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>; (b) K<sub>3</sub>[Fe(CN)<sub>6</sub>]; (c) K<sub>2</sub>[Ni(CN)<sub>4</sub>]; and (d) Ca<sub>2</sub>[PtBr<sub>4</sub>Cl<sub>2</sub>]

# 16

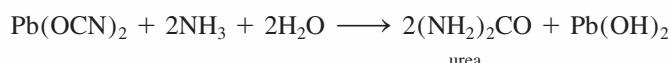
Chapter

## Organic and Polymer Chemistry

- 16.1 Hydrocarbons Are Organic Compounds Containing Only Hydrogen and Carbon 801
- 16.2 Hydrocarbons Undergo a Number of Important Chemical Reactions 811
- 16.3 The Structure and Properties of Organic Compounds Are Greatly Influenced by the Presence of Functional Groups 815
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- 16.5 Proteins Are Polymer Chains Composed of Amino Acid Monomers 833
- 16.6 DNA and RNA Are Polymers Composed of Nucleic Acids 841



**Organic chemistry** is the study of carbon compounds. The word *organic* was originally used by eighteenth-century chemists to describe substances obtained from living sources—plants and animals. These chemists believed that nature possessed a certain vital force and that only living things could produce organic compounds. This romantic notion was disproved in 1828 by Friedrich Wöhler, a German chemist who prepared urea, an organic compound, from the reaction between the inorganic compounds lead cyanate and aqueous ammonia:



Today, well over 14 million synthetic and natural organic compounds are known. This number is significantly greater than the 100,000 or so known inorganic compounds.

## 16.1 | Hydrocarbons Are Organic Compounds Containing Only Hydrogen and Carbon

Carbon can form more compounds with itself and/or other atoms than any other element because carbon atoms can form single, double, and triple bonds to other carbon atoms and because carbon atoms can link up with each other in chains and ring structures. Classes of organic compounds can be distinguished based on the functional groups they contain. A ***functional group*** is an atom or group of atoms that gives characteristic chemical properties to the parent molecule. Different molecules containing the same kind of functional group or groups undergo similar reactions. Thus, by learning the characteristic properties of a few functional groups, we can understand the properties of many organic compounds. In Section 16.3, we will discuss the functional groups known as alcohols, ethers, aldehydes, ketones, carboxylic acids, and amines.

### Aliphatic Hydrocarbons

All organic compounds are derived from a group of compounds known as ***hydrocarbons*** because they are *made up only of hydrogen and carbon*. On the basis of structure, hydrocarbons can be classified as aliphatic or aromatic. ***Aliphatic hydrocarbons*** do not contain the benzene group, or the benzene ring, whereas ***aromatic hydrocarbons*** contain one or more benzene rings. In addition, aliphatic hydrocarbons are further divided into alkanes, alkenes, and alkynes (Figure 16.1).

#### Alkanes

***Alkanes*** have the general formula  $C_nH_{2n+2}$ , where  $n$  is a positive integer ( $n = 1, 2, 3, \dots$ ). They contain only C—H and C—C single covalent bonds. Alkanes are also known as ***saturated hydrocarbons*** because they contain the maximum number of hydrogen atoms that can bond with the number of carbon atoms present.

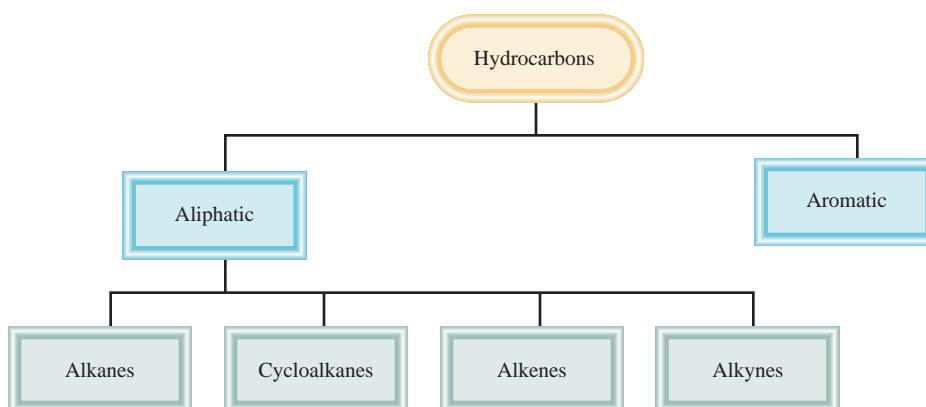
The simplest alkane (that is, with  $n = 1$ ) is methane ( $CH_4$ ), which, in addition to several natural sources, is a natural product of the anaerobic bacterial decomposition of vegetable matter under water. Because it was first collected in marshes, methane became known as “marsh gas.” A rather improbable but proven source of methane is termites. When these voracious insects consume wood, the microorganisms that inhabit their digestive system break down cellulose (the major component of wood) into methane, carbon dioxide, and other compounds. It is estimated that termites produce 170 million tons of methane annually! Methane is also produced in some sewage treatment processes. Commercially, methane is obtained from natural gas.

1A	2A							8A
		B	C	N	O	F		
		Si	P	S	Cl			
						Br		
						I		

Common elements in organic compounds



Termites are a natural source of methane.



**Figure 16.1** Classification of hydrocarbons.

**Figure 16.2** Structures of the first four alkanes. Butane has two different structural isomers, as discussed in Section 4.4.

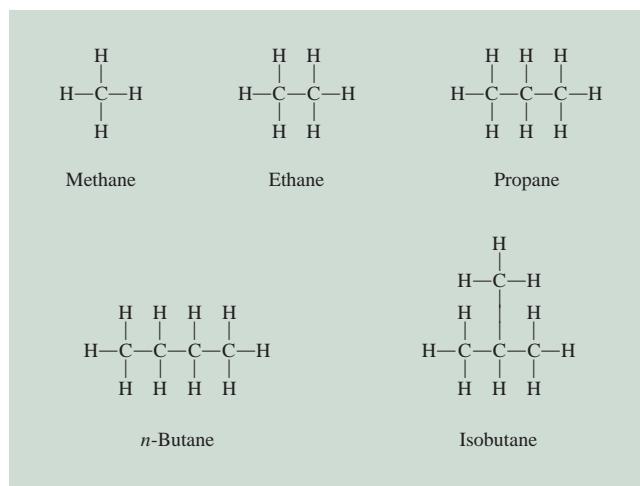


Figure 16.2 shows the structures of methane, ethane, propane, and butane, the first four alkanes ( $n = 1$  to  $n = 4$ ). Natural gas is a mixture of methane, ethane, and a small amount of propane. Recall from Section 4.3 that the carbon atom of methane is  $sp^3$ -hybridized. In fact, the carbon atoms in all the alkanes are  $sp^3$ -hybridized. There is only one way to join the carbon atoms in ethane and propane, but there are two possible ways in butane, resulting in the *structural isomers* *n*-butane and isobutane. (See Section 4.4 to review structural isomers.) All alkanes with  $n \geq 4$  can exist in a variety of different structural isomers with the number of possibilities increasing rapidly with increasing  $n$ .

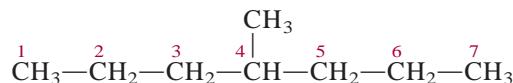
The nomenclature of alkanes and all other organic compounds is based on the recommendations of the International Union of Pure and Applied Chemistry (IUPAC). The first four alkanes (methane, ethane, propane, and butane) have nonsystematic names. As Table 16.1 shows, the number of carbon atoms is reflected in the Greek prefixes for the alkanes containing 5 to 10 carbons.

**Table 16.1** The First Ten Straight-Chain Alkanes

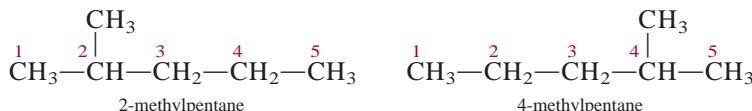
Name of Hydrocarbon	Molecular Formula	Number of Carbon Atoms	Melting Point (°C)	Boiling Point (°C)
Methane	$\text{CH}_4$	1	−182.5	−161.6
Ethane	$\text{CH}_3\text{—CH}_3$	2	−183.3	−88.6
Propane	$\text{CH}_3\text{—CH}_2\text{—CH}_3$	3	−189.7	−42.1
Butane	$\text{CH}_3\text{—}(\text{CH}_2)_2\text{—CH}_3$	4	−138.3	−0.5
Pentane	$\text{CH}_3\text{—}(\text{CH}_2)_3\text{—CH}_3$	5	−129.8	36.1
Hexane	$\text{CH}_3\text{—}(\text{CH}_2)_4\text{—CH}_3$	6	−95.3	68.7
Heptane	$\text{CH}_3\text{—}(\text{CH}_2)_5\text{—CH}_3$	7	−90.6	98.4
Octane	$\text{CH}_3\text{—}(\text{CH}_2)_6\text{—CH}_3$	8	−56.8	125.7
Nonane	$\text{CH}_3\text{—}(\text{CH}_2)_7\text{—CH}_3$	9	−53.5	150.8
Decane	$\text{CH}_3\text{—}(\text{CH}_2)_8\text{—CH}_3$	10	−29.7	174.0

Use the following IUPAC rules to name alkanes:

- The parent name of the hydrocarbon is that given to the longest continuous chain of carbon atoms in the molecule. Thus, the parent name of the following compound is heptane because there are seven carbon atoms in the longest chain.



- An alkane less one hydrogen atom is an **alkyl group**. When a hydrogen atom is removed from methane, for example, the  $\text{CH}_3$  fragment remains, which is called a *methyl* group. Similarly, removing a hydrogen atom from ethane leaves an *ethyl* group ( $\text{C}_2\text{H}_5$ ). Table 16.2 lists the names of several common alkyl groups. Any chain branching off the longest chain is named as an alkyl group.
- When one or more hydrogen atoms are replaced by other groups, the name of the compound must indicate the locations of the carbon atoms where the replacements are made. The procedure is to number each carbon atom on the longest chain in the direction that gives the smaller numbers for the locations of all branches. Consider the two different systems for the *same* compound shown here:



The compound on the left is numbered correctly because the methyl group is located at carbon 2 of the pentane chain; in the compound on the right, the methyl group is located at carbon 4. Thus, the name of the compound is 2-methylpentane, not 4-methylpentane. Note that the branch name and the parent name are written as a single word, and a hyphen follows the number.

**Table 16.2 Common Alkyl Groups**

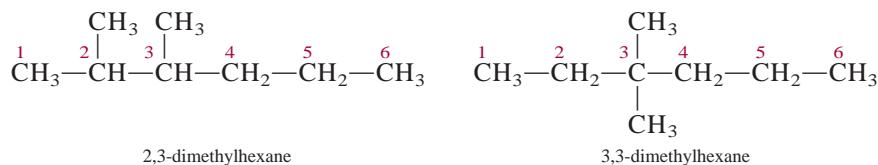
Name	Formula
Methyl	$-\text{CH}_3$
Ethyl	$-\text{CH}_2-\text{CH}_3$
<i>n</i> -Propyl	$-\text{CH}_2-\text{CH}_2-\text{CH}_3$
<i>n</i> -Butyl	$-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$
Isopropyl	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{C}-\text{H} \\   \\ \text{CH}_3 \end{array}$
<i>t</i> -Butyl*	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{C}-\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$

\*The letter *t* stands for tertiary.

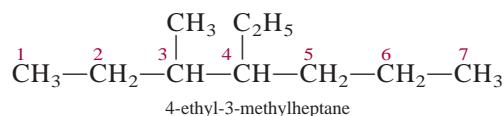
**Table 16.3**

Functional Group	Name
$-\text{NH}_2$	Amino
$-\text{F}$	Fluoro
$-\text{Cl}$	Chloro
$-\text{Br}$	Bromo
$-\text{I}$	Iodo
$-\text{NO}_2$	Nitro
$-\text{CH}=\text{CH}_2$	Vinyl

4. When there is more than one alkyl branch of the same kind present, we use a prefix such as *di*-, *tri*-, or *tetra*- with the name of the alkyl group. Consider the following examples:



When there are two or more different alkyl groups, the names of the groups are listed alphabetically. For example,



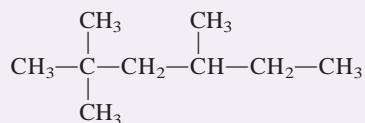
5. Alkanes can have many different types of substituents. Table 16.3 lists the names of some substituents, including nitro- and bromo-. Thus, the compound



is called 3-bromo-2-nitrohexane. Note that the substituent groups are listed alphabetically in the name and the chain is numbered in the direction that gives the lowest number to the first substituted carbon. Substituted alkanes, like 3-bromo-2-nitrobutane, that contain asymmetric carbon atoms (that is, carbon atoms that are bonded to four different substituents) can exhibit optical isomerism (Section 4.3).

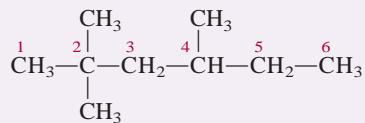
### Example 16.1

Give the IUPAC name of the following compound:



**Strategy** Follow the IUPAC rules and use the information in Table 16.2 to name the compound. How many C atoms are there in the longest continuous chain?

**Solution** The longest continuous chain has six C atoms so the parent compound is called hexane. The chain is numbered from left to right, putting the two methyl groups on carbon 2 and the other methyl group on carbon 4, because numbering the chain from right to left would give these substituents higher numbers.

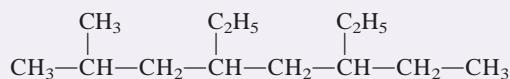


*—Continued*

*Continued—*

Therefore, the IUPAC name of the compound is 2,2,4-trimethylhexane.

**Practice Exercise** Give the IUPAC name of the following compound:



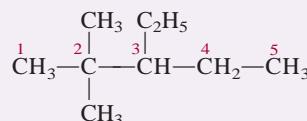
Example 16.2 shows that prefixes such as di-, tri-, and tetra- are used as needed, but are ignored when alphabetizing.

### Example 16.2

Write the structural formula of 3-ethyl-2,2-dimethylpentane.

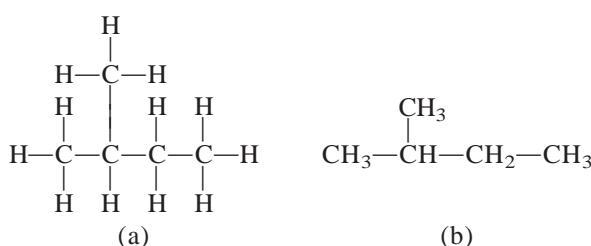
**Strategy** Follow the preceding procedure and the information in Table 16.2 to write the structural formula of the compound. How many C atoms are there in the longest continuous chain?

**Solution** The parent compound is pentane, so the longest chain has five C atoms. There are two methyl groups attached to carbon 2 and one ethyl group attached to carbon 3. Therefore, the structure of the compound is

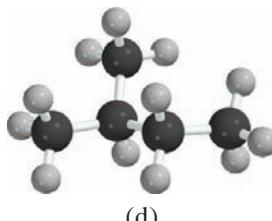
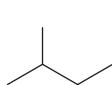


**Practice Exercise** Write the structural formula of 5-ethyl-2,4,6-trimethyloctane.

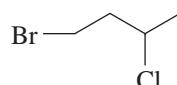
Before proceeding further, it is necessary to learn different ways of drawing the structure of organic compounds. To see how atoms are connected in 2-methylbutane ( $C_5H_{12}$ ), for example, we must first write the “expanded” molecular formula,  $CH_3CH(CH_3)CH_2CH_3$ , and draw its structural formula, shown in Figure 16.3(a).



**Figure 16.3** Four representations of the structure of 2-methylbutane: (a) structural formula, (b) abbreviated structural formula, (c) skeletal structure, (d) ball-and-stick model.



Although informative, the structural formula is time-consuming to draw. Therefore, chemists have devised ways to simplify the representation. Figure 16.3(b) is an abbreviated version, and the structure shown in Figure 16.3(c) is called the *skeletal structure* in which all the C and H letters are omitted. A carbon atom is assumed to be at each intersection of two lines (bond) and at the end of each line. Because every C atom forms four bonds, we can always deduce the number of H atoms bonded to any C atom. The element symbols for substituent atoms in the skeletal structure are always shown explicitly, such as in 1-bromo-3-chlorobutane [ $C_4H_8BrCl$ ]:



What is lacking in these structures, however, is the three dimensionality of the molecule, which for 2-methylbutane is shown by the ball-and-stick molecular model in Figure 16.3(d). Depending on the purpose of the discussion, any of these representations can be used to describe the properties of the molecule.

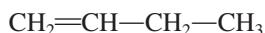
### Cycloalkanes

*Alkanes whose carbon atoms are joined in rings* are known as *cycloalkanes*. They have the general formula  $C_nH_{2n}$ , where  $n = 3, 4, \dots$ , giving them two fewer hydrogen atoms than the acyclic alkane with the same number of carbon atoms. The simplest cycloalkane is cyclopropane ( $C_3H_6$ ). The structures for the first four cycloalkanes are shown in Figure 16.4. Many biologically significant substances such as cholesterol, testosterone, and progesterone contain a ring system.

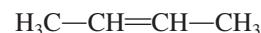
### Alkenes

*Alkenes* (also called *olefins*) contain at least one carbon-carbon double bond. Alkenes with one  $C=C$  bond have the general formula  $C_nH_{2n}$ , where  $n = 2, 3, \dots$ , giving them the same general formula as cycloalkanes (that is, two fewer hydrogen atoms than the acyclic alkane with the same number of carbon atoms). The simplest alkene is ethene ( $C_2H_4$ ), in which both carbon atoms are  $sp^2$ -hybridized and the double bond is made up of a sigma ( $\sigma$ ) bond and a pi ( $\pi$ ) bond (see Section 4.4). Ethene is also commonly known as ethylene. In fact, many organic compounds have common names in addition to their IUPAC names and, when appropriate, we will list both (with the common name in parenthesis).

As with alkanes, the name of the parent alkene is determined by the number of carbon atoms in the longest chain containing the carbon-carbon double bond (see Table 16.1). Consider two examples:

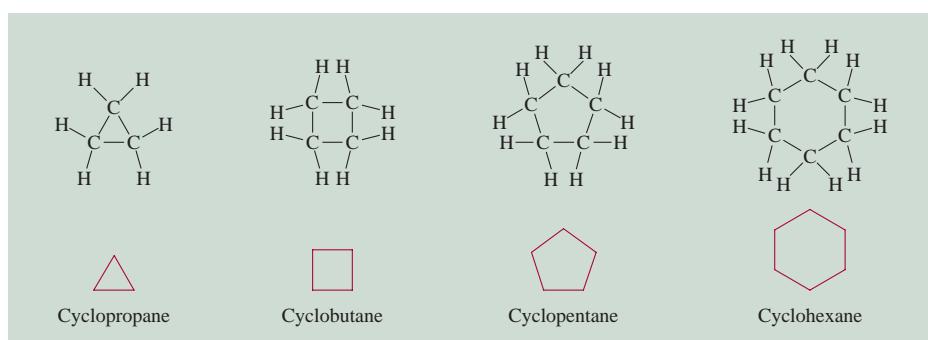


1-butene

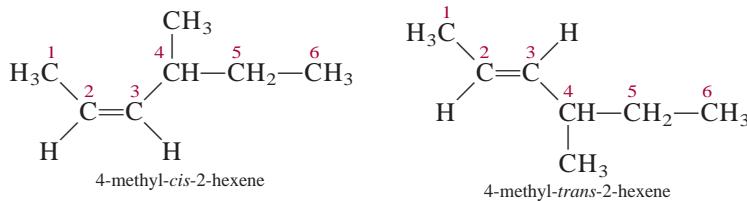


2-butene

**Figure 16.4** Structures of the first four cycloalkanes and their simplified skeletal forms.

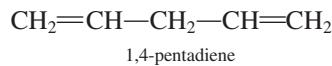
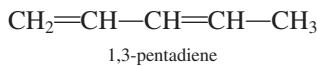


As these two examples demonstrate, the names of alkanes end with *-ene* and numbers are used to indicate the position of the double bond. The parent chain is numbered so that the lowest number possible is given to one of the carbon atoms in the double bond, regardless of any other substituents present in the compound (for example, alkyl groups or halides). The numbers in the names of alkenes refer to the lowest numbered carbon atom in the chain that is part of the C=C bond of the alkene. The name *butene* means that there are four carbon atoms in the longest chain. Because of restricted rotation about the carbon-carbon double bond, alkenes can form geometric isomers (Section 4.4). In this case, the name of an alkene must also specify whether the isomer is *cis* or *trans*:



In the *cis* isomer, the two H atoms are on the same side of the C=C bond. In the *trans* isomer, the two H atoms are across from each other.

If more than one double bond is present in an alkene, the prefixes *di-*, *tri-*, etc. precede the *-ene* suffix, as shown for the following isomers of pentadiene:



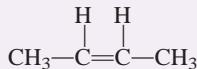
(Note: 1,3-Pentadiene will have *cis* and *trans* geometric isomers.)

### Example 16.3

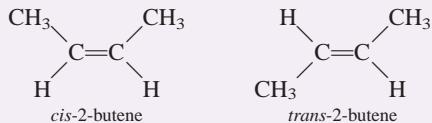
Draw and name the geometric isomers of 2-butene.

**Strategy** This is an alkene, so geometric *cis* and *trans* isomers are possible. First draw the structural formula and examine the groups attached to the double bonded carbon atoms to see if you can construct *cis* and *trans* isomers.

**Solution** The structural formula is



In this formula we could put the methyl ( $-\text{CH}_3$ ) groups on either the same (*cis*) or opposite (*trans*) sides of the double bond:



Because there is only one double bond, these are the only geometric isomers possible.

**Practice Exercise** Draw and name the geometric isomers of 2,6-dimethyl-3-heptene.

### Alkynes

Alkynes contain at least one carbon-carbon triple bond. Those that have one carbon-carbon triple bond have the general formula  $\text{C}_n\text{H}_{2n-2}$ , where  $n = 2, 3, \dots$ . As a result, alkynes have two fewer hydrogen atoms than the alkene or cycloalkane with the same

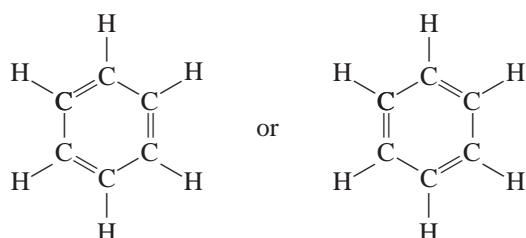
number of carbon atoms, and four fewer hydrogen atoms than the corresponding alkane.

Names of compounds containing  $\text{C}\equiv\text{C}$  bonds end with *-yne*. The name of the parent compound is determined by the number of carbon atoms in the longest chain containing the triple bond (see Table 16.1 for names of alkane counterparts). The simplest alkyne is ethyne ( $\text{C}_2\text{H}_2$ ), commonly known as acetylene. As with alkenes, the parent chain of alkynes is numbered so that the position of the carbon-carbon triple bond is given the lowest number possible:



### Aromatic Hydrocarbons

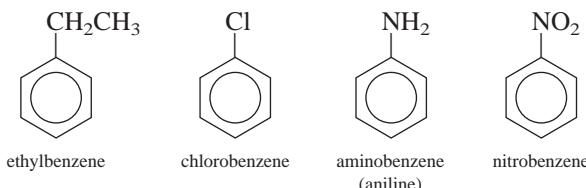
Benzene ( $\text{C}_6\text{H}_6$ ), the parent compound of the aromatic hydrocarbons, was discovered by Michael Faraday in 1826. Over the next 40 years, chemists were preoccupied with determining its molecular structure. Despite the small number of atoms in the molecule, there are quite a few ways to represent the structure of benzene without violating the tetravalency of carbon. Most of the proposed structures were rejected, however, because they did not explain the known properties of benzene. Finally, in 1865, August Kekulé<sup>1</sup> deduced that the benzene molecule could be best represented by a ring structure—a cyclic compound consisting of six carbon atoms:



As discussed in Section 4.3, the properties of benzene are best represented by both of the preceding resonance structures. Alternatively, the properties of benzene can be explained in terms of delocalized molecular orbitals (see Section 4.5):

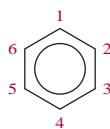


The naming of monosubstituted benzenes (that is, benzenes in which one H atom has been replaced by another atom or a group of atoms) consists of the name of the substituent followed by *benzene*:

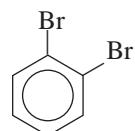


1. August Kekulé (1829–1896). German chemist. Kekulé was a student of architecture before he became interested in chemistry. He supposedly solved the riddle of the structure of the benzene molecule after having a dream in which dancing snakes bit their own tails. Kekulé's work is regarded by many as the crowning achievement of theoretical organic chemistry of the nineteenth century.

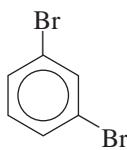
If more than one substituent is present, the location of the second group must be indicated relative to the first. The systematic way to accomplish this is to number the carbon atoms as follows:



Three different dibromobenzenes are possible:



1,2-dibromobenzene  
(*o*-dibromobenzene)

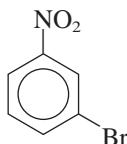


1,3-dibromobenzene  
(*m*-dibromobenzene)



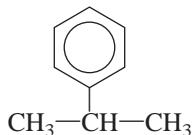
1,4-dibromobenzene  
(*p*-dibromobenzene)

The prefixes *o*- (*ortho*-), *m*- (*meta*-), and *p*- (*para*-) are also used to denote the relative positions of the two substituted groups, as shown previously for the dibromobenzenes. Compounds in which the two substituted groups are different are named accordingly. Thus,



is named 3-bromonitrobenzene, or *m*-bromonitrobenzene.

Finally, the group consisting of benzene minus a hydrogen atom ( $C_6H_5$ ) is called the *phenyl* group. Thus, the following molecule is called 2-phenylpropane:



This compound is also called isopropyl benzene (see Table 16.2).

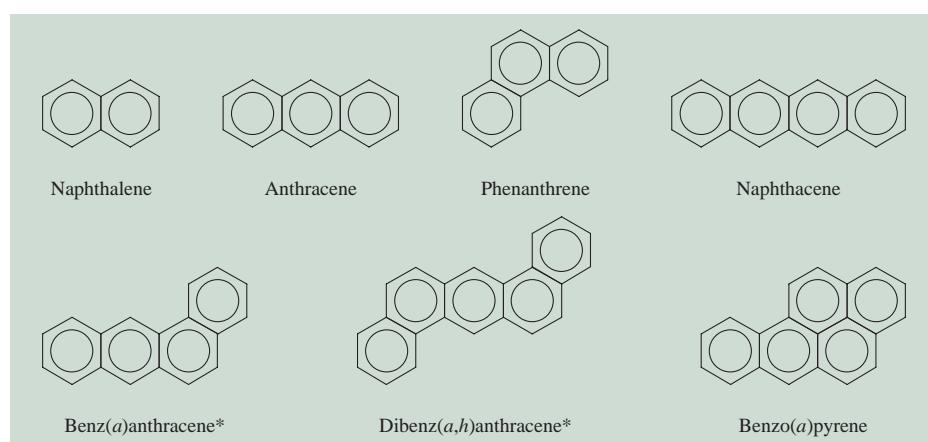
An enormously large number of compounds can be generated from substances in which benzene rings are fused together. Some of these *polycyclic* aromatic hydrocarbons are shown in Figure 16.5. The best known of these compounds is naphthalene, which is used in mothballs. These and many other similar compounds are present in coal tar. Some of the compounds with several rings are powerful carcinogens.

## Configurations of Organic Molecules

Molecular geometry gives the spatial arrangement of atoms in a molecule. However, because of internal molecular motions, atoms are not held rigidly in position. For this reason, even a simple molecule like ethane may be structurally more complicated than we might think.

The two C atoms in ethane are  $sp^3$ -hybridized and they are joined by a sigma bond. As discussed in Chapter 4, sigma bonds have cylindrical symmetry, that is, the overlap of the  $sp^3$  orbitals is the same regardless of the rotation about the C—C bond.

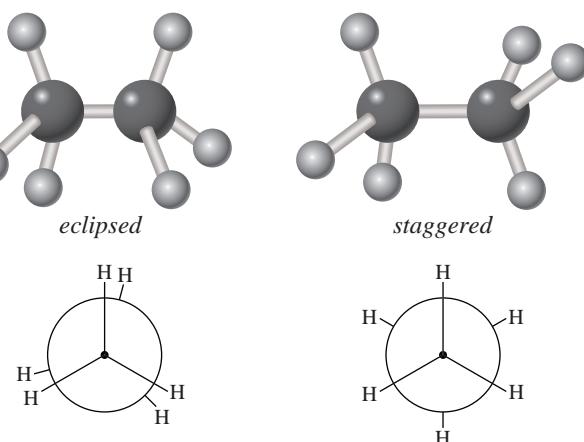
**Figure 16.5** Some polycyclic aromatic hydrocarbons. Compounds denoted by \* are potent carcinogens. An enormous number of such compounds exist in nature.

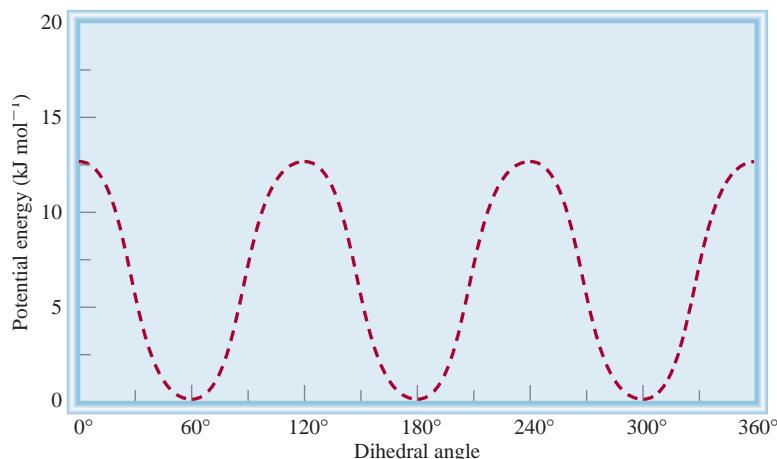


This bond rotation is not totally free, however, because there are interactions between the H atoms on the two different C atoms. Figure 16.6 shows the two extreme *conformations* of ethane. **Conformations** are different spatial arrangements of a molecule that are generated by rotation about single bonds. In the staggered configuration, the three H atoms on one C atom are pointing away from the three H atoms on the other C atom, whereas in the eclipsed conformation the two groups of H atoms are aligned parallel to one another.

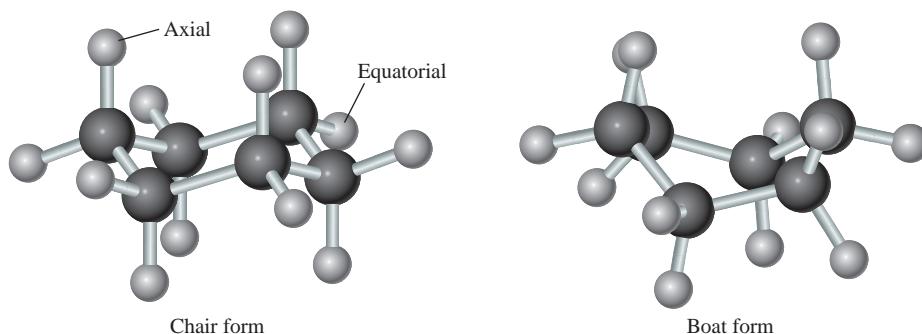
A simpler and more effective way of viewing these two conformations is by using a **Newman projection**, also shown in Figure 16.6. When looking at the C–C bond end-on, the rear carbon atom is represented by a circle and the front carbon atom is represented by a dot in the center of the circle. The C–H bonds attached to the front carbon are the lines emanating from the dot at the center of the circle, and the C–H bonds attached to the rear carbon appear as lines emanating from the edge of the circle. The eclipsed form of ethane is less stable than the staggered form. Figure 16.7 shows the variation of the potential energy of ethane as a function of rotation. The rotation of one CH<sub>3</sub> group relative to the other is described in terms of the angle between the C–H bonds on the front and back carbon atoms, called the *dihedral angle*. The dihedral angle for the first eclipsed configuration is zero. A clockwise rotation of 60° about the C–C bond generates a staggered configuration, which is converted to another eclipsed confirmation by a similar rotation, and so on.

**Figure 16.6** Staggered and eclipsed conformations of ethane shown in both ball-and-stick representations (top) and Newman projections (bottom).





**Figure 16.7** Potential energy for ethane conformations as a function of dihedral angle.



**Figure 16.8** Cyclohexane can exist in various shapes (or conformations). The most stable conformation is the chair form and a less stable one is the boat form. The two types of H atoms are labeled axial and equatorial, respectively.

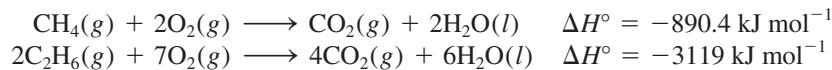
Another molecule with more than one stable conformation is cyclohexane. Theoretical analysis shows that cyclohexane can assume two different conformations that are relatively free of strain (Figure 16.8). By *strain*, we mean that bonds are compressed, stretched, or twisted out of normal geometric shapes as predicted by  $sp^3$  hybridization. The most stable configuration of cyclohexane is the *chair* form.

Configurational analysis of molecules is of great importance in understanding the details of reactions ranging from simple hydrocarbons to proteins and DNA.

## 16.2 | Hydrocarbons Undergo a Number of Important Chemical Reactions

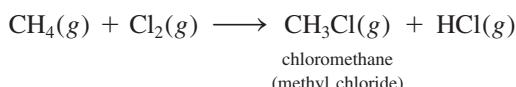
### Reactions of Alkanes

Alkanes are not very reactive substances. Under suitable conditions, however, they do react. Methane and ethane, for example, are alkanes that undergo highly exothermic combustion reactions:

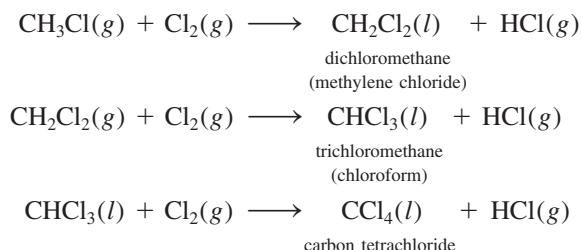


These, and similar combustion reactions, such as those for gasoline (a mixture of alkanes) and fuel oil, have long been utilized in industrial processes and in domestic heating and cooking.

The *halogenation* of alkanes, that is, the replacement of one or more hydrogen atoms by halogen atoms, is another type of reaction that alkanes undergo. When a mixture of methane and chlorine is heated above 100°C or irradiated with light of a suitable wavelength, methyl chloride is produced:



If excess chlorine gas is present, the reaction can proceed further:



A great deal of experimental evidence suggests that the initial step of the first halogenation reaction occurs as follows:

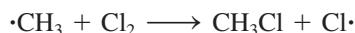


that is, the covalent bond in  $\text{Cl}_2$  breaks and two chlorine atoms form. We know it is the Cl—Cl bond that breaks when the mixture is heated or irradiated because the bond enthalpy of  $\text{Cl}_2$  is 242.7 kJ mol<sup>-1</sup> (see Table 6.6), whereas about 414 kJ mol<sup>-1</sup> is needed to break each of the C—H bonds in  $\text{CH}_4$ .

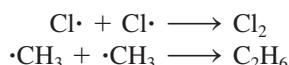
A chlorine atom is a *free radical*, which contains an unpaired electron (shown by a single dot). Chlorine atoms are highly reactive and attack methane molecules according to the following reaction



This reaction produces hydrogen chloride and the methyl radical ( $\cdot\text{CH}_3$ ). The methyl radical is another reactive species; it combines with molecular chlorine to give chloromethane (methyl chloride) and a chlorine atom:



The production of dichloromethane (methylene chloride) from chloromethane (methyl chloride) and any further reactions can be explained in the same way. The actual mechanism is more complex than the scheme we have shown because “side reactions” that do not lead to the desired products often take place, such as



Alkanes in which one or more hydrogen atoms have been replaced by a halogen atom are called *alkyl halides*. Among the large number of alkyl halides, the best known are trichloromethane (chloroform) ( $\text{CHCl}_3$ ), carbon tetrachloride ( $\text{CCl}_4$ ), dichloromethane (methylene chloride) ( $\text{CH}_2\text{Cl}_2$ ), and the chlorofluorocarbons (CFCs).

Trichloromethane (chloroform) is a volatile, sweet-tasting liquid that was used for many years as an anesthetic. However, because of its toxicity (it can severely damage the liver, kidneys, and heart), it has been replaced by other compounds. Carbon tetrachloride, also a toxic substance, was once used as a solvent in the dry cleaning industry for its ability to remove grease stains from clothing. Dichloromethane (methylene chloride) is used as a paint remover and was once used to decaffeinate coffee. Chlorofluorocarbons are used as refrigerant gases but are being phased out because of their role in the depletion of stratospheric ozone.

## Reactions of Alkenes and Alkynes

Ethene (or ethylene), the simplest alkene, is used in large quantities for the manufacture of organic polymers (to be discussed in Section 16.4) and to prepare many other organic chemicals. Ethylene is prepared industrially by the *cracking* process, that is, by the thermal decomposition of a large hydrocarbon into smaller molecules. When ethane is heated to about 800°C in the presence of a catalyst, it undergoes the following reaction:

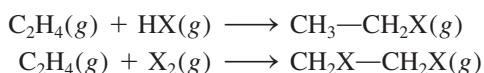


Other alkenes can be prepared by cracking the higher members of the alkane family.

Alkenes and alkynes are called *unsaturated hydrocarbons* because they can add hydrogen atoms to their carbon-carbon double and triple bonds. Unsaturated hydrocarbons commonly undergo **addition reactions** in which one molecule adds to another to form a single product. An industrially useful example of an addition reaction is **hydrogenation**, the addition of hydrogen to compounds containing multiple bonds. A simple hydrogenation reaction is the conversion of ethylene to ethane:

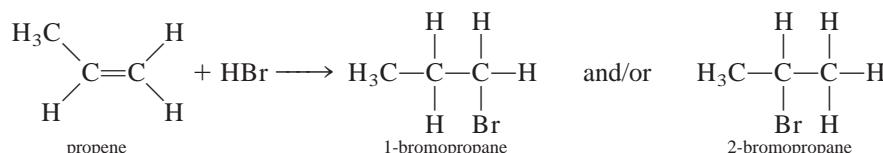


Other addition reactions to the C=C bond include

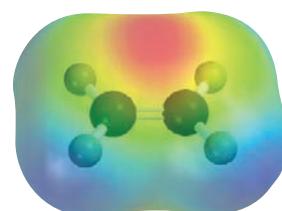
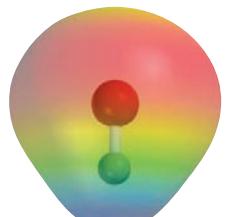


where X represents a halogen (Cl, Br, or I).

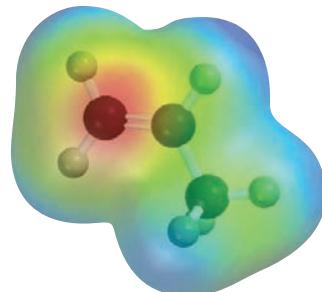
The addition of a hydrogen halide to an unsymmetrical alkene such as propene (propylene) is more complicated because two products are possible:



In reality, however, only 2-bromopropane is formed. This phenomenon was observed in all reactions between unsymmetrical reagents and alkenes. In 1871, Vladimir Markovnikov<sup>2</sup> postulated a generalization that enables us to predict the outcome of such an addition reaction: in the addition of unsymmetrical (i.e., polar) reagents to alkenes, the positive portion of the reagent (usually hydrogen) adds to the carbon atom that already has the most hydrogen atoms. This generalization, now known as *Markovnikov's rule*, makes it possible to predict the outcome of addition reactions to alkenes.



The addition reaction between HCl and ethylene. The initial interaction is between the positive end of HCl (blue) and the electron-rich region of ethylene (red), which is associated with the pi electrons of the C=C bond.



The electron density is higher on the carbon atom in the CH<sub>2</sub> group in propene.

2. Vladimir W. Markovnikov (1838–1904). Russian chemist. Markovnikov's observations of the addition reactions to alkenes were published a year after his death.



The reaction of calcium carbide with water produces acetylene, a flammable gas.

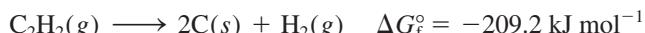
Ethyne ( $\text{C}_2\text{H}_2$ ), better known as acetylene, is a colorless gas (b.p.  $-84^\circ\text{C}$ ) prepared by the reaction between calcium carbide and water:



Acetylene has many important uses in industry. Because of its high heat of combustion

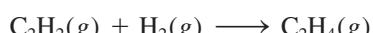


acetylene burned in an “oxyacetylene torch” gives an extremely hot flame (about 3000°C). Thus, oxyacetylene torches are used to weld metals. The standard free energy of formation of acetylene is positive ( $\Delta G_f^\circ = +209.2 \text{ kJ mol}^{-1}$ ), unlike that of the alkanes. This means that acetylene is unstable (relative to its elements) and has a tendency to decompose:

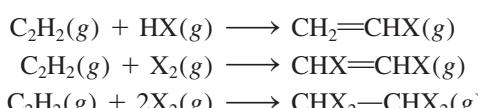


In the presence of a suitable catalyst or when the gas is kept under pressure, this reaction can occur with explosive violence. To be transported safely, the gas must be dissolved in an inert organic solvent such as acetone at moderate pressure. In the liquid state, acetylene is very sensitive to shock and is highly explosive.

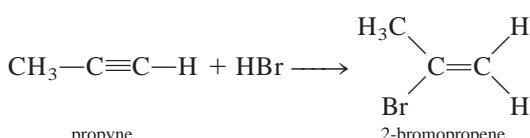
Acetylene, an unsaturated hydrocarbon, can be hydrogenated to yield ethylene:



It also undergoes the following addition reactions with hydrogen halides and halogens:

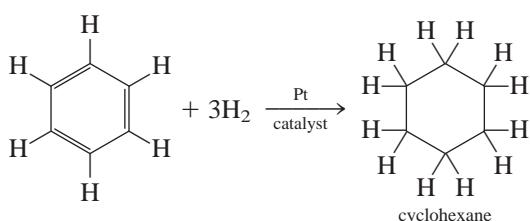


Propyne (methylacetylene) ( $\text{CH}_3\text{—C}\equiv\text{C—H}$ ) is the next member in the alkyne family. It undergoes reactions similar to those of acetylene. The addition reactions of propyne also obey Markovnikov's rule:

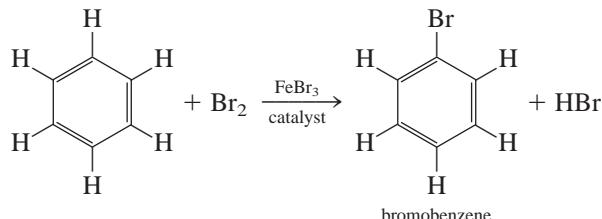


# Reactions of Aromatic Hydrocarbons

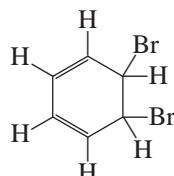
Benzene is a colorless, flammable liquid (b.p. 80.1°C) obtained chiefly from petroleum and coal tar. Although it has the same empirical formula as acetylene ( $\text{CH}$ ) and a high degree of unsaturation, it is much less reactive than either ethylene or acetylene. The stability of benzene is due to electron delocalization. In fact, benzene can be hydrogenated, but only with difficulty. The following reaction is carried out at significantly higher temperatures and pressures than are needed for similar reactions of alkenes:



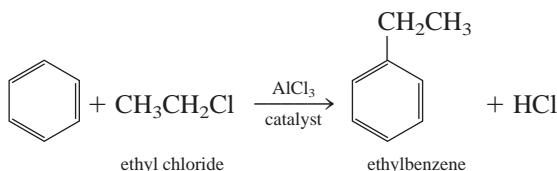
Recall that alkenes react readily with halogens to form addition products because the pi bond portion of the carbon-carbon double bond can be broken easily. The most common reaction of halogens with benzene is the ***substitution reaction***, in which *an atom or group of atoms replaces an atom or groups of atoms in another molecule*. For example,



If this were an addition reaction, the electron delocalization of the benzene ring would be destroyed in the product and the molecule would lack the stability characteristic of aromatic compounds.



Alkyl groups can be introduced onto the ring system by reacting benzene with an alkyl halide in the presence of a Lewis acid catalyst, such as AlCl<sub>3</sub>:



## 16.3 The Structure and Properties of Organic Compounds Are Greatly Influenced by the Presence of Functional Groups

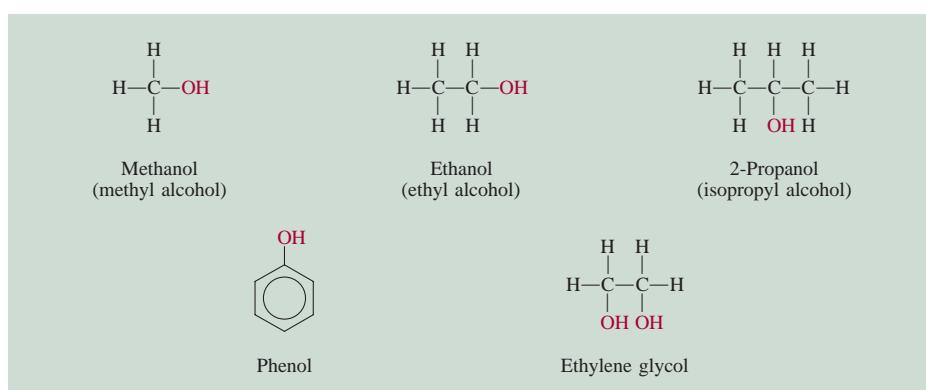
Organic functional groups are responsible for most of the reactions of the parent compounds. In this section, we focus on oxygen-containing functional groups (alcohols, ethers, aldehydes, ketones, carboxylic acids, and esters) and nitrogen-containing functional groups (amines).

## Alcohols

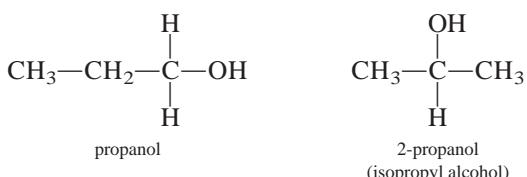
All **alcohols** contain the hydroxyl functional group,  $-OH$ . Some common alcohols are shown in Figure 16.9. Like hydrocarbons, alcohols are named according to the number of carbon atoms in the longest continuous chain containing the hydroxy group.

The prefixes from Table 16.1 are used, combined with the suffix *-ol*. Thus, the simplest alcohol is methanol (methyl alcohol, CH<sub>3</sub>OH). If the —OH group is not on the terminal carbon, then a numerical prefix is used to indicate the specific carbon to which the hydroxyl group is attached. The parent chain is numbered so as to give the carbon with the hydroxyl group the lowest possible number. For example, there are

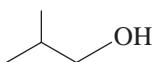
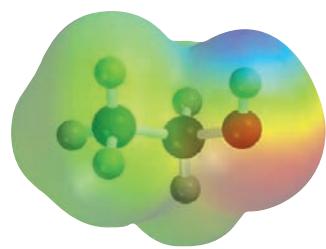
**Figure 16.9** Common alcohols. All of them contain the  $\text{—OH}$  group. The properties of phenol are quite different from those of aliphatic alcohols.



two isomers of the alcohol  $C_3H_7OH$ : 1-propanol (or just propanol) and 2-propanol (also called isopropyl alcohol):



Alcohols containing substituents are named in a similar manner as for hydrocarbons. For example, the molecule



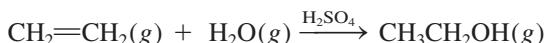
is called 2-methylpropanol

Ethanol (ethyl alcohol,  $C_2H_5OH$ ) is by far the best-known alcohol. It is produced biologically by the fermentation of sugar or starch. In the absence of oxygen, the enzymes present in bacterial cultures or yeast catalyze the reaction

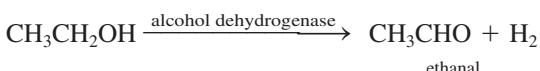


This process gives off energy, which microorganisms, in turn, use for growth and other functions.

Commercially, ethanol is prepared by an addition reaction in which water is combined with ethene at about 280°C and 300 bar



Ethanol has countless applications as a solvent for organic chemicals and as a starting compound for the manufacture of dyes, synthetic drugs, cosmetics, and explosives. It is also a constituent of alcoholic beverages. Ethanol is the only nontoxic (more properly, the least toxic) of the straight-chain alcohols; our bodies produce an enzyme, called *alcohol dehydrogenase*, that helps metabolize ethanol by oxidizing it to ethanal (acetaldehyde):

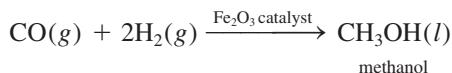


This equation is a simplified version of what actually takes place; in your body the H atoms are taken up by other molecules, so that no H<sub>2</sub> gas is evolved.

Ethanol can also be oxidized by inorganic oxidizing agents, such as acidified dichromate, to ethanal (acetaldehyde) and then to ethanoic acid (acetic acid):

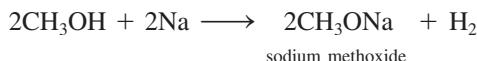


Ethanol is called an aliphatic alcohol because it is derived from an alkane (ethane). The simplest aliphatic alcohol is methanol ( $\text{CH}_3\text{OH}$ ). Methanol is sometimes called *wood alcohol* because it was prepared at one time by the dry distillation of wood. It is now synthesized industrially by the reaction of carbon monoxide and molecular hydrogen at high temperatures and pressures:



Methanol is highly toxic. Ingestion of only a few milliliters can cause nausea and blindness. Ethanol intended for industrial use is often mixed with methanol to prevent people from drinking it. Ethanol containing methanol or other toxic substances is called *denatured alcohol*.

Alcohols are very weakly acidic, but they do not react with strong bases, such as NaOH. The alkali metals react with alcohols to produce hydrogen:



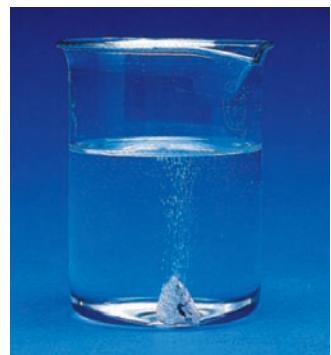
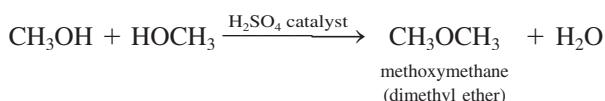
Although the reaction is vigorous, it is much less violent than the analogous reaction between Na and water:



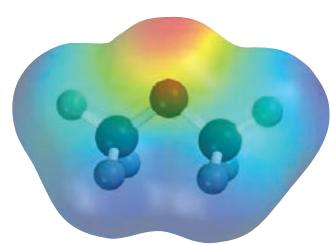
Two other aliphatic alcohols used in everyday products are 2-propanol (isopropyl alcohol), commonly known as rubbing alcohol, and, ethylene glycol (see Figure 16.9), which is used in commercial automobile antifreeze.<sup>3</sup> Ethylene glycol has two —OH groups and so can form hydrogen bonds with water more effectively than compounds that have only a single —OH group. Most alcohols—especially those with low molar masses—are highly flammable.

## Ethers

**Ethers** have the general structure  $R—O—R'$ , where  $R$  and  $R'$  are a hydrocarbon (aliphatic or aromatic) group. To name an ether, we chose the hydrocarbon group ( $R$  or  $R'$ ) with the longest carbon chain as the parent group and then treat the remaining  $R—O—$  group as a substituent on the parent hydrocarbon using the suffix *-oxy*. Thus, the ether  $CH_3—O—CH_2CH_3$  is called methoxyethane. Ethers can be formed by the reaction between two alcohols in the presence of a strong acid catalyst (such as  $H_2SO_4$ ):



Alcohols react more slowly with sodium metal than does water.



CH<sub>3</sub>OCH<sub>3</sub>

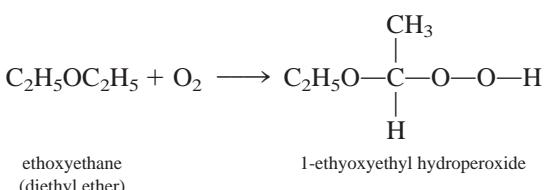
3. Some commercial automobile antifreeze products use propylene glycol ( $C_3H_8O_2$ ) instead of ethylene glycol, because of its lower toxicity (especially in pets).

Ethoxyethane (diethyl ether) is prepared on an industrial scale by heating ethanol with sulfuric acid at 140°C

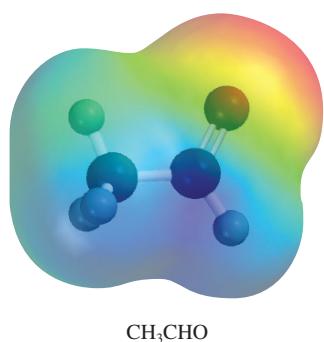


The formation of ethers is an example of a **condensation reaction**, in which *two molecules are joined together and a small molecule, usually water, is eliminated*.

Like alcohols, ethers are extremely flammable. When left standing in air, they have a tendency to slowly form explosive peroxides:

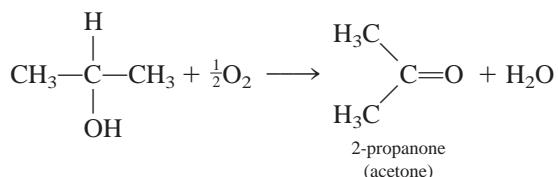
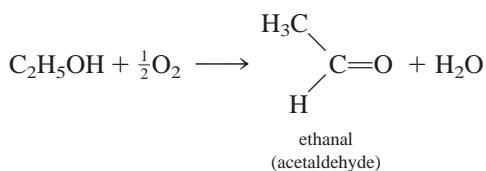
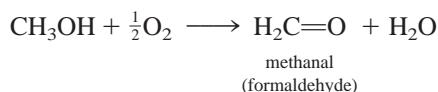


Peroxides contain the —O—O— linkage. The simplest peroxide is hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). Ethoxyethane ( $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ ), commonly known as diethyl ether (or just “ether”), was used as an anesthetic for many years. It produces unconsciousness by depressing the activity of the central nervous system. The major disadvantages of diethyl ether are its irritating effects on the respiratory system and the occurrence of postanesthetic nausea and vomiting. “Neothyl,” or methoxypropane (methyl propyl ether,  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$ ), is currently favored as an anesthetic because it is relatively free of side effects.



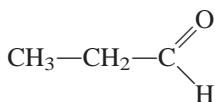
## Aldehydes and Ketones

Under mild oxidation conditions, it is possible to convert alcohols to aldehydes and ketones:

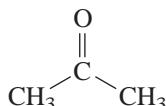


The functional group in these compounds is the *carbonyl group*,  $\text{C}=\text{O}$ . In an *aldehyde*, at least one hydrogen atom is bonded to the carbon in the carbonyl group. In a *ketone*, the carbon atom in the carbonyl group is bonded to two hydrocarbon groups. The official naming conventions for aldehydes and ketones are similar to those

for alcohols, except that aldehydes carry the suffix *-al* and ketones have the suffix *-one*. For example, the compound



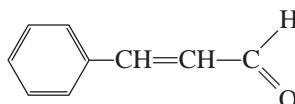
is an aldehyde with three carbons and is called *propanal*. Similarly, the molecule



is a three-carbon ketone with the name 2-propanone (acetone). In an aldehyde, the carbon atom of the carbonyl group is always number 1. In a ketone, though, the carbon chain is numbered so as to give the carbonyl carbon the lowest possible number.

The simplest aldehyde, methanal (formaldehyde,  $\text{H}_2\text{C}=\text{O}$ ) has a tendency to *polymerize*, that is, the individual molecules join together to form a compound of high molar mass. This reaction gives off tremendous amounts of heat and is often explosive, so methanal is usually prepared and stored in aqueous solution (to reduce the concentration). This rather disagreeable-smelling liquid is used as a starting material in the polymer industry (see Section 16.4) and in the laboratory as a preservative for animal specimens. Interestingly, the higher molar mass aldehydes, such as cinnamic aldehyde,

Cinnamic aldehyde gives cinnamon its characteristic aroma.

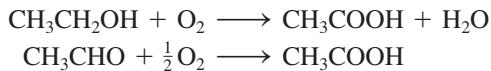


have a pleasant odor and are used in the manufacture of perfumes.

Ketones generally are less reactive than aldehydes. The simplest ketone is 2-propanone (acetone), a volatile liquid that is used mainly as a solvent for organic compounds and nail polish remover.

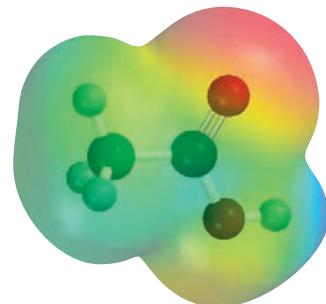
## Carboxylic Acids

Under appropriate conditions, both alcohols and aldehydes can be oxidized to **carboxylic acids**, acids that contain the carboxyl group,  $-\text{COOH}$ . For example, ethanol and ethanal can be oxidized to form ethanoic acid (acetic acid,  $\text{CH}_3\text{COOH}$ ):



These reactions occur so readily, in fact, that wine must be protected from atmospheric oxygen while in storage. Otherwise, it would soon turn to vinegar as a result of the formation of acetic acid. Figure 16.10 shows the structure of some of the common carboxylic acids. The IUPAC names for carboxylic acids are formed by adding the suffix *-oic acid* to the parent hydrocarbon. The parent hydrocarbon includes the carboxyl carbon, so the compounds  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$  are ethanoic acid (acetic acid) and butanoic acid (butyric acid), respectively.

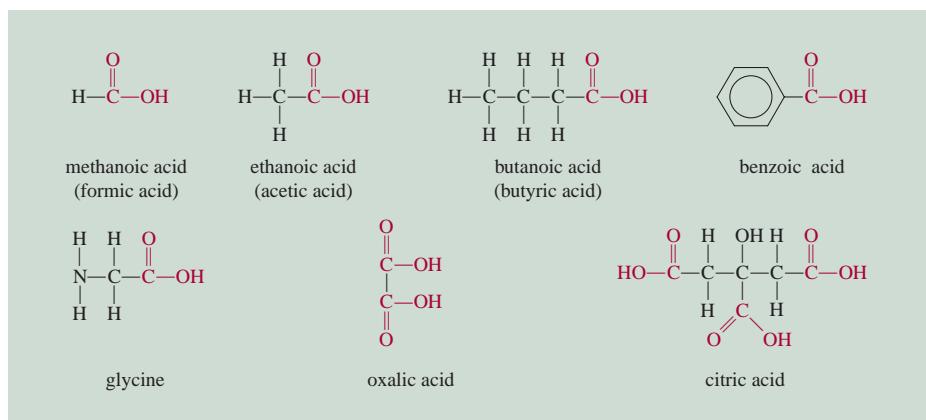
Carboxylic acids are widely distributed in nature; they are found in both the plant and animal kingdoms. All protein molecules are made of amino acids, a special kind of carboxylic acid containing an amino group ( $-\text{NH}_2$ ) and a carboxyl group ( $-\text{COOH}$ ).



$\text{CH}_3\text{COOH}$

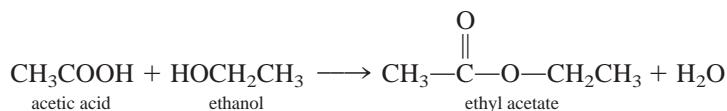
The oxidation of ethanol to acetic acid in wine is catalyzed to enzymes.

**Figure 16.10** Some common carboxylic acids. They all contain the  $\text{—COOH}$  group. (Glycine is one of the amino acids found in proteins.)



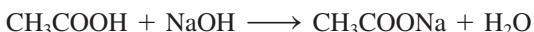
This is a condensation reaction.

Unlike the inorganic acids HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>, carboxylic acids are usually weak acids. They react with alcohols to form pleasant-smelling esters in a process called *esterification*:

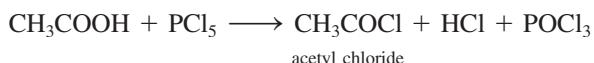


Esterification reactions are condensation reactions because two reactants (in this case, an alcohol and a carboxylic acid) are joined together and a small molecule (water) is eliminated.

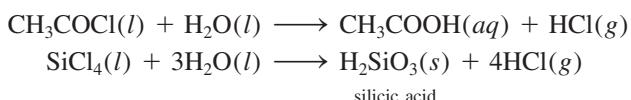
Other common reactions of carboxylic acids include neutralization



and the formation of acid halides, such as acetyl chloride,

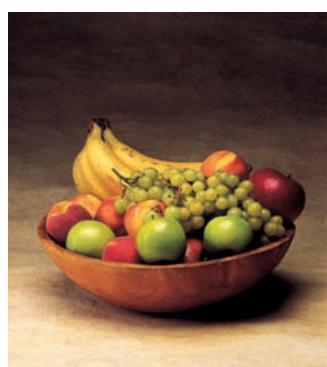


Acid halides are reactive compounds used as intermediates in the preparation of many other organic compounds. They hydrolyze in much the same way as many nonmetallic halides, such as  $\text{SiCl}_4$ :



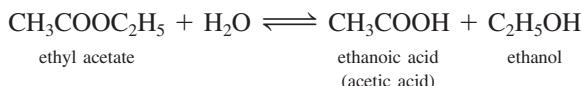
## Esters

**Esters** have the general formula  $R'COOR$ , where  $R'$  can be H or a hydrocarbon group and  $R$  is a hydrocarbon group. Esters are used in the manufacture of perfumes and as flavoring agents in the confectionery and soft-drink industries. Many fruits owe their characteristic smell and flavor to the presence of small quantities of esters. For example, bananas contain 3-methylbutyl acetate [ $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$ ], oranges contain octyl acetate ( $\text{CH}_3\text{COOC}_8\text{H}_{17}$ ), and apples contain methyl butyrate ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_3$ ). As mentioned previously, esters are formed through the esterification (condensation reaction) of a carboxylic acid with an alcohol.

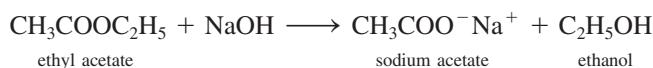


The odor of fruits is mainly due to the ester compounds in them.

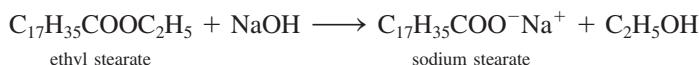
The functional group in esters is the  $\text{—COOR}$  group. In the presence of an acid catalyst, such as HCl, esters hydrolyze to yield a carboxylic acid and an alcohol (the opposite of esterification). For example, in an acid solution, ethyl acetate hydrolyzes to ethanoic acid (acetic acid) and ethanol:



The hydrolysis of an ester does not go to completion, however, because the reverse reaction, that is, the formation of an ester from an alcohol and an acid, also occurs to an appreciable extent. When an ester is hydrolyzed in basic solution (such as aqueous NaOH), on the other hand, the reaction does go to completion from left to right because the sodium acetate that is formed does not react with ethanol:



As a result, ester hydrolysis is usually carried out in basic solutions. Note that NaOH is a reactant in this reaction and not a catalyst because NaOH is consumed (not regenerated) in the reaction. The term **saponification** (meaning *soap making*) was originally used to describe the alkaline hydrolysis of fatty acid esters to yield soap molecules (sodium stearate):



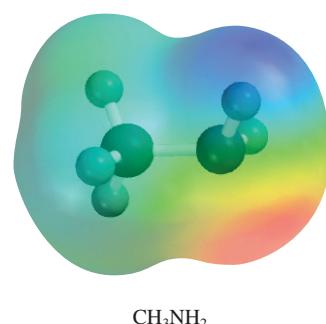
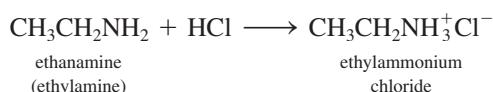
Saponification has now become *a general term for alkaline hydrolysis of any type of ester.*

## Amines

**Amines** are organic bases with the general formula  $R_3N$ , where R may be H or a hydrocarbon group. As with ammonia, the reaction of amines with water is

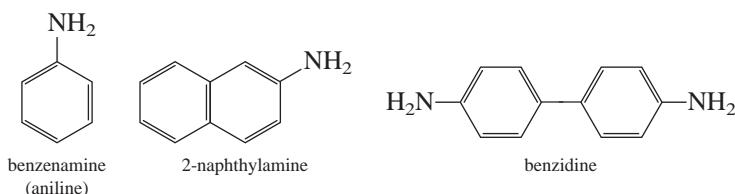


where R represents a hydrocarbon group. Like all bases, amines form salts when they react with acids:



These salts are usually colorless, odorless solids.

Aromatic amines are used mainly in the manufacture of dyes. Benzenamine (aniline), the simplest aromatic amine, is a toxic compound; a number of other aromatic amines such as 2-naphthylamine and benzidine are potent carcinogens:

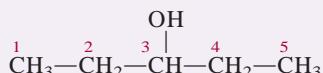


### Example 16.4

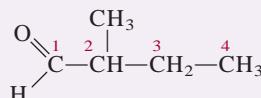
Draw structures for the following organic compounds: (a) 3-pentanol (b) 2-methylbutanal, (c) 1,2-dimethoxyethane, and (d) 2,2-dimethylpropanoic acid.

**Strategy** Find the longest carbon chain containing the functional group and use the naming rules discussed previously.

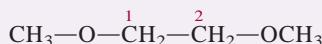
**Solution** (a) The suffix *-ol* indicates that the compound is an alcohol and the prefix *pentan-* indicates that the parent hydrocarbon is pentane. The numerical prefix (3-) tells us that the —OH group is attached to the third carbon in the pentane chain, so the structure is



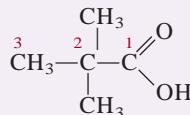
(b) The suffix *-al* means that the compound is an aldehyde, so it has a carbonyl ( $\text{—C=O}$ ) group attached to a terminal carbon of the parent hydrocarbon chain. The parent chain is four carbons long because the prefix is *butan-*. Additionally, a methyl group is attached to the second carbon of the parent (the carbon adjacent to the carbonyl carbon because the carbonyl carbon is always the first carbon in an aldehyde):



(c) This compound is an ether and the parent hydrocarbon chain is ethane. The *dimethoxy-* prefix indicates that there are two methoxy groups ( $\text{CH}_3\text{—O—}$ ) groups attached to the parent ethane at the first and second carbon positions:



(d) This compound is a carboxylic acid and the longest chain (including the carboxyl carbon) consists of three carbons (*propan-*). Attached to this chain at the second carbon position (the carbon adjacent to the carboxyl carbon) are two methyl groups, giving a structure of



The common name for this compound is *pivalic acid*.

**Practice Exercise** Write structural formulas for the following compounds: (a) 1,3-dibromo-2-pentanol, (b) 2-methoxy-3-methylpentane, (c) 2-methyl-3-pentanone, and (d) 3-phenyl-pentanoic acid.

### Summary of Functional Groups

Table 16.4 summarizes the common functional groups, including the  $\text{C}=\text{C}$  and  $\text{C}\equiv\text{C}$  groups. Organic compounds commonly contain more than one functional group. Generally, the reactivity of a compound is determined by the number and types of functional groups it contains.

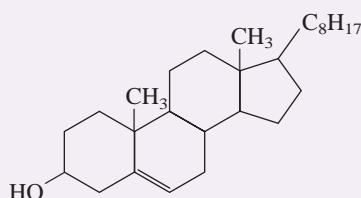
Example 16.5 shows how we can use the functional groups to predict reactions.

**Table 16.4** Important Functional Groups and Their Reactions

Functional Group	Name	Typical Reactions
$\begin{array}{c} \diagup \\ \diagdown \end{array} \text{C=C} \begin{array}{c} \diagdown \\ \diagup \end{array}$	Carbon-carbon double bond	Addition reactions with halogens, hydrogen halides, and water; hydrogenation to yield alkanes
$-\text{C}\equiv\text{C}-$	Carbon-carbon triple bond	Addition reactions with halogens, hydrogen halides; hydrogenation to yield alkenes and alkanes
$\begin{array}{c} \cdot\cdot \\ -\text{X}: \\ (\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}) \end{array}$	Halogen	Exchange reactions: $\text{CH}_3\text{CH}_2\text{Br} + \text{KI} \longrightarrow \text{CH}_3\text{CH}_2\text{I} + \text{KBr}$
$\begin{array}{c} \cdot\cdot \\ -\ddot{\text{O}}-\text{H} \end{array}$	Hydroxyl	Esterification (formation of an ester) with carboxylic acids; oxidation to aldehydes, ketones, and carboxylic acids
$\begin{array}{c} \diagup \\ \diagdown \end{array} \text{C=}\begin{array}{c} \cdot\cdot \\ \text{O} \end{array}$	Carbonyl	Reduction to yield alcohols; oxidation of aldehydes to yield carboxylic acids
$\begin{array}{c} :\text{O}: \\ \parallel \\ -\text{C}-\begin{array}{c} \cdot\cdot \\ \text{O}-\text{H} \end{array} \end{array}$	Carboxyl	Esterification with alcohols; reaction with phosphorus pentachloride to yield acid chlorides
$\begin{array}{c} :\text{O}: \\ \parallel \\ -\text{C}-\begin{array}{c} \cdot\cdot \\ \text{O}-\text{R} \end{array} \\ (\text{R} = \text{hydrocarbon}) \end{array}$	Ester	Hydrolysis to yield acids and alcohols
$\begin{array}{c} \cdot\cdot \\ \diagup \\ \diagdown \\ -\text{N}-\text{R} \\ \diagdown \\ \diagup \\ \text{R} \\ (\text{R} = \text{H or hydrocarbon}) \end{array}$	Amine	Formation of ammonium salts with acids

**Example 16.5**

Cholesterol is a major component of gallstones, and it is believed that the cholesterol level in the blood is a contributing factor in certain types of heart disease. From the following structure of the compound, predict its reaction with (a)  $\text{Br}_2$ , (b)  $\text{H}_2$  (in the presence of a Pt catalyst), and (c)  $\text{CH}_3\text{COOH}$ .



An artery becoming blocked by cholesterol.

**Strategy** To predict the type of reactions a molecule may undergo, we must first identify the functional groups present (see Table 16.4).

—Continued

## Important Experimental Technique: Nuclear Magnetic Resonance Spectroscopy

There are a number of experimental techniques that are useful in the identification and characterization of organic compounds. Two techniques, mass spectrometry and IR spectroscopy, were discussed in Chapters 0 and 4, respectively. Here, we will discuss another important technique, **nuclear magnetic resonance (NMR) spectroscopy**.

Like electrons (Section 1.4), the nucleus of an atom has an intrinsic spin and a corresponding magnetic moment. Unlike electrons, which have a total spin of  $1/2$  (with possible orientations of  $+1/2$  and  $-1/2$ ), the total spin ( $I$ ) of a nucleus can take on both integer and half-integer values:

$$I = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots$$

The value of  $I$  depends upon the number of protons (atomic number) and neutrons present in the nucleus:

- ▶ If an even number of both protons and neutrons are present (for example, carbon-12) the nucleus will have zero spin ( $I = 0$ ).
- ▶ If the number of protons is odd and the number of neutrons is even (or vice versa), the nucleus will have half-integer spin (for example, carbon-13 with  $I = 1/2$ ).
- ▶ If both protons and neutrons are present in odd numbers, the nuclear spin will be a positive integer (for example, nitrogen-14 has  $I = 1$ ).

A nucleus with a total spin  $I$  possesses  $(2I + 1)$  possible spin orientations, each denoted by a different value of the nuclear spin quantum number,  $m_I$ , which can take on any value in the set  $\{-I, -I + 1, \dots, I - 1, I\}$ . In the absence of a magnetic field, these  $2I + 1$  spin orientation states corresponding to a nucleus of spin  $I$  are degenerate, that is, they are equal in energy. In the presence of an external magnetic field of strength  $B_0$ , this degeneracy is lifted and the nuclear spin energy ( $E_I$ ) is proportional to the value of  $m_I$ :

$$E_I = -m_I B_0 \gamma \hbar \quad (1)$$

where  $\gamma$  is called the *gyromagnetic ratio* and  $\hbar = h/(2\pi)$ .

The proton ( $^1\text{H}$ ), for example, has a nuclear spin  $I = 1/2$ , with two possible orientations:  $m_I = +1/2$  or  $m_I = -1/2$ . In the presence of a magnetic field of strength  $B_0$ , the difference in energy ( $\Delta E$ ) between the two spin states ( $+1/2$  and  $-1/2$ ) is

$$\Delta E = E_{-1/2} - E_{1/2} = -B_0 \left[ \left( -\frac{1}{2} \right) - \left( +\frac{1}{2} \right) \right] \gamma \hbar = \gamma B_0 \hbar$$

A transition from the  $m_I = +\frac{1}{2}$  level to the  $m_I = -\frac{1}{2}$  level (called a NMR) can be induced by electromagnetic radiation with a frequency corresponding to the energy gap:

$$\nu = \Delta E / h = \frac{\gamma B_0}{2\pi} \quad (2)$$

This resonance frequency is called the *Larmor frequency*. In nuclear magnetic resonance spectroscopy, the resonance is determined either by varying the radiation frequency (typically in the radio wave region) or by varying the applied magnetic field strength.

The strength of the magnetic field is measured in *tesla*<sup>4</sup> (T), after the Greek engineer and inventor Nikola Tesla.<sup>4</sup> Another common unit is the *gauss* ( $10^4$  gauss = 1 T). The gyromagnetic ratio has units of  $\text{T}^{-1} \text{s}^{-1}$  and will vary depending on the nucleus type. The most common isotopes used in NMR spectroscopy are  $^1\text{H}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ , and  $^{13}\text{C}$ . The most abundant isotope of carbon,  $^{12}\text{C}$ , cannot be studied with NMR because it has a nuclear spin of zero.)

### NMR Spectra of Organic Molecules

The usefulness of NMR in organic chemistry arises from the fact that the resonance frequency of a given nucleus is affected by its local environment within the molecule; that is, nuclei with different environments will have slightly different resonance frequencies. Thus, the pattern of nuclear magnetic resonance frequencies observed (the NMR spectrum) will differ from compound to compound, which allows NMR to be used as a method for identifying and characterizing chemical substances. The shape of an NMR spectrum for a given compound is determined primarily by three effects: *chemical shift*, *spin-spin coupling*, and *kinetic exchange processes*.

4. Nikola Tesla (1856–1943) Serbian-American physicist, engineer and inventor. Tesla immigrated to the United States in 1884. He worked for a short time in the laboratory of Thomas Edison but soon left to devote himself full time to independent experimentation and invention. In 1888, he devised a method to produce and transmit alternating electric current. He is credited with a number of inventions including the Tesla coil, a type of transformer.



An NMR spectrometer. The instrument is surrounded by a insulated container of liquid nitrogen, which is used to cool the large electromagnets required to generate the magnetic field.

### Chemical Shift

The resonance frequency of a nucleus depends on the *local* magnetic field, which is a combination of the applied external field and the field due to neighboring nuclei and electrons. The difference between the actual resonance frequency and that predicted by Equation 2 is called the *chemical shift*. The figure below shows a low-resolution proton ( $^1\text{H}$ ) NMR spectrum of ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ). Three separate peaks are observed because there are three different types of H atoms in ethanol with respect to local environment: the hydroxyl hydrogen ( $-\text{OH}$ ), two methylene hydrogen atoms ( $-\text{CH}_2-$ ) and three methyl ( $-\text{CH}_3$ ) hydrogen atoms. The relative areas under the hydroxyl, methylene, and methyl hydrogen peaks have relative areas in the ratio 1:2:3, respectively, reflecting the relative number of hydrogen atoms of each type.

In practice the chemical shift of a nucleus is generally measured relative to the chemical shift for a standard reference nucleus. We define the chemical shift parameter ( $\delta$ ) as the relative difference in resonance frequencies between a nucleus of interest ( $\nu$ ) and that of a reference nucleus ( $\nu_{\text{ref}}$ )

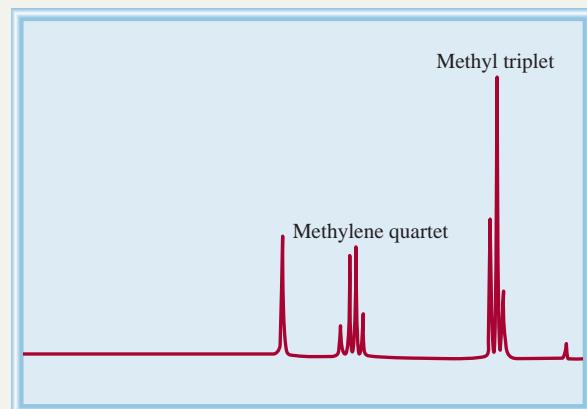
$$\delta = \frac{\nu - \nu_{\text{ref}}}{\nu_{\text{ref}}} \times 10^6 \quad (3)$$

Because of the factor of  $10^6$  present in Equation 3, chemical shifts are reported as parts per million (ppm). For proton ( $^1\text{H}$ ) NMR, the reference compound is usually tetramethylsilane (TMS),  $(\text{CH}_3)_4\text{Si}$ .

### Spin-Spin Coupling

By increasing the magnetic field strength, the resolution of an NMR spectrum can be improved. The high-resolution  $^1\text{H}$  spectrum of ethanol is shown.

In high-resolution, we see that the  $-\text{CH}_2-$  and  $-\text{CH}_3$  peaks in the low-resolution spectrum are made up of four and three peaks, respectively. Because the hydrogen atoms in each group are equivalent the splitting of the lines at high resolution is not due to chemical shift. Instead, the splitting is caused by an interaction between nuclear spins and nearby nonequivalent spins that is transmitted through the bonding electrons. This phenomenon is called *spin-spin coupling*. In



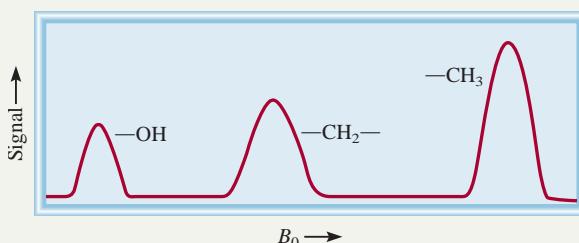
High-resolution NMR spectrum of ethanol.

the methylene group in ethanol, each nuclear spin has two possible orientations. The methyl peak is split into two peaks by interaction with the magnetic field generated by the first methylene proton. Interaction with the second methylene proton further splits these two peaks to give a total of four lines. Two of these peaks are coincident so only three peaks are observed—a pattern called a *triplet*. In a similar manner, spin-spin coupling with the methyl group splits the methylene peak into four separate peaks, called a *quartet*. When examining an unknown compound, the observed peak patterns (singlet, triplet, etc.) can be used to deduce the local bonding environment.

### Kinetic Exchange Processes

In ethanol, the hydroxyl peak should be split by spin-spin interaction with the methylene protons. However, the high-resolution NMR spectrum shows only a single hydroxyl peak. The lack of apparent spin-spin coupling in this peak is due to the fact that this spectrum was taken on a sample that contained a small amount of water. In the NMR spectrum of pure ethanol, the hydroxyl peak will be a triplet as we expect. However, if a small amount of water is present, a rapid proton-exchange reaction between the  $-\text{OH}$  proton in ethanol and  $\text{H}_3\text{O}^+$  in the water will occur that has the effect of broadening the three peaks in the  $-\text{OH}$  triplet so that they coalesce into a single observed peak.

If the rate of exchange in a proton-exchange reaction is slow, the split peaks will not completely coalesce, but would be broader and less distinct than in the absence of exchange. In such cases, the rate constant for the exchange can be determined. Therefore, NMR spectroscopy can be used as a tool to study the kinetics of proton-exchange reactions and of many other processes such as the rotation about a chemical bond and diffusion.



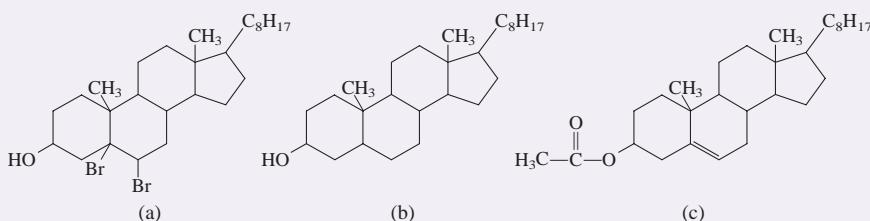
The low-resolution proton NMR spectrum of ethanol

*Continued—*

**Solution** Despite a relatively complex structure, there are only two functional groups in cholesterol: the hydroxyl group and the carbon-carbon double bond.

- (a) The reaction with bromine results in the addition of bromine to the double-bonded carbons, which become single-bonded.
  - (b) This is a hydrogenation reaction. Again, the carbon-carbon double bond is converted to a carbon-carbon single bond.
  - (c) The acid reacts with the hydroxyl group to form an ester and water (esterification, a type of condensation reaction).

The products formed in (a), (b), and (c) are



**Practice Exercise** Predict the products of the following reaction:



**16.4 Polymers Are Very Large Molecular Weight Compounds Formed from the Joining Together of Many Subunits Called Monomers**

A ***polymer*** is a molecular compound with a high molar mass, ranging into thousands and millions of grams, and made up of many repeating units called ***monomers***. The word *polymer* is a combination of the Greek prefix *poly-*, meaning “many,” and the Greek suffix *-mer*, meaning “parts.” The physical properties of these so-called ***macromolecules*** differ greatly from those of small molecules, and special techniques are required to study them.

Naturally occurring polymers include proteins, nucleic acids, cellulose (polysaccharides), and rubber (polyisoprene). Most synthetic polymers are organic compounds. Familiar examples are nylon, poly(hexamethylene adipamide); Dacron, poly(ethylene terephthalate); and Lucite or Plexiglas, poly(methyl methacrylate).

The development of polymer chemistry began in the 1920s with the investigation into some unusual properties of certain materials, including wood, gelatin, cotton, and rubber. Rubber, for example, had a known empirical formula of  $C_5H_8$ , but it exhibited high viscosity, low osmotic pressure, and negligible freezing-point depression when it was dissolved in an organic solvent. These observations strongly suggested the presence of solutes of very high molar mass. Chemists at that time, however, were not ready to accept the idea that such giant molecules could exist. Instead, they postulated that materials such as rubber consisted of aggregates of small molecular units, like  $C_5H_8$  or  $C_{10}H_{16}$ , held together by intermolecular forces. This misconception

persisted until Hermann Staudinger<sup>5</sup> clearly showed that these so-called aggregates were, in fact, enormously large molecules, each of which contained many thousands of atoms held together by covalent bonds.

Once the structures of these macromolecules were understood, the way was open for manufacturing polymers, which now pervade almost every aspect of our daily lives. About 90 percent of today's chemists, including biochemists, work with polymers.

Because of their size, we might expect molecules containing thousands of carbon and hydrogen atoms to form an enormous number of structural and geometric isomers (if C=C bonds are present). Polymers, however, are made up of *monomers*, simple repeating units, and this composition severely restricts the number of possible isomers. Synthetic polymers are created by joining monomers together, one at a time, by means of addition reactions and condensation reactions.

## Addition Reactions

**Addition reactions** involve the addition of atoms to compounds containing double or triple bonds, particularly C=C and C≡C. Examples include hydrogenation and the reactions of hydrogen halides and halogens with alkenes and alkynes.

Polyethylene, a very stable polymer used in packaging wraps, is made by joining ethylene monomers via an addition-reaction mechanism. First an *initiator* molecule ( $R_2$ ) is heated to produce two radicals:



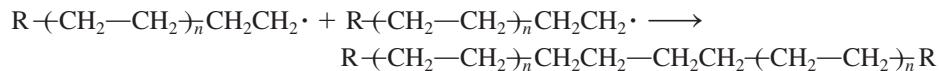
The reactive radical attacks an ethylene molecule to generate a new radical:



which further reacts with another ethylene molecule, and so on:



Very quickly a long chain of CH<sub>2</sub> groups is built. Eventually, this process is terminated by the combination of two long-chain radicals to give the polymer called polyethylene:



where  $\overset{\circ}{(CH_2-CH_2)_n}$  is a convenient shorthand convention for representing the repeating unit in the polymer. The value of  $n$  is understood to be very large (on the order of hundreds).

The individual chains of polyethylene pack together well, giving it distinctive crystalline properties (Figure 16.11). Polyethylene is mainly used in films in frozen food packaging and other product wrappings. A specially treated type of polyethylene called Tyvek is used for home insulation.

5. Hermann Staudinger (1881–1963). German chemist. One of the pioneers in polymer chemistry. Staudinger was awarded the Nobel Prize in Chemistry in 1953.

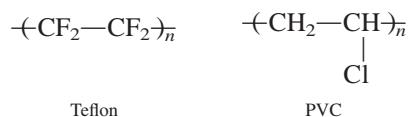


**Figure 16.11** The structure of polyethylene. Each carbon atom is  $sp^3$ -hybridized.

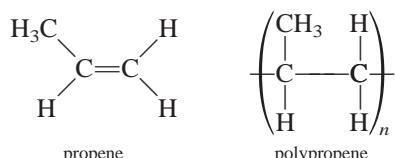


**Figure 16.12** A cooking utensil coated with Silverstone, which contains polytetrafluoroethylene (Teflon).

Polyethylene is a **homopolymer** because it is a polymer made up of only one type of monomer. Other homopolymers that are synthesized by a radical mechanism are polytetrafluoroethylene (Teflon; Figure 16.12) and poly(vinyl chloride) (PVC):



The chemistry of polymers is more complex if the monomers are asymmetric:



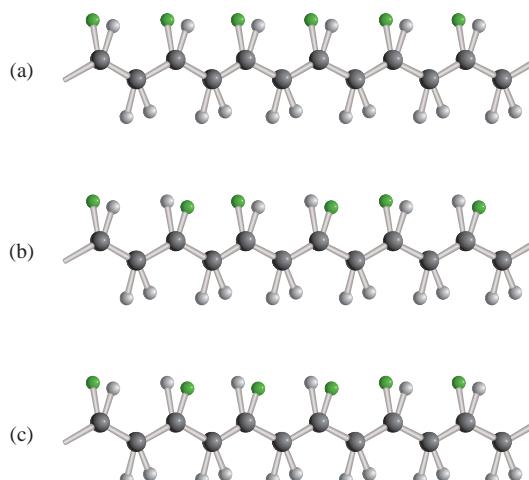
Several stereoisomers can result from an addition reaction of propylenes (Figure 16.13). If the additions occur randomly, *atactic* polypropylenes form, which do not pack together well. These polymers are rubbery, amorphous, and relatively weak. Two other possibilities are an *isotactic* structure, in which the R groups are all on the same side of the asymmetric carbon atoms, and a *syndiotactic* form, in which the R groups alternate to the left and right of the asymmetric carbons. Of these, the isotactic isomer has the highest melting point and greatest crystallinity and is endowed with superior mechanical properties.

A major problem that the polymer industry faced in the beginning was how to selectively synthesize either the isotactic or syndiotactic polymer without having it contaminated by other products. Giulio Natta<sup>6</sup> and Karl Ziegler<sup>7</sup> discovered, however, that certain catalysts, including triethylaluminum [Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>] and titanium trichloride (TiCl<sub>3</sub>), could promote the formation of specific isomers only. Using Natta-Ziegler catalysts, chemists have been able to design polymers to suit almost any purpose.

6. Giulio Natta (1903–1979). Italian chemist. Natta received the Nobel Prize in Chemistry in 1963 for discovering stereospecific catalysts for polymer synthesis.

7. Karl Ziegler (1898–1976). German chemist. Ziegler shared the Nobel Prize in Chemistry in 1963 with Natta for his work in polymer synthesis.

**Figure 16.13** Stereoisomers of polymers. When the R group (green sphere) is CH<sub>3</sub>, the polymer is polypropylene. (a) When the R groups are all on one side of the chain, the polymer is isotactic. (b) When the R groups alternate from side to side, the polymer is syndiotactic. (c) When the R groups are disposed at random, the polymer is atactic.

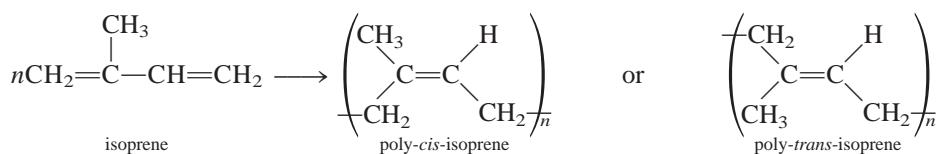




**Figure 16.14** Latex (an aqueous suspension of rubber particles) being collected from a rubber tree.

### Rubber

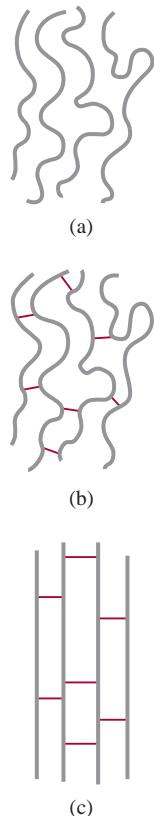
Rubber is probably the best-known organic polymer and the only true hydrocarbon polymer found in nature. It is formed by the radical addition of the monomer isoprene. Actually, polymerization can result in poly-*cis*-isoprene, poly-*trans*-isoprene, or a mixture of both, depending on reaction conditions:



Note that in the *cis* isomer, the two CH<sub>2</sub> groups are on the same side of the C=C bond, whereas the same groups are across from each other in the *trans* isomer. Natural rubber is poly-*cis*-isoprene, which is extracted from the tree *Hevea brasiliensis* (Figure 16.14).

An unusual and very useful property of rubber is its elasticity. Rubber will stretch up to 10 times its length and, if released, will return to its original size. In contrast, a piece of copper wire can be stretched only a small percentage of its length and still return to its original size. Unstretched rubber has no regular X-ray diffraction pattern and is therefore amorphous. Stretched rubber, however, possesses a fair amount of crystallinity and order. The elasticity of rubber is due to the flexibility of each individual long-chain molecule. In the bulk state, however, where rubber is a tangle of polymeric chains, a strong external force can make individual chains slip past one another instead of stretch, thereby causing the rubber to lose most of its elasticity. In 1839, Charles Goodyear<sup>8</sup> discovered that natural rubber could be cross-linked with sulfur (using zinc oxide as the catalyst) to prevent chain slippage (Figure 16.15). His process, known as *vulcanization*, paved the way for many practical and commercial uses of rubber, such as in automobile tires and dentures.

8. Charles Goodyear (1800–1860). American chemist. Goodyear was the first person to realize the potential of natural rubber. His vulcanization process made rubber usable in countless ways and opened the way for the development of the automobile industry.

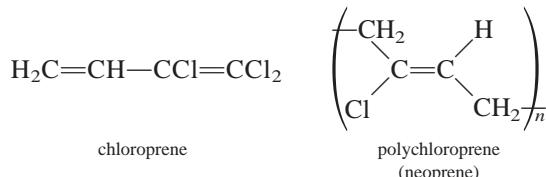


**Figure 16.15** Rubber molecules ordinarily are bent and convoluted. Parts (a) and (b) represent the long chains before and after vulcanization, respectively; (c) shows the alignment of molecules when stretched. Without vulcanization these molecules would slip past one another, and rubber would lose its elastic properties.

**Table 16.5** Some Monomers and Their Common Synthetic Polymers

Monomer		Polymer	
Formula	Name	Name and Formula	Uses
$\text{H}_2\text{C}=\text{CH}_2$	Ethylene	Polyethylene $(-\text{CH}_2-\text{CH}_2)_n$	Plastic piping, bottles, electrical insulation, toys
$\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{C}=\text{C} \\   \\ \text{CH}_3 \end{array}$	Propene	Polyethylene $\left(\begin{array}{c} \text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2 \\   \\ \text{CH}_3 \quad \text{CH}_3 \end{array}\right)_n$	Packaging film, carpets, crates for soft-drink bottles, lab wares, toys
$\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{C}=\text{C} \\   \\ \text{Cl} \\   \\ \text{H} \\   \\ \text{H}_2\text{C}=\text{C} \\   \\ \text{CN} \end{array}$	Vinyl chloride	Poly(vinyl chloride) (PVC) $(-\text{CH}_2-\text{CH}-)_n$   Cl	Piping, siding, gutters, floor tile, clothing, toys
$\text{H}_2\text{C}=\text{C}$	Acrylonitrile	Polyacrylonitrile (PAN) $\left(\begin{array}{c} \text{CH}_2-\text{CH} \\   \\ \text{CN} \end{array}\right)_n$	Carpets, knitwear
$\text{F}_2\text{C}=\text{CF}_2$	Tetrafluoroethylene	Polytetrafluoroethylene (Teflon) $(-\text{CF}_2-\text{CF}_2)_n$	Coating on cooking utensils, electrical insulation, bearings
$\begin{array}{c} \text{COOCH}_3 \\   \\ \text{H}_2\text{C}=\text{C} \\   \\ \text{CH}_3 \end{array}$	Methyl methacrylate	Poly(methyl methacrylate) (Plexiglas) $(-\text{CH}_2-\overset{\text{COOCH}_3}{\underset{\text{CH}_3}{\text{C}}})_n$	Optical equipment, home furnishings
$\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{C}=\text{C} \\   \\ \text{C}_6\text{H}_5 \end{array}$	Styrene	Polystyrene $(-\text{CH}_2-\text{CH}-)_n$ $\text{C}_6\text{H}_5$	Containers, thermal insulation (ice buckets, water coolers), toys
$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}_2\text{C}=\text{C}-\text{C}=\text{CH}_2 \end{array}$	Butadiene	Polybutadiene $(-\text{CH}_2\text{CH}=\text{CHCH}_2)_n$	Tire tread, coating resin
See above structures	Butadiene and styrene	Styrene-butadiene rubber (SBR) $(-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2)_n$ $\text{C}_6\text{H}_5$	Synthetic rubber

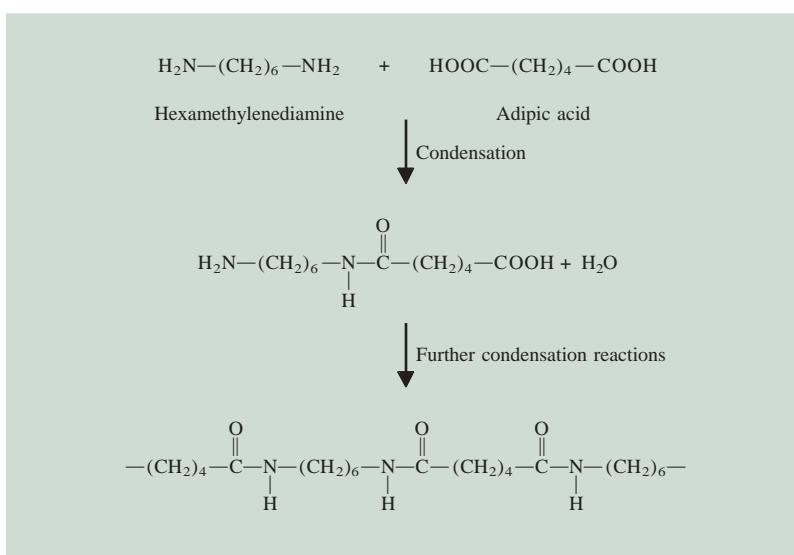
During World War II, a shortage of natural rubber in the United States prompted an intensive program to produce synthetic rubber. Most synthetic rubbers (called *elastomers*) are made from petroleum products such as ethylene, propylene, and butadiene. For example, chloroprene molecules polymerize readily to form polychloroprene, commonly known as *neoprene*, which has properties that are comparable or even superior to those of natural rubber:



Another important synthetic rubber is formed by the addition of butadiene to styrene in a 3:1 ratio to give styrene-butadiene rubber (SBR). SBR is a *copolymer* because it is a *polymer containing two or more different monomers*. Table 16.5 lists some common homopolymers and one copolymer produced by addition reactions.

### Condensation Reactions

One of the best-known polymer condensation processes is the reaction between hexamethylenediamine and adipic acid, shown in Figure 16.16. The final product, called nylon-66 (because there are six carbon atoms each in hexamethylenediamine and adipic acid), was first made by Wallace Carothers<sup>9</sup> at Du Pont in 1931. The versatility of nylons is so great that the annual production of nylons and related substances now amounts to several billion pounds. Figure 16.17 shows how nylon-66 is prepared in the laboratory.



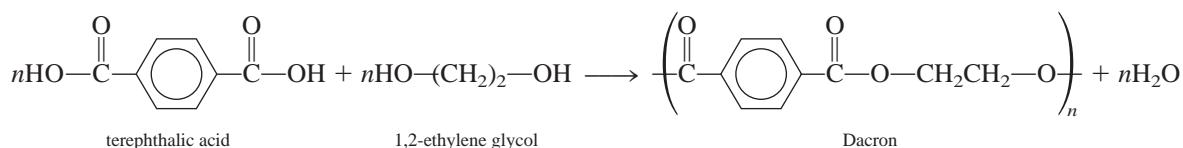
**Figure 16.16** The formation of nylon by the condensation reaction between hexamethylenediamine and adipic acid.

9. Wallace H. Carothers (1896–1937). American chemist. Besides its enormous commercial success, Carothers' work on nylon is ranked with that of Staudinger in clearly elucidating macromolecular structure and properties. Depressed by the death of his sister and convinced that his life's work was a failure, Carothers committed suicide at the age of 41.



**Figure 16.17** The nylon rope trick. Adding a solution of adipoyl chloride (an adipic acid derivative in which the OH groups have been replaced by Cl groups) in cyclohexane to an aqueous solution of hexamethylenediamine causes nylon to form at the interface of the two solutions, which do not mix. It can then be drawn off.

Condensation reactions are also used to manufacture Dacron (polyester).

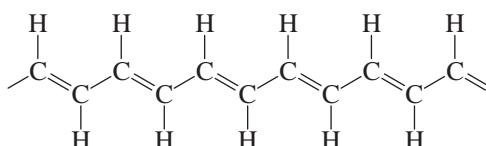


Polyesters are used in fibers, films, and plastic bottles.

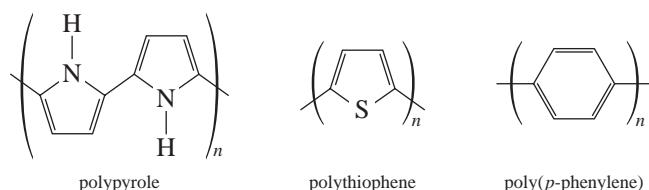
### Conducting Polymers

Recall from Chapter 6 that the conductivity in metals and semiconductors is due to electrons moving within the delocalized electron states of the conduction band. In contrast to metals and semiconductors, most organic compounds do not conduct electricity to any appreciable extent, that is, they are electrical insulators. **Conducting polymers**, however, are organic materials that exhibit significant electrical conduction. Although their conductivity is generally low relative to metals, such as aluminum and copper, conducting polymers have a number of properties (including low cost, low density, and flexibility) that give them significant potential for future technological use.

Electrical conduction in conducting polymers, like that in metals and semiconductors, occurs because some of the electrons in the material occupy a partially filled band of electron states called a *conduction band* (see Section 6.4). In most conducting polymers, the conduction band arises from delocalized molecular orbitals in a *conjugated  $\pi$  system*—an alternating carbon-carbon single and carbon-carbon double bond pattern that gives rise to a geometry in which there is significant overlap between the  $\pi$  orbitals forming the double bonds. The simplest conducting polymer is *trans*-polyacetylene



Just as  $\pi$ -orbital overlap between the alternating single and double bonds in benzene ( $C_6H_6$ ) leads to delocalized molecular orbitals in the benzene ring (see Section 4.5), the  $\pi$ -orbital overlap in *trans*-polyacetylene gives rise to delocalized molecular orbitals along the conjugated  $\pi$  chain. Polyacetylene is unstable in the presence of air and moisture, so its commercial potential is limited, but other more stable (and thus more commercially promising) polymers with conjugated  $\pi$  systems include polypyrole, polythiophene, and poly(*p*-phenylene):



The conductivity of materials,  $\sigma$ , is measured in units of siemens (S) per centimeter, where a siemen is the inverse of the ohm, the SI unit of electrical resistance, that is,  $1\text{ S} = 1\text{ } \Omega^{-1}$ . Materials can be classified as conducting ( $\sigma > 10^2\text{ S cm}^{-1}$ ), semiconducting ( $10^{-7}\text{ S cm}^{-1} < \sigma < 10^2\text{ S cm}^{-1}$ ), or as insulating ( $\sigma < 10^{-8}\text{ S cm}^{-1}$ ). Pure conducting polymers are generally semiconductors. For example, pure

*trans*-polyacetylene has a conductivity of  $4.4 \times 10^{-5}$  S cm<sup>-1</sup>, which makes it weakly semiconducting. Metal-like conductivity in conducting polymers can be achieved by doping the polymer with impurities, such as I<sub>2</sub> or AsI<sub>5</sub>. As discussed in Section 6.4, the presence of these dopants acts to increase the number of charge carriers on the conducting polymer backbone by either adding electrons (*n*-type) or removing electrons (*p*-type). Doped polyacetylene can achieve conductivities approaching 10<sup>5</sup> S cm<sup>-1</sup>, which is on the order of that for pure copper ( $\sigma = 4.1 \times 10^5$  S cm<sup>-1</sup>). For this reason, doped conducting polymers are often referred to as “synthetic metals.”

## 16.5 | Proteins Are Polymer Chains Composed of Amino Acid Monomers

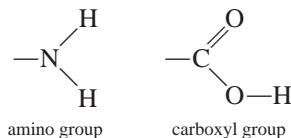
**Proteins**, which play a key role in nearly all biological processes, are *polymers of amino acids*. Enzymes, the catalysts of biochemical reactions, are mostly proteins. Proteins also facilitate a wide range of other functions, such as the transport and storage of vital substances, coordinated motion, mechanical support, and protection against diseases.

The human body contains an estimated 100,000 different kinds of proteins, each of which has a specific physiological function. As we will see in this section, the chemical composition and structure of these complex natural polymers are the basis of their specificity.

### Amino Acids

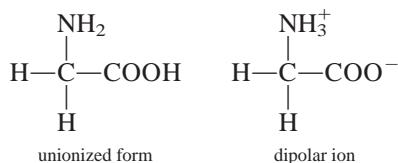
Proteins have high molar masses, ranging from about 5000 g to  $1 \times 10^7$  g, and yet the percent composition by mass of the elements in proteins is remarkably constant: carbon, approximately 53 percent; hydrogen, 7 percent; oxygen, 23 percent; nitrogen, 16 percent; and sulfur, 1 percent.

The basic structural units of proteins are *amino acids*. An **amino acid** is a compound that contains at least one amino group ( $-NH_2$ ) and at least one carboxyl group ( $-COOH$ ):



Twenty different amino acids are the building blocks of all the proteins in the human body. Table 16.6 shows the structures of these vital compounds along with their three-letter abbreviations.

Amino acids in solution at neutral pH exist as *dipolar ions* because the proton on the carboxyl group has migrated to the amino group. Compare, for example, the unionized form and the dipolar ion form of glycine, the simplest amino acid, shown here:



The first step in the synthesis of a protein molecule is a condensation reaction between an amino group on one amino acid and a carboxyl group on another. The

**Table 16.6** The 20 Amino Acids Essential to Living Organisms\*

Name	Abbreviation	Structure
Alanine	Ala	The structure shows a central carbon atom bonded to a hydrogen atom (top), an amino group ( $\text{NH}_3^+$ , bottom), a methyl group ( $\text{CH}_3$ , left), and a carboxylate group ( $\text{COO}^-$ , right). A blue shaded box highlights the methyl group ( $\text{CH}_3$ ).
Arginine	Arg	The structure shows a guanidino group ( $\text{H}_2\text{N}-\text{C}(=\text{NH})-\text{N}$ , top), a methylene group ( $\text{CH}_2$ , middle), and a carboxylate group ( $\text{COO}^-$ , right). A blue shaded box highlights the guanidino group ( $\text{H}_2\text{N}-\text{C}(=\text{NH})-\text{N}$ ).
Asparagine	Asn	The structure shows an amide group ( $\text{H}_2\text{N}-\text{C}(=\text{O})-\text{CH}_2$ , top), a methylene group ( $\text{CH}_2$ , middle), and a carboxylate group ( $\text{COO}^-$ , right). A blue shaded box highlights the amide group ( $\text{H}_2\text{N}-\text{C}(=\text{O})-\text{CH}_2$ ).
Aspartic acid	Asp	The structure shows a carboxylic acid group ( $\text{HOOC}-\text{CH}_2$ , top), a methylene group ( $\text{CH}_2$ , middle), and a carboxylate group ( $\text{COO}^-$ , right). A blue shaded box highlights the carboxylic acid group ( $\text{HOOC}-\text{CH}_2$ ).
Cysteine	Cys	The structure shows a thiomethyl group ( $\text{HS}-\text{CH}_2$ , top), a methylene group ( $\text{CH}_2$ , middle), and a carboxylate group ( $\text{COO}^-$ , right). A blue shaded box highlights the thiomethyl group ( $\text{HS}-\text{CH}_2$ ).
Glutamic acid	Glu	The structure shows a carboxylic acid group ( $\text{HOOC}-\text{CH}_2$ , top), a methylene group ( $\text{CH}_2$ , middle), and a carboxylate group ( $\text{COO}^-$ , right). A blue shaded box highlights the carboxylic acid group ( $\text{HOOC}-\text{CH}_2$ ).
Glutamine	Gln	The structure shows an amide group ( $\text{H}_2\text{N}-\text{CH}_2$ , top), a methylene group ( $\text{CH}_2$ , middle), and a carboxylate group ( $\text{COO}^-$ , right). A blue shaded box highlights the amide group ( $\text{H}_2\text{N}-\text{CH}_2$ ).
Glycine	Gly	The structure shows a methyl group ( $\text{H}-\text{CH}_2$ , top), a methylene group ( $\text{CH}_2$ , middle), and a carboxylate group ( $\text{COO}^-$ , right). A blue shaded box highlights the methyl group ( $\text{H}-\text{CH}_2$ ).
Histidine	His	The structure shows an imidazole ring system ( $\text{HC}=\text{C}-\text{CH}_2-\text{C}(=\text{NH})-\text{NH}_3^+$ , top), and a carboxylate group ( $\text{COO}^-$ , right). A blue shaded box highlights the imidazole ring system ( $\text{HC}=\text{C}-\text{CH}_2-\text{C}(=\text{NH})-\text{NH}_3^+$ ).
Isoleucine	Ile	The structure shows a methyl group ( $\text{H}_3\text{C}-\text{CH}_2$ , top), a methylene group ( $\text{CH}_2$ , middle), and a carboxylate group ( $\text{COO}^-$ , right). A blue shaded box highlights the methyl group ( $\text{H}_3\text{C}-\text{CH}_2$ ).

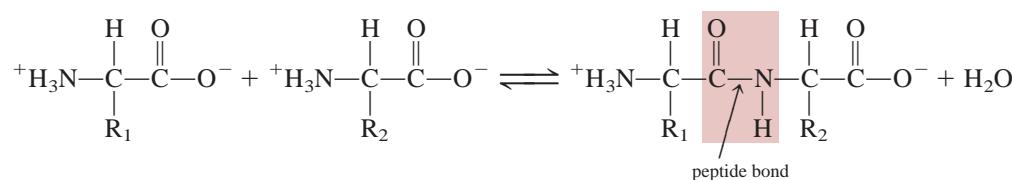
(Continued)

\*The shaded portion is the R group of the amino acid.

**Table 16.6** The 20 Amino Acids Essential to Living Organisms—Cont.

Name	Abbreviation	Structure
Leucine	Leu	The structure shows a central alpha-carbon atom bonded to four groups: a methyl group (H <sub>3</sub> C) pointing up, another methyl group (H <sub>3</sub> C) pointing down, a hydrogen atom (H) pointing up, and an amino acid side chain (CH <sub>2</sub> -C(=O)NH <sub>3</sub> <sup>+</sup> ) pointing down.
Lysine	Lys	The structure shows a central alpha-carbon atom bonded to four groups: a hydrogen atom (H) pointing up, a side chain (H <sub>2</sub> N-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -) pointing left, a hydrogen atom (H) pointing up, and an amino acid side chain (C(=O)NH <sub>3</sub> <sup>+</sup> ) pointing down.
Methionine	Met	The structure shows a central alpha-carbon atom bonded to four groups: a hydrogen atom (H) pointing up, a side chain (H <sub>3</sub> C-S-CH <sub>2</sub> -CH <sub>2</sub> -) pointing left, a hydrogen atom (H) pointing up, and an amino acid side chain (C(=O)NH <sub>3</sub> <sup>+</sup> ) pointing down.
Phenylalanine	Phe	The structure shows a central alpha-carbon atom bonded to four groups: a hydrogen atom (H) pointing up, a side chain (C <sub>6</sub> H <sub>5</sub> -CH <sub>2</sub> -) pointing left, a hydrogen atom (H) pointing up, and an amino acid side chain (C(=O)NH <sub>3</sub> <sup>+</sup> ) pointing down.
Proline	Pro	The structure shows a central alpha-carbon atom bonded to four groups: a hydrogen atom (H) pointing up, a side chain (NH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -) pointing left, a hydrogen atom (H) pointing up, and an amino acid side chain (C(=O)NH <sub>3</sub> <sup>+</sup> ) pointing down.
Serine	Ser	The structure shows a central alpha-carbon atom bonded to four groups: a hydrogen atom (H) pointing up, a side chain (HO-CH <sub>2</sub> -) pointing left, a hydrogen atom (H) pointing up, and an amino acid side chain (C(=O)NH <sub>3</sub> <sup>+</sup> ) pointing down.
Threonine	Thr	The structure shows a central alpha-carbon atom bonded to four groups: a hydrogen atom (H) pointing up, a side chain (CH <sub>3</sub> -C(OH)-CH <sub>2</sub> -) pointing left, a hydrogen atom (H) pointing up, and an amino acid side chain (C(=O)NH <sub>3</sub> <sup>+</sup> ) pointing down.
Tryptophan	Trp	The structure shows a central alpha-carbon atom bonded to four groups: a hydrogen atom (H) pointing up, a side chain (C <sub>6</sub> H <sub>5</sub> -CH=CH <sub>2</sub> -) pointing left, a hydrogen atom (H) pointing up, and an amino acid side chain (C(=O)NH <sub>3</sub> <sup>+</sup> ) pointing down.
Tyrosine	Tyr	The structure shows a central alpha-carbon atom bonded to four groups: a hydrogen atom (H) pointing up, a side chain (HO-C <sub>6</sub> H <sub>4</sub> -CH <sub>2</sub> -) pointing left, a hydrogen atom (H) pointing up, and an amino acid side chain (C(=O)NH <sub>3</sub> <sup>+</sup> ) pointing down.
Valine	Val	The structure shows a central alpha-carbon atom bonded to four groups: a methyl group (H <sub>3</sub> C) pointing up, another methyl group (H <sub>3</sub> C) pointing down, a hydrogen atom (H) pointing up, and an amino acid side chain (CH <sub>2</sub> -C(=O)NH <sub>3</sub> <sup>+</sup> ) pointing down.

molecule formed from the condensation reaction between two amino acids is called a *dipeptide*, and the bond joining them together is a *peptide bond*:



where  $R_1$  and  $R_2$  represent an H atom or some other group, and  $-\text{CO}-\text{NH}-$  is called the *amide group*. Because the equilibrium of the reaction joining two amino acids lies to the left, the process is coupled to the hydrolysis of ATP (see p. 459).

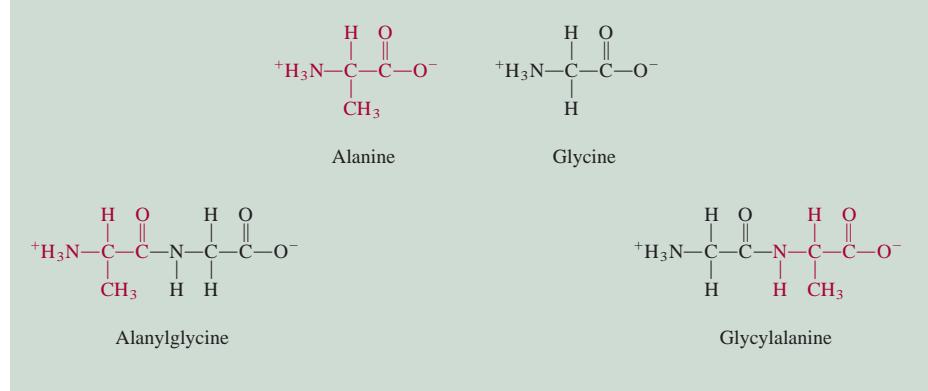
Either end of a dipeptide can engage in a condensation reaction with another amino acid to form a *tripeptide*, a *tetrapeptide*, and so on. The final product, the protein molecule, is a *polypeptide*; it can also be thought of as a polymer of amino acids. An amino acid unit in a polypeptide chain is called a *residue*. Typically, a polypeptide chain contains 100 or more amino acid residues. The sequence of amino acids in a polypeptide chain is written conventionally from left to right, starting with the amino-terminal residue and ending with the carboxyl-terminal residue. Figure 16.18 shows that alanylglucose and glycylalanine, two dipeptides that can form from alanine and glycine, are different molecules.

With 20 different amino acids to choose from,  $20^2 = 400$  different dipeptides can be generated. Even for a very small protein such as insulin, which contains only 50 amino acid residues, the number of chemically different structures that are possible is on the order of  $20^{50}$  or  $10^{65}$ ! This is an incredibly large number when you consider that the total number of atoms in our galaxy is about  $10^{68}$ . With so many possibilities for protein synthesis, it is remarkable that generation after generation of cells can produce identical proteins for specific physiological functions.

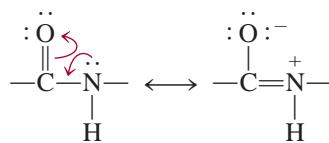
## Protein Structure

The type and number of amino acids in a given protein along with the sequence or order in which these amino acids are joined together determine the structure of the protein. In the 1930s, Linus Pauling and coworkers conducted a systematic investigation of protein structure. First they studied the geometry of the basic repeating

**Figure 16.18** The formation of two dipeptides from two different amino acids.



group (that is, the amide group), which is represented by the following resonance structures:



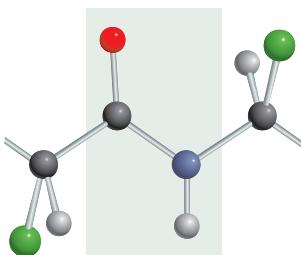
Because it is more difficult (i.e., it would take more energy) to twist a double bond than a single bond, the four atoms in the amide group become locked in the same plane (Figure 16.19). Figure 16.20 depicts the repeating amide group in a polypeptide chain.

On the basis of models and X-ray diffraction data, Pauling deduced that there are two common structures for protein molecules, called the  $\alpha$  helix and the  $\beta$ -pleated sheet. The  $\alpha$ -helical structure of a polypeptide chain is shown in Figure 16.21. The helix is stabilized by *intramolecular* hydrogen bonds between the NH and CO groups of the main chain, giving rise to an overall rodlike shape. The CO group of each amino acid is hydrogen-bonded to the NH group of the amino acid that is four residues away in the sequence. In this manner all the main-chain CO and NH groups take part in hydrogen bonding. X-ray studies have shown that the structure of a number of proteins, including myoglobin and hemoglobin, consist of  $\alpha$  helices to a great extent.

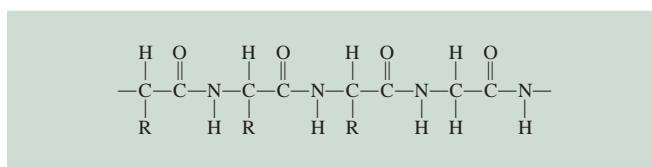
The  $\beta$ -pleated structure gives the protein a sheet-like structure rather than the rodlike structure of the  $\alpha$  helix. The polypeptide chain is almost fully extended, and each chain forms many *intermolecular* hydrogen bonds with adjacent chains. Figure 16.22 shows the two different types of  $\beta$ -pleated structures, called *parallel* and *antiparallel*. Silk molecules possess the antiparallel structure. Because its polypeptide chains are already in an extended form, silk lacks elasticity and extensibility, but it is quite strong due to the many intermolecular hydrogen bonds.

It is customary to divide protein structure into four levels of organization. The *primary structure* refers to the unique amino acid sequence of the polypeptide chain. The *secondary structure* includes those parts of the polypeptide chain that are stabilized by a regular pattern of hydrogen bonds between the CO and NH groups of the backbone (for example, the  $\alpha$  helix or  $\beta$ -pleated sheet). The term *tertiary structure* applies to the three-dimensional structure stabilized by dispersion forces, hydrogen bonding, and other intermolecular forces. It differs from secondary structure because the amino acids taking part in these interactions may be far apart in the polypeptide chain.

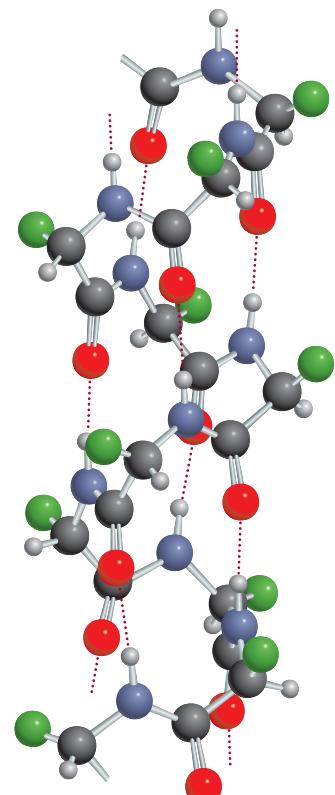
A protein molecule may be made up of more than one polypeptide chain. Thus, in addition to the various interactions *within* a chain that give rise to the secondary and tertiary structures, we must also consider the interaction *between* chains. The



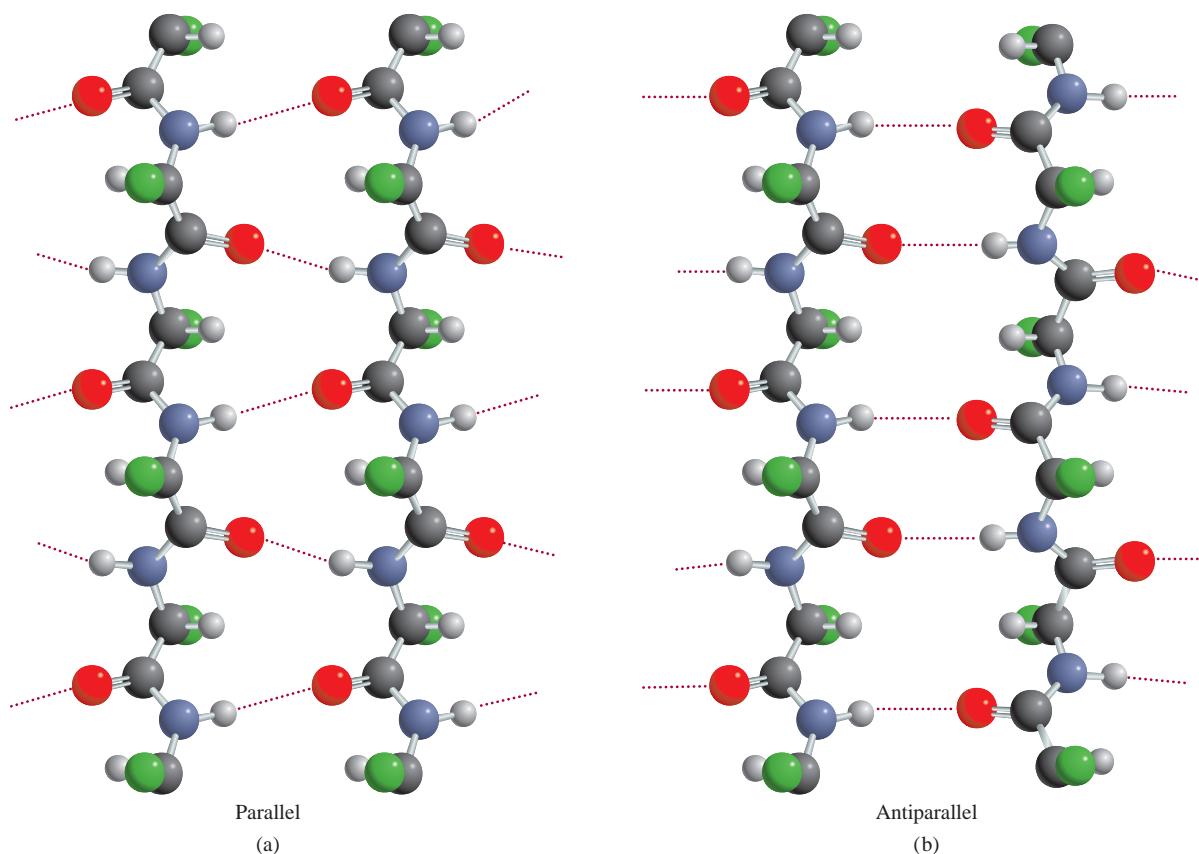
**Figure 16.19** The planar amide group in proteins. Rotation about the peptide bond in the amide group is hindered by its double-bond character. The black atoms represent carbon; blue, nitrogen; red, oxygen; green, R group; and gray, hydrogen.



**Figure 16.20** A polypeptide chain. Note the repeating units of the amide group. The symbol R represents part of the structure characteristic of the individual amino acids. For glycine, R is simply an H atom.



**Figure 16.21** The  $\alpha$ -helical structure of a polypeptide chain. The structure is held in position by intramolecular hydrogen bonds, shown as dotted lines. For color key, see Figure 16.19.

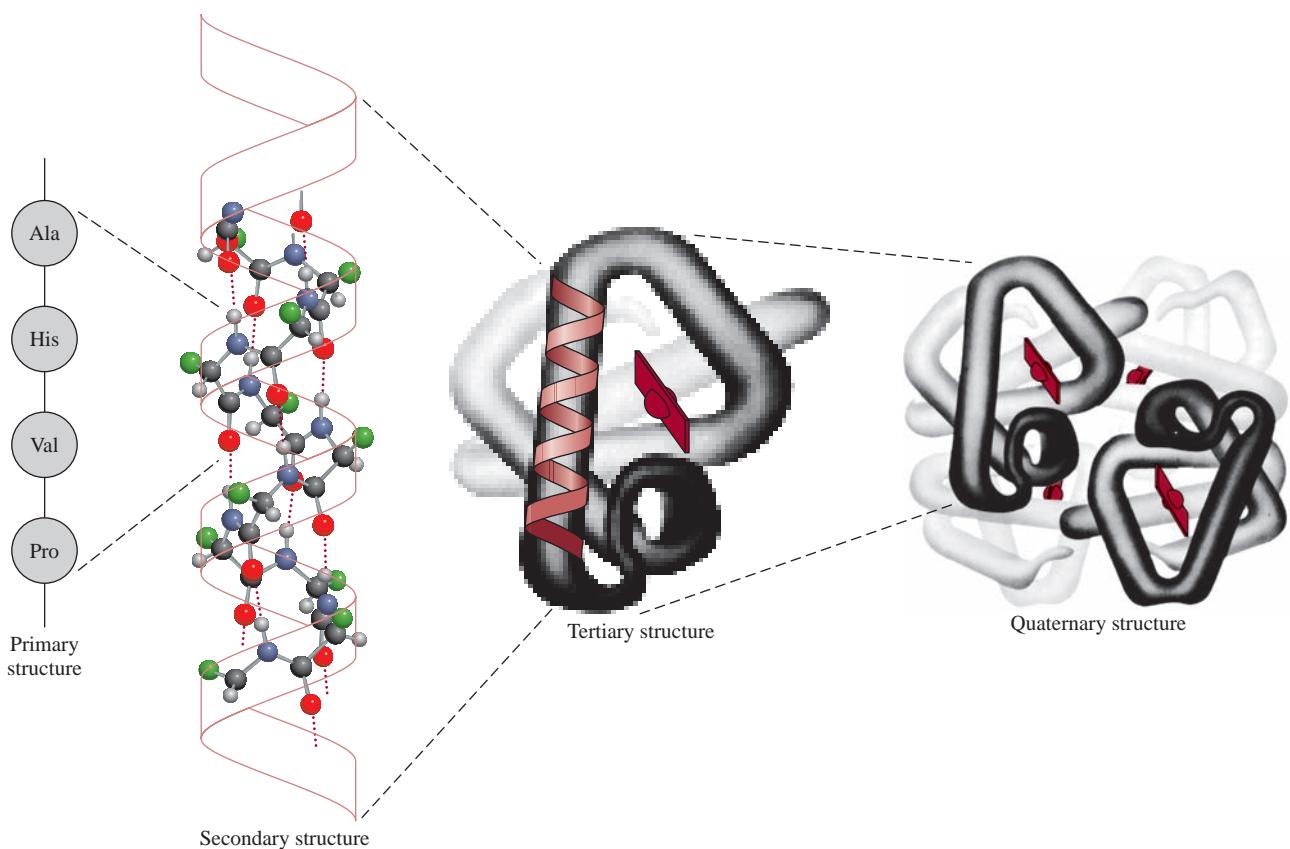


**Figure 16.22** Hydrogen bonds (a) in a parallel  $\beta$ -pleated sheet structure, in which all the polypeptide chains are oriented in the same direction, and (b) in an antiparallel  $\beta$ -pleated sheet, in which adjacent polypeptide chains run in opposite directions. For color key, see Figure 16.19.

overall arrangement of the polypeptide chains is called the *quaternary structure*. Hemoglobin, for example, consists of four separate polypeptide chains, or *subunits*. These subunits are held together by van der Waals forces and ionic (electrostatic) forces (Figure 16.23).

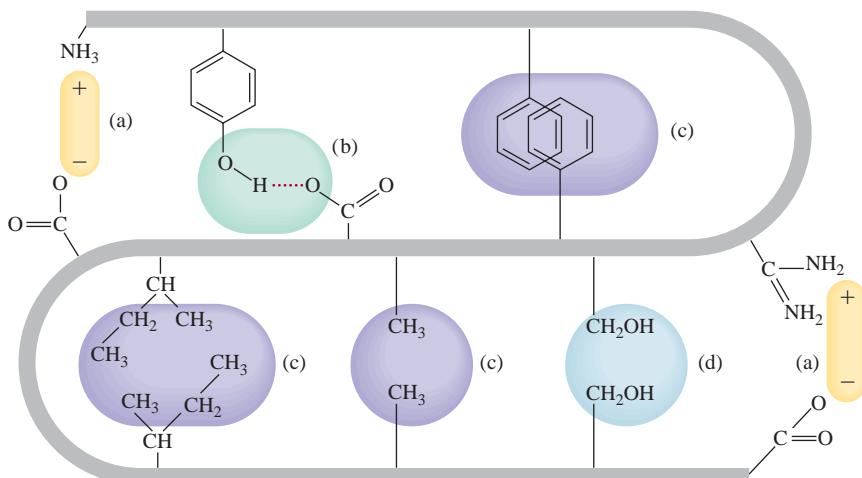
Pauling's work was a great triumph in protein chemistry. It showed for the first time how to predict a protein structure purely from knowledge of the geometry of its fundamental building blocks—its amino acids. There are many proteins, however, whose structures do not consist of  $\alpha$  helices or  $\beta$ -pleated sheets. Chemists now know that the three-dimensional structures of these biopolymers are maintained by several types of intermolecular forces in addition to hydrogen bonding (Figure 16.24). The delicate balance of the various interactions can be appreciated by considering what happens when a glutamic acid residue in two of the four polypeptide chains in hemoglobin is replaced by valine, an amino acid with very different properties than glutamic acid. The resulting protein molecules aggregate to form insoluble polymers, causing the disease known as sickle cell anemia (see the boxed text on p. 840).

In spite of all the forces that give proteins their structural stability, most proteins have a certain amount of flexibility. Enzymes, for example, are flexible enough to change their geometries to fit substrates of various sizes and shapes. Another interesting



**Figure 16.23** The primary, secondary, tertiary, and quaternary structures of the hemoglobin molecule.

of protein flexibility is found in the binding of hemoglobin to oxygen. Each of the four polypeptide chains in hemoglobin contains a heme group that can bind to an oxygen molecule. In deoxyhemoglobin, the affinity of each of the heme groups for oxygen is about the same. As soon as one of the heme groups becomes oxygenated, however, the affinity of the other three hemes for oxygen is greatly enhanced. This



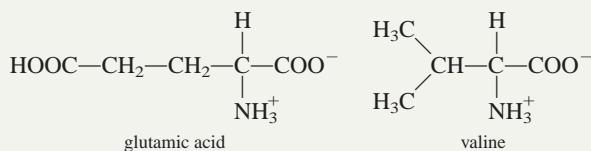
**Figure 16.24** Intermolecular forces in a protein molecule: (a) ionic forces, (b) hydrogen bonding, (c) dispersion forces, and (d) dipole-dipole forces.

## Sickle Cell Anemia: A Molecular Disease

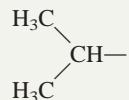
**S**ickle cell anemia is a hereditary disease in which abnormally shaped red blood cells restrict the flow of blood to vital organs in the human body, causing swelling, severe pain, and in many cases a shortened life span. There is currently no cure for this condition, but its painful symptoms are known to be caused by a defect in hemoglobin, the oxygen-carrying protein in red blood cells.

The hemoglobin molecule is a large protein with a molar mass of about 65,000 g. Normal human hemoglobin (HbA) consists of two  $\alpha$  chains, each containing 141 amino acids, and two  $\beta$  chains made up of 146 amino acids each. These four polypeptide chains, or subunits, are held together by ionic and van der Waals forces.

There are many mutant hemoglobin molecules—molecules with an amino acid sequence that differs somewhat from the sequence in HbA. Most mutant hemoglobins are harmless, but sickle cell hemoglobin (HbS) and others are known to cause serious diseases. HbS differs from HbA in only one very small detail. A valine molecule replaces a glutamic acid molecule on each of the two  $\beta$  chains:



This change may seem small (two amino acids out of 292), but it has a profound effect on the stability of HbS in solution. The valine groups are located at the bottom outside of the molecule to form a protruding “key” on each of the  $\beta$  chains. The nonpolar portion of valine

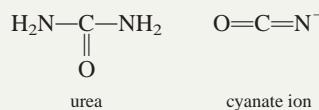


can attract another nonpolar group in the  $\alpha$  chain of an adjacent HbS molecule through dispersion forces. Biochemists often refer to this kind of attraction between nonpolar groups as a *hydrophobic* (see Chapter 9) interaction. Gradually, enough HbS molecules aggregate to form a “superpolymer.”

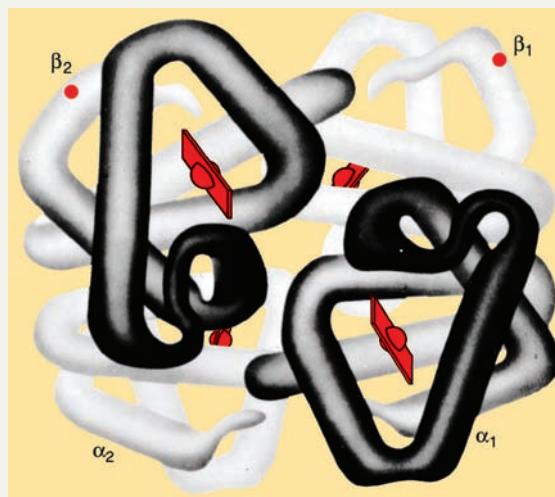
Generally speaking, the solubility of a substance decreases as its size increases because the solvation process becomes unfavorable with increasing molecular surface area. As a result, proteins are not usually very soluble in water. In fact, the aggregated HbS molecules eventually precipitate out of solution. The precipitate causes normal disk-shaped red blood cells to assume a warped crescent or sickle shape

(see the figure on page 109). These deformed cells clog the narrow capillaries, thereby restricting blood flow to the organs of the body. It is the reduced blood flow that gives rise to the symptoms of sickle cell anemia. Sickle cell anemia has been termed a molecular disease by Linus Pauling, who did some of the early important chemical research on the nature of the affliction, because the destructive action occurs at the molecular level and the disease is, in effect, due to a molecular defect.

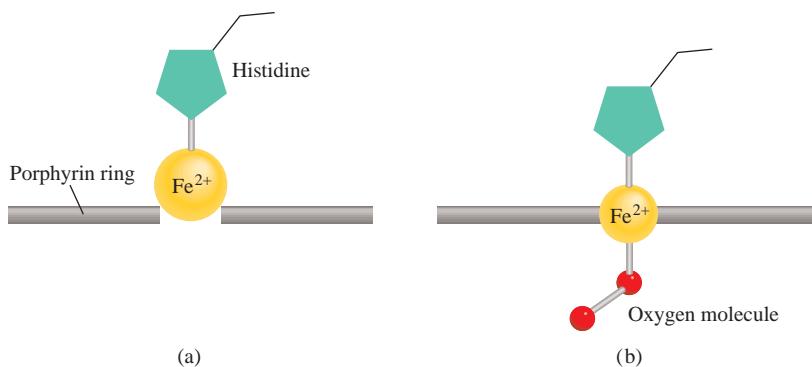
Some substances, such as urea and the cyanate ion,



can break up the hydrophobic interaction between HbS molecules and have been applied with some success to reverse the “sickling” of red blood cells. This approach may alleviate the pain and suffering of sickle cell patients, but it does not prevent the body from making more HbS. To cure sickle cell anemia, researchers must find a way to alter the genetic machinery that directs the production of HbS.



The overall structure of hemoglobin. Each hemoglobin molecule contains two  $\alpha$  chains and two  $\beta$  chains. Each of the four chains is similar to a myoglobin molecule in structure, and each also contains a heme group for binding oxygen. In sickle cell hemoglobin, the defective regions (the valine groups) are located near the ends of the  $\beta$  chains, as indicated by the dots.

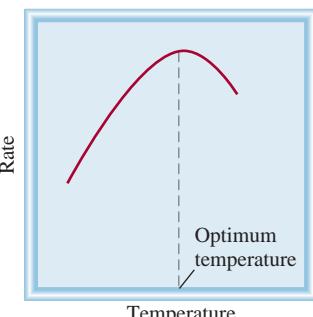


**Figure 16.25** The structural changes that occur when the heme group in hemoglobin binds to an oxygen molecule. (a) The heme group in deoxyhemoglobin. (b) Oxyhemoglobin.

phenomenon, called *cooperativity*, makes hemoglobin a particularly suitable substance for the uptake of oxygen in the lungs. By the same token, once a fully oxygenated hemoglobin molecule releases an oxygen molecule (to myoglobin in the tissues), the other three oxygen molecules will depart with increasing ease. The cooperative nature of the binding is such that information about the presence (or absence) of oxygen molecules is transmitted from one subunit to another along the polypeptide chains, a process made possible by the flexibility of the three-dimensional structure (Figure 16.25).

The  $\text{Fe}^{2+}$  ion at the center of the heme group may have too large a radius to fit into the porphyrin ring of deoxyhemoglobin. When  $\text{O}_2$  binds to  $\text{Fe}^{2+}$ , however, the ion shrinks somewhat so that it can fit into the plane of the ring. As the ion slips into the ring, it pulls the histidine residue opposite  $\text{O}_2$  toward the ring and thereby sets off a sequence of structural changes from one subunit to another. Although the details of the changes are unclear, biochemists believe that this is how the binding of an oxygen molecule to one heme group affects binding to the remaining three heme groups.

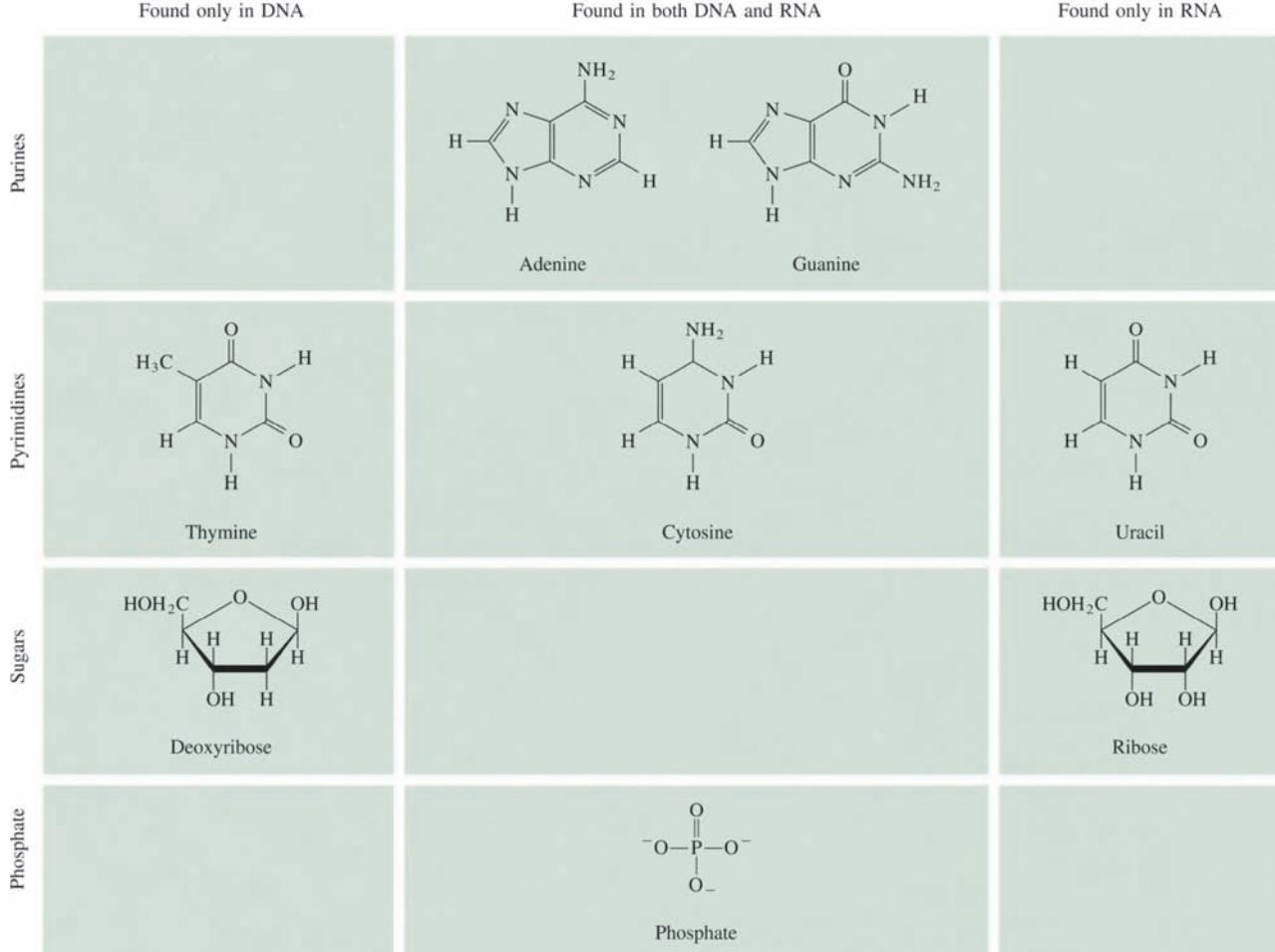
When proteins are heated above body temperature or when they are subjected to unusual acid or base conditions or treated with special reagents called *denaturants*, they lose some or all of their tertiary and secondary structure. Called *denatured proteins*, proteins in this state *no longer exhibit normal biological activity*. Figure 16.26 shows the variation of rate with temperature for a typical enzyme-catalyzed reaction. Initially, the rate increases with increasing temperature, as we would expect. Beyond the optimum temperature, however, the enzyme begins to denature and the rate decreases rapidly. If a protein is denatured under mild conditions, its original structure can often be regenerated by removing the denaturant or by restoring the temperature to normal conditions. This process is called *reversible denaturation*.



**Figure 16.26** Dependence of the rate of an enzyme-catalyzed reaction on temperature. Above the optimum temperature at which an enzyme is most effective, its activity drops off as a consequence of denaturation.

## 16.6 | DNA and RNA Are Polymers Composed of Nucleic Acids

**Nucleic acids** are high-molar-mass polymers that play an essential role in protein synthesis. **Deoxyribonucleic acid (DNA)** and **ribonucleic acid (RNA)** are the two types of nucleic acid. DNA molecules are among the largest molecules known; they have molar masses of up to tens of billions of grams. RNA molecules, on the other hand, vary greatly in size, some having a molar mass of about 25,000 g. Compared with proteins, which are made of up to 20 different amino acids, nucleic acids are fairly simple in composition. A DNA or RNA molecule contains only four types of building



**Figure 16.27** The components of the nucleic acids DNA and RNA.

blocks: purines, pyrimidines, furanose sugars, and phosphate groups (Figure 16.27). Each purine or pyrimidine is called a *base*.

In the 1940s, Erwin Chargaff<sup>10</sup> studied DNA molecules obtained from various sources and observed certain regularities. *Chargaff's rules*, as his findings are now known, describe these patterns:

1. The amount of adenine (a purine) is equal to that of thymine (a pyrimidine), that is, A = T, or A/T = 1.
2. The amount of cytosine (a pyrimidine) is equal to that of guanine (a purine), that is, C = G, or C/G = 1.
3. The total number of purine bases is equal to the total number of pyrimidine bases, that is, A + G = C + T.

10. Erwin Chargaff (1905–2002). American biochemist of Austrian origin. Chargaff was the first to show that different biological species contain different DNA molecules.

## DNA Fingerprinting

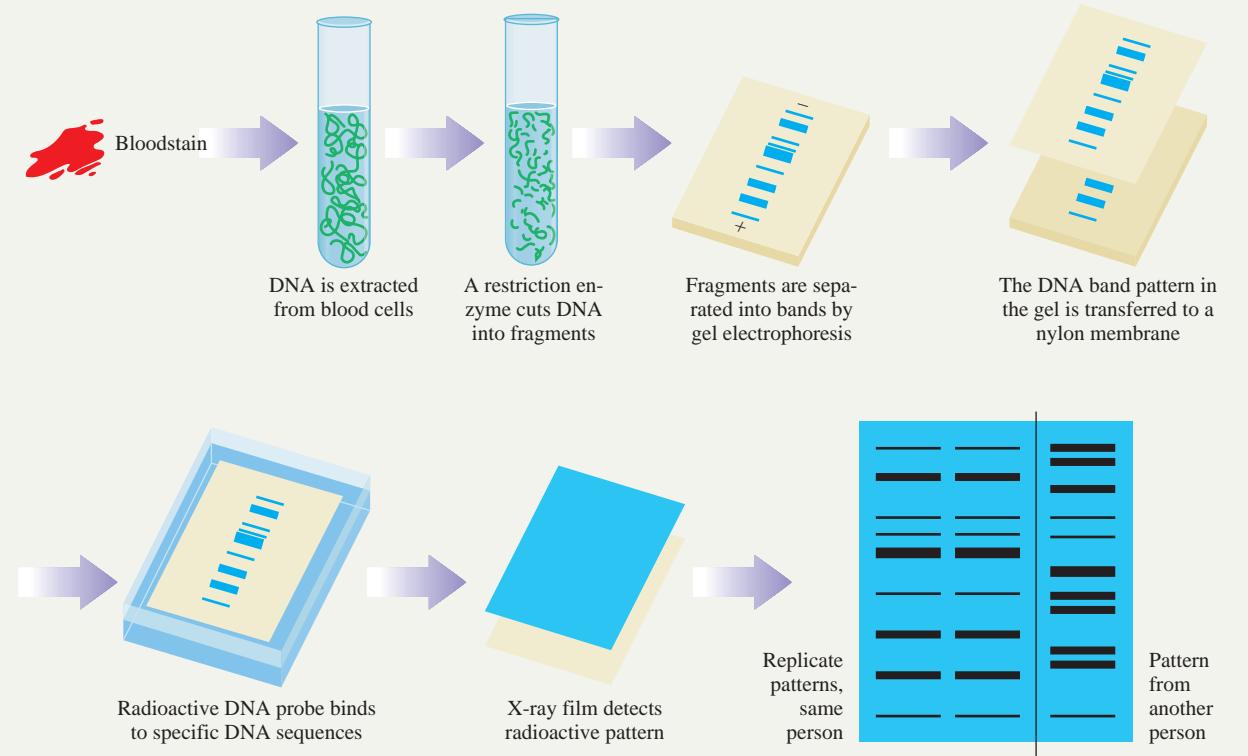
The human genetic makeup, or *genome*, consists of about 3 billion nucleotides. These 3 billion units compose the 23 pairs of chromosomes, which are continuous strands of DNA ranging in length from 50 million to 500 million nucleotides. Encoded in this DNA and stored in units called *genes* are the instructions for protein synthesis. Each of about 100,000 genes is responsible for the synthesis of a particular protein. In addition to instructions for protein synthesis, each gene contains a sequence of bases, repeated several times, that has no known function. What is interesting about these sequences, called *minisatellites*, is that they appear many times in different locations, not just in a particular gene. Furthermore, each person has a unique number of repeats. Only identical twins have the same number of minisatellite sequences.

In 1985, a British chemist named Alec Jeffreys suggested that minisatellite sequences provide a means of identification, much like fingerprints. *DNA fingerprinting* has since gained prominence with law enforcement officials as a way to identify crime suspects.

To make a DNA fingerprint, a chemist needs a sample of any tissue, such as blood or semen; even hair and saliva contain DNA. The DNA is extracted from cell nuclei and cut into

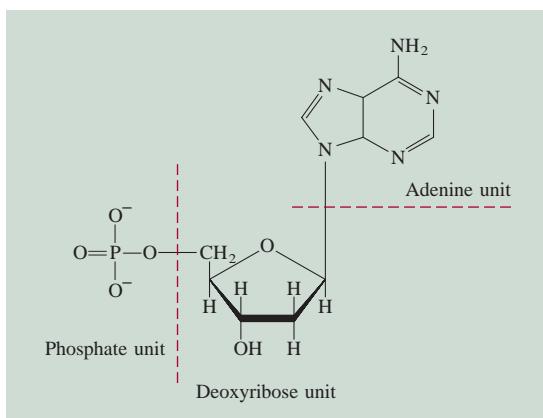
fragments by the addition of so-called restriction enzymes. These fragments, which are negatively charged, are separated by an electric field in a gel. The smaller fragments move faster than the larger ones, so they eventually separate into bands. The bands of DNA fragments are transferred from the gel to a plastic membrane, and their position is thereby fixed. Then a DNA probe—a DNA fragment that has been tagged with a radioactive label—is added. The probe binds to the fragments that have a complementary DNA sequence. An X-ray film is laid directly over the plastic sheet, and bands appear on the exposed film in the positions corresponding to the fragments recognized by the probe. About four different probes are needed to obtain a profile that is unique to just one individual. The probability of finding identical patterns in the DNA of two randomly selected individuals is estimated to be on the order of 1 in 10 billion.

The first U.S. case in which a person was convicted of a crime with the help of DNA fingerprints was tried in 1987. Today, DNA fingerprinting has become an indispensable tool of law enforcement. It is also used by those who believe they were falsely accused or convicted to prove their innocence.



Procedure for obtaining a DNA fingerprint. The developed film shows the DNA fingerprint, which is compared with patterns from known subjects.

**Figure 16.28** Structure of a nucleotide, one of the repeating units in DNA.



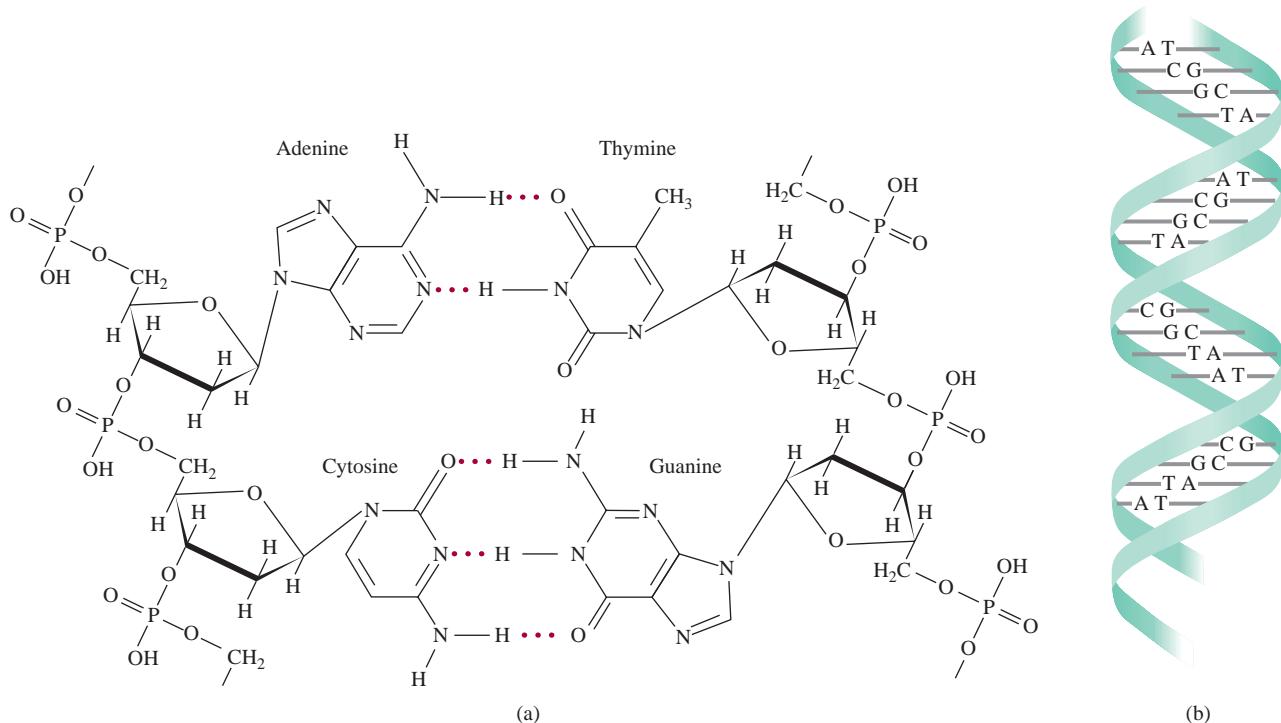
Based on chemical analyses and information obtained from X-ray diffraction measurements, James Watson<sup>11</sup> and Francis Crick<sup>12</sup> formulated the double-helical structure for the DNA molecule in 1953. Watson and Crick determined that the DNA molecule has two helical strands. Each strand is made up of **nucleotides**, which consist of a base, a deoxyribose, and a phosphate group linked together (Figure 16.28).

The key to the double-helical structure of DNA is the formation of hydrogen bonds between bases in the two strands of a molecule. Although hydrogen bonds can form between any two bases, called *base pairs*, Watson and Crick found that the most favorable couplings were between adenine and thymine and between cytosine and guanine (Figure 16.29). This scheme is consistent with Chargaff's rules because every purine base is hydrogen-bonded to a pyrimidine base, and vice versa ( $A + G = C + T$ ). Other attractive forces such as dipole-dipole interactions and van der Waals forces between the base pairs also help to stabilize the double helix.

The structure of RNA differs from that of DNA in several respects. First, as shown in Figure 16.27, the four bases found in RNA molecules are adenine, cytosine, guanine, and uracil (instead of thymine). Second, RNA contains the sugar ribose rather than the 2-deoxyribose of DNA. Third, chemical analysis shows that the composition of RNA does not obey Chargaff's rules. In other words, the purine-to-pyrimidine ratio is not equal to 1 as in the case of DNA. This and other evidence rule out a double-helical structure. In fact, the RNA molecule exists as a single-stranded polynucleotide. There are three types of RNA molecules—messenger RNA (mRNA), ribosomal RNA (rRNA), and transfer RNA (tRNA). These RNAs have similar nucleotides but differ from one another in molar mass, overall structure, and biological functions.

11. James Dewey Watson (1928– ). American biologist. Watson shared the 1962 Nobel Prize in Physiology or Medicine with Crick and Maurice Wilkins for their work on the DNA structure, which is considered by many to be the most significant development in biology in the twentieth century.

12. Francis Harry Compton Crick (1916–2004). British biologist. Crick started as a physicist but became interested in biology after reading the book *What Is Life?* by Erwin Schrödinger (see Chapter 1). In addition to elucidating the structure of DNA, for which he was a corecipient of the Nobel Prize in Physiology or Medicine in 1962, Crick has made many significant contributions to molecular biology.



**Figure 16.29** (a) Base-pair formation by adenine and thymine and by cytosine and guanine. (b) The double-helical strand of a DNA molecule held together by hydrogen bonds (and other intermolecular forces) between base pairs A-T and C-G.

## Summary of Facts and Concepts

### Sections 16.1 and 16.2

- ▶ Because carbon atoms can link up with other carbon atoms in straight and branched chains, carbon can form more compounds than any other element. The naming of organic compounds follows systematic guidelines set down by the IUPAC, although many compounds have common names that are different than their systematic names.
- ▶ Organic compounds are derived from two types of hydrocarbons: aliphatic hydrocarbons and aromatic hydrocarbons. Methane ( $\text{CH}_4$ ) is the simplest of the alkanes, a family of hydrocarbons with the general formula  $\text{C}_n\text{H}_{2n+2}$ .
- ▶ Cyclopropane ( $\text{C}_3\text{H}_6$ ) is the simplest of the cycloalkanes, a family of alkanes whose carbon atoms are joined in a ring. Alkanes and cycloalkanes are saturated hydrocarbons.
- ▶ Ethylene ( $\text{CH}_2=\text{CH}_2$ ) is the simplest of the olefins, or alkenes, a class of hydrocarbons containing carbon-carbon double bonds and having the general formula  $\text{C}_n\text{H}_{2n}$ .
- ▶ Acetylene ( $\text{CH}\equiv\text{CH}$ ) is the simplest of the alkynes, which are compounds that have the general formula  $\text{C}_n\text{H}_{2n-2}$  and contain carbon-carbon triple bonds.

- ▶ Compounds that contain one or more benzene rings are called aromatic hydrocarbons. These compounds undergo substitution by halogens and alkyl groups.

### Section 16.3

- ▶ Functional groups impart specific types of chemical reactivity to molecules.
- ▶ Classes of compounds characterized by their functional groups include alcohols, ethers, aldehydes and ketones, carboxylic acids and esters, and amines.

### Section 16.4

- ▶ Polymers are large molecules made up of small, repeating units called monomers.
- ▶ Proteins, nucleic acids, cellulose, and rubber are natural polymers. Nylon, Dacron, and Lucite are examples of synthetic polymers.
- ▶ Organic polymers can be synthesized via addition reactions or condensation reactions.
- ▶ Stereoisomers of a polymer made up of asymmetric monomers have different properties, depending on how the starting units are joined together.

- ▶ Synthetic rubbers include polychloroprene and styrene-butadiene rubber, which is a copolymer of styrene and butadiene.

### Section 16.5

- ▶ Structure determines the function and properties of proteins. To a great extent, hydrogen bonding and other intermolecular forces determine the structure of proteins.
- ▶ The primary structure of a protein is its amino acid sequence. Secondary structure is the shape defined by hydrogen bonds joining the CO and NH groups of the amino acid backbone. Tertiary and quaternary structures

are the three-dimensional folded arrangements of proteins that are stabilized by hydrogen bonds and other intermolecular forces.

### Section 16.6

- ▶ Nucleic acids—DNA and RNA—are high-molar-mass polymers that carry genetic instructions for protein synthesis in cells. Nucleotides are the building blocks of DNA and RNA. DNA nucleotides contain a purine or pyrimidine base, a deoxyribose molecule, and a phosphate group. RNA nucleotides are similar but contain different bases and ribose instead of deoxyribose.

## Key Words

addition reactions, p. 813	carboxylic acid, p. 819	functional group, p. 801	nucleotides, p. 844
alcohol, p. 815	condensation reaction, p. 818	homopolymer, p. 828	organic chemistry, p. 800
aldehyde, p. 818	conducting polymers, p. 832	hydrocarbon, p. 801	polymer, p. 826
aliphatic hydrocarbon, p. 801	conformations, p. 810	hydrogenation, p. 813	proteins, p. 833
alkane, p. 801	copolymer, p. 831	ketone, p. 818	ribonucleic acid (RNA), p. 841
alkene, p. 806	cycloalkane, p. 806	macromolecules, p. 826	saponification, p. 821
alkyl group, p. 803	denatured proteins, p. 841	monomer, p. 826	saturated hydrocarbon, p. 801
alkyne, p. 807	deoxyribonucleic acids (DNA), p. 841	Newman projection, p. 810	substitution reaction, p. 815
amine, p. 821	ester, p. 820	nuclear magnetic resonance spectroscopy, p. 824	unsaturated
amino acid, p. 833	ether, p. 817	nucleic acids, p. 841	hydrocarbon, p. 813
aromatic hydrocarbon, p. 801			

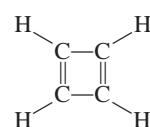
## Problems

### Hydrocarbons Are Organic Compounds Containing Only Hydrogen and Carbon

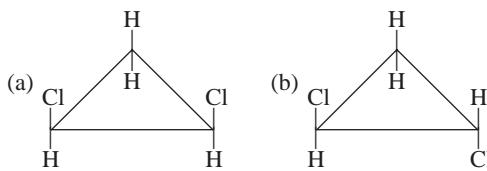
- 16.1 What do *saturated* and *unsaturated* mean when applied to hydrocarbons? Give examples of a saturated hydrocarbon and an unsaturated hydrocarbon.
- 16.2 Alkenes have geometric isomers, so why is it that alkanes and alkynes do not?
- 16.3 Give examples of a chiral substituted alkane and an achiral substituted alkane.
- 16.4 Draw and name all possible structural isomers for alkanes with the formula  $C_7H_{16}$ .
- 16.5 How many distinct chloropentanes ( $C_5H_{11}Cl$ ) could be produced in the direct chlorination of *n*-pentane [ $CH_3(CH_2)_3CH_3$ ]? Draw the structure of each molecule.
- 16.6 Draw all possible isomers for the molecule  $C_4H_8$ .
- 16.7 Draw all possible isomers for the molecule  $C_3H_5Br$ .
- 16.8 The structural isomers of pentane ( $C_5H_{12}$ ) have quite different boiling points. Explain the observed variation in boiling point, in terms of their different structures.
- 16.9 Discuss how you can determine which of the following compounds might be alkanes, cyclo-

kanes, alkenes, or alkynes, without drawing their structures: (a)  $C_6H_{12}$ , (b)  $C_4H_6$ , (c)  $C_5H_{12}$ , (d)  $C_7H_{14}$ , and (e)  $C_3H_4$ .

- 16.10 Draw the structures of *cis*-2-butene and *trans*-2-butene. Which of the two compounds has the higher heat of hydrogenation? Explain.
- 16.11 Would you expect cyclobutadiene to be a stable molecule? Explain.

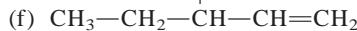
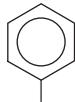
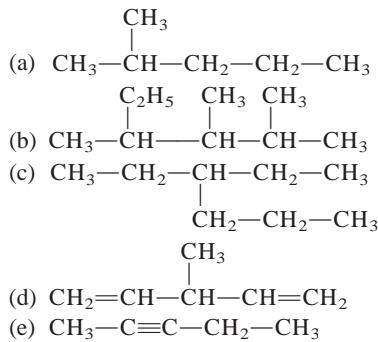


- 16.12 How many different isomers can be derived from ethylene if two hydrogen atoms are replaced by a fluorine atom and a chlorine atom? Draw their structures and name them. Indicate which are structural isomers and which are geometric isomers.
- 16.13 Geometric isomers are not restricted to compounds containing the  $C=C$  bond. For example, certain disubstituted cycloalkanes can exist in the *cis* and the *trans* forms. Label the following molecules as the *cis* and *trans* isomers of the same compound:



- 16.14 Which of the following amino acids are chiral: (a)  $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$ , (b)  $\text{CH}_2(\text{NH}_2)\text{COOH}$ , (c)  $\text{CH}_2(\text{OH})\text{CH}(\text{NH}_2)\text{COOH}$ ?

- 16.15 Name the following compounds:



- 16.16 Write structural formulas for the following organic compounds: (a) 3-methylhexane, (b) 1,3,5-trichlorocyclohexane, (c) 2,3-dimethylpentane, (d) 2-bromo-4-phenylpentane, and (e) 3,4,5-trimethyloctane.

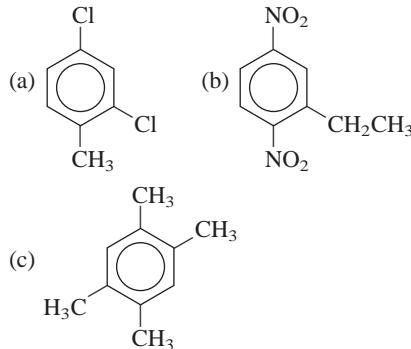
- 16.17 Write structural formulas for the following compounds: (a) *trans*-2-pentene, (b) 2-ethyl-1-butene, (c) 4-ethyl-*trans*-2-heptene, and (d) 3-phenylbutyne.

- 16.18 Draw and name the two geometric isomers of 1,3-pentadiene.

- 16.19 Benzene and cyclohexane both contain six-membered rings. Benzene is planar, whereas cyclohexane is nonplanar. Explain.

- 16.20 Write structures for the following compounds: (a) 1-bromo-3-methylbenzene, (b) 1-chloro-2-propylbenzene, and (c) 1,2,4,5-tetramethylbenzene.

- 16.21 Name the following compounds:



## Hydrocarbons Undergo a Number of Important Chemical Reactions

- 16.22 Suggest two chemical tests that would help you distinguish between  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ .
- 16.23 Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) adds to the double bond of alkenes as  $\text{H}^+$  and  $\text{OSO}_3\text{H}$ . Predict the products when sulfuric acid reacts with (a) ethylene and (b) propylene.
- 16.24 Acetylene is an unstable compound. It has a tendency to form benzene as follows:

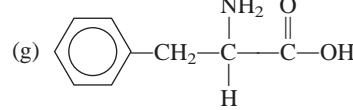


Calculate the standard enthalpy change in  $\text{kJ mol}^{-1}$  for this reaction at  $25^\circ\text{C}$ .

- 16.25 Predict the products when  $\text{HBr}$  is added to (a) 1-butene and (b) 2-butene.

## The Structure and Properties of Organic Compounds Are Greatly Influenced by the Presence of Functional Groups

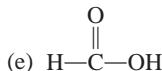
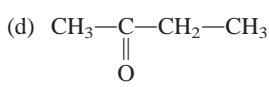
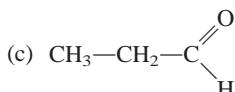
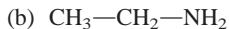
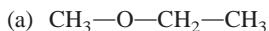
- 16.26 Draw the Lewis structure for each of the following functional groups: alcohol, ether, aldehyde, ketone, carboxylic acid, ester, and amine.
- 16.27 Draw structures for molecules with the following formulas: (a)  $\text{CH}_4\text{O}$ , (b)  $\text{C}_2\text{H}_6\text{O}$ , (c)  $\text{C}_3\text{H}_6\text{O}_2$ , and (d)  $\text{C}_3\text{H}_8\text{O}$ .
- 16.28 Classify each of the following molecules as an alcohol, aldehyde, ketone, carboxylic acid, amine, or ether:
- (a)  $\text{CH}_3-\text{O}-\text{CH}_2-\text{CH}_3$
- (b)  $\text{CH}_3-\text{CH}_2-\text{NH}_2$
- (c)  $\text{CH}_3-\text{CH}_2-\overset{\text{O}}{\underset{|}{\text{C}}}-\text{H}$
- (d)  $\text{CH}_3-\overset{\text{O}}{\underset{||}{\text{C}}}-\text{CH}_2-\text{CH}_3$
- (e)  $\text{H}-\overset{\text{O}}{\underset{||}{\text{C}}}-\text{OH}$
- (f)  $\text{CH}_3-\text{CH}_2\text{CH}_2-\text{OH}$



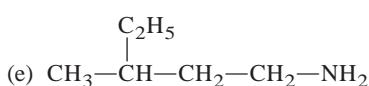
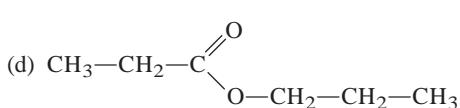
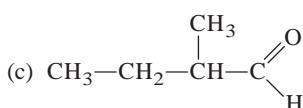
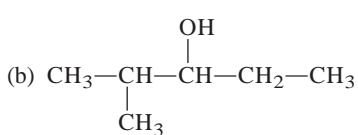
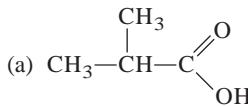
- 16.29 Aldehydes are generally more susceptible to oxidation in air than are ketones. Use ethanal (or acetaldehyde) and 2-propanone (or acetone) as examples and show why ketones are more stable than aldehydes in this respect.
- 16.30 Draw structures for the following compounds: (a) 3-hexanol, (b) 2,2-dibromo-3-pentanol, (c) 3-pentanone, (d) 2-phenylbutanal, and (e) ethoxypentane.

- 16.31 Draw structures for the following compounds:  
 (a) 1,2-diethoxybutane, (b) pentanoic acid, (c) 1,2-dimethoxybenzene, (d) 3-bromo-2-chloro-4-heptanol, and (e) dichloroethanoic acid.

- 16.32 Give IUPAC names for the following compounds:



- 16.33 Give IUPAC names for the following compounds:



(Be careful with this one!)

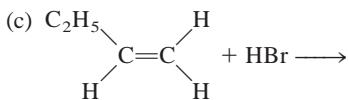
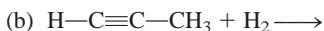
- 16.34 Complete the following equation and identify the products:



- 16.35 A compound has the empirical formula  $\text{C}_5\text{H}_{12}\text{O}$ . Upon controlled oxidation, it is converted into a compound of empirical formula  $\text{C}_5\text{H}_{10}\text{O}$ , which behaves as a ketone. Draw possible structures for the original compound and the final compound.

- 16.36 A compound having the molecular formula  $\text{C}_4\text{H}_{10}\text{O}$  does not react with sodium metal. In the presence of light, the compound reacts with  $\text{Cl}_2$  to form three compounds having the formula  $\text{C}_4\text{H}_9\text{OCl}$ . Draw a structure for the original compound that is consistent with this information.

- 16.37 Predict the product or products of each of the following reactions:



- 16.38 Identify the functional groups in each of the following molecules:



### Polymers Are Very Large Molecular Weight Compounds Formed from the Joining Together of Many Subunits Called Monomers

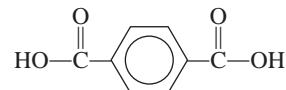
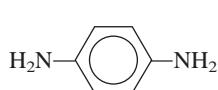
- 16.39 Calculate the molar mass of a particular polyethylene sample,  $(-\text{CH}_2\text{—CH}_2-)_n$ , where  $n = 4600$ .

- 16.40 In Chapter 8, you learned about the colligative properties of solutions. Which of the colligative properties is best suited for determining the molar mass of a polymer? Why?

- 16.41 Teflon is formed by a radical addition reaction involving the monomer tetrafluoroethylene. Show the mechanism for this reaction.

- 16.42 Vinyl chloride ( $\text{H}_2\text{C}=\text{CHCl}$ ) undergoes copolymerization with 1,1-dichloroethylene ( $\text{H}_2\text{C}=\text{CCl}_2$ ) to form a polymer commercially known as Saran. Draw the structure of the polymer, showing the repeating monomer units.

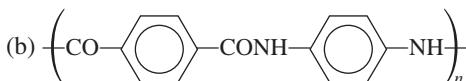
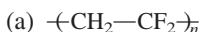
- 16.43 Kevlar is a copolymer used in bulletproof vests. It is formed in a condensation reaction between 1,4-diaminobenzene and 1,4-dicarboxybenzene.



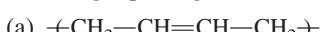
Sketch a portion of the polymer chain showing several monomer units. Write the overall equation for the condensation reaction.

- 16.44 Describe the formation of polystyrene.

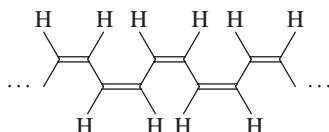
- 16.45 Deduce plausible monomers for polymers with the following repeating units:



- 16.46 Deduce plausible monomers for polymers with the following repeating units:



- 16.47 The conductivity of *cis*-polyacetylene ( $1.7 \times 10^{-9}$  S cm $^{-1}$ ) is much smaller than that of *tran*-polyacetylene (see page 832). Can you explain this difference by examining the structures of these two polymers? The structure of *cis*-polyacetylene is



### Proteins Are Polymer Chains Composed of Amino Acid Monomers

- 16.48 Discuss the characteristics of an amide group and its importance in protein structure.
- 16.49 Briefly explain the phenomenon of cooperativity exhibited by the hemoglobin molecule in binding oxygen.
- 16.50 Why is sickle cell anemia called a molecular disease?
- 16.51 Draw the structures of the dipeptides that can be formed from the reaction between the amino acids glycine and valine.
- 16.52 Draw the structures of the dipeptides that can be formed from the reaction between the amino acids glycine and lysine.
- 16.53 The amino acid glycine can be condensed to form a polymer called polyglycine. Draw the repeating monomer unit.
- 16.54 The folding of a polypeptide chain depends not only on its amino acid sequence but also on the nature of the solvent. Discuss the types of interactions that might occur between water molecules and the amino acid residues of the polypeptide chain. Which groups would be exposed on the exterior of the protein in contact with water and which groups would be buried in the interior of the protein?
- 16.55 The following are data obtained on the rate of product formation of an enzyme-catalyzed reaction:

Temperature (°C)	Rate of Product Formation (M s $^{-1}$ )
10	0.0025
20	0.0048
30	0.0090
35	0.0086
45	0.0012

Comment on the dependence of the rate on temperature. (No calculations are required.)

- 16.56 The pitch of a helix is the distance required for the helix to make a full turn. The average pitch of an  $\alpha$  helix (Figure 16.21) is 5.4 Å. Assuming this pitch is

the same for human hair and that hair grows at the rate of 0.6 inches per month, how many turns of the  $\alpha$  helix are generated each second (assume 1 month = 30 days).

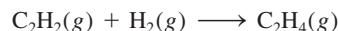
### DNA and RNA Are Polymers Composed of Nucleic Acids

- 16.57 What is the difference between ribose and deoxyribose?
- 16.58 A standard DVD can store approximately 4.7 gigabytes of information, where each byte consists of 8 bits. Each bit can be either "0" or "1". Could the entire human genome be stored on a single DVD?
- 16.59 Describe the role of hydrogen bonding in maintaining the double-helical structure of DNA.

### Additional Problems

- 16.60 Draw all the possible structural isomers for the molecule having the formula C<sub>7</sub>H<sub>7</sub>Cl. The molecule contains one benzene ring.
- 16.61 Given
- $$\text{C}_2\text{H}_4(g) + 3\text{O}_2(g) \longrightarrow 2\text{CO}_2(g) + 2\text{H}_2\text{O}(l)$$
- $$\Delta H^\circ = -1411 \text{ kJ mol}^{-1}$$
- $$2\text{C}_2\text{H}_2(g) + 5\text{O}_2(g) \longrightarrow 4\text{CO}_2(g) + 2\text{H}_2\text{O}(l)$$
- $$\Delta H^\circ = -2599 \text{ kJ mol}^{-1}$$
- $$\text{H}_2(g) + \text{O}_2(g) \longrightarrow \text{H}_2\text{O}(l)$$
- $$\Delta H^\circ = -285.8 \text{ kJ mol}^{-1}$$

calculate the enthalpy change of hydrogenation for acetylene:

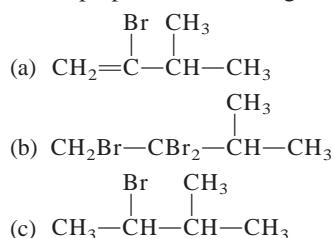


- 16.62 State which member of each of the following pairs of compounds is the more reactive and explain why:  
(a) propane and cyclopropane, (b) ethylene and methane, and (c) acetaldehyde and acetone.
- 16.63 State which of the following types of compounds can form hydrogen bonds with water molecules:  
(a) carboxylic acids, (b) alkenes, (c) ethers, (d) aldehydes, (e) alkanes, (f) amines.
- 16.64 An organic compound is found to contain 37.5 percent carbon, 3.2 percent hydrogen, and 59.3 percent fluorine by mass. The following pressure and volume data were obtained for 1.00 g of this substance at 90°C:

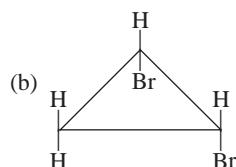
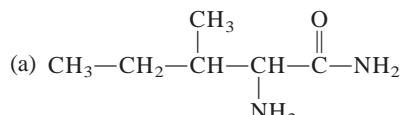
P (bar)	V (L)
2.0	0.332
1.5	0.409
1.0	0.564
0.50	1.028

- The molecule is known to have a dipole moment of zero. (a) What is the empirical formula of this substance? (b) Does this substance behave as an ideal gas? (c) What is its molecular formula? (d) Draw the Lewis structure of this molecule and describe its geometry. (e) What is the systematic name of this compound?
- 16.65 State at least one commercial use for each of the following compounds: (a) 2-propanol (isopropanol), (b) acetic acid, (c) naphthalene, (d) methanol, (e) ethanol, (f) ethylene glycol, (g) methane, and (h) ethylene.
- 16.66 How many liters of air (78 percent N<sub>2</sub>, 22 percent O<sub>2</sub> by volume) at 20°C and 1.00 bar are needed for the complete combustion of 1.0 L of octane, C<sub>8</sub>H<sub>18</sub>, a typical gasoline component that has a density of 0.70 g mL<sup>-1</sup>?
- 16.67 How many carbon-carbon sigma bonds are present in each of the following molecules? (a) 2-butyne, (b) anthracene (see Figure 16.5), and (c) 2,3-dimethylpentane.
- 16.68 How many carbon-carbon sigma bonds are present in each of the following molecules: (a) benzene, (b) cyclobutane, and (c) 2-methyl-3-ethylpentane?
- 16.69 The combustion of 20.63 mg of compound Y, which contains only C, H, and O, with excess oxygen gave 57.94 mg of CO<sub>2</sub> and 11.85 mg of H<sub>2</sub>O. (a) Calculate how many milligrams of C, H, and O were present in the original sample of Y. (b) Derive the empirical formula of Y. (c) Suggest a plausible structure for Y if the empirical formula is the same as the molecular formula.
- 16.70 Draw all the structural isomers of compounds with the formula C<sub>4</sub>H<sub>8</sub>Cl<sub>2</sub>. Indicate which isomers are chiral, and give them systematic names.
- 16.71 Discuss the importance of hydrogen bonding in biological systems. Use proteins and nucleic acids as examples.
- 16.72 Proteins vary widely in structure, whereas nucleic acids have rather uniform structures. How do you account for this major difference?
- 16.73 If untreated, fevers of 40°C or higher may lead to brain damage. Why?
- 16.74 The “melting point” of a DNA molecule is the temperature at which the double-helical strand breaks apart. Suppose you are given two DNA samples. One sample contains 45 percent C-G base pairs, and the other contains 64 percent C-G base pairs. The total number of bases is the same in each sample. Which of the two samples has a higher melting point? Why?
- 16.75 When fruits such as apples and pears are cut, the exposed parts begin to turn brown. This is the result of an oxidation reaction catalyzed by enzymes present in the fruit. Often the browning action can be prevented or slowed by adding a few drops of lemon juice to the exposed areas. What is the chemical basis for this treatment?
- 16.76 “Dark meat” and “white meat” are one’s choices when eating a turkey. Explain what causes the meat to assume different colors. (*Hint:* The more active muscles in a turkey have a higher rate of metabolism and need more oxygen.)
- 16.77 Nylon can be destroyed easily by strong acids. Explain the chemical basis for the destruction. (*Hint:* The products are the starting materials of the polymerization reaction.)
- 16.78 Despite what you may have read in science fiction novels or seen in horror movies, it is extremely unlikely that insects can ever grow to human size. Why? (*Hint:* Insects do not have hemoglobin molecules in their blood.)
- 16.79 How many different tripeptides can be formed by lysine and alanine?
- 16.80 Chemical analysis shows that hemoglobin contains 0.34 percent Fe by mass. What is the minimum possible molar mass of hemoglobin? The actual molar mass of hemoglobin is four times this minimum value. What conclusion can you draw from these data?
- 16.81 What kind of intermolecular forces are responsible for the aggregation of hemoglobin molecules that leads to sickle cell anemia? Draw structures of the nucleotides containing the following components: (a) deoxyribose and cytosine, and (b) ribose and uracil.
- 16.82 When a nonapeptide (containing nine amino acid residues) isolated from rat brains was hydrolyzed, it gave the following smaller peptides as identifiable products: Gly-Ala-Phe, Ala-Leu-Val, Gly-Ala-Leu, Phe-Glu-His, and His-Gly-Ala. Reconstruct the amino acid sequence in the nonapeptide, giving your reasons. (Remember the convention for writing peptides.)
- 16.83 At neutral pH, amino acids exist as dipolar ions. Using glycine as an example, and given that the pK<sub>a</sub> of the carboxyl group is 2.3 and that of the ammonium group is 9.6, predict the predominant form of the molecule at pH 1, 7, and 12. Justify your answers using the Henderson-Hasselbalch equation (Equation 12.2).
- 16.84 The combustion of 3.795 mg of liquid B, which contains only C, H, and O, with excess oxygen gave 9.708 mg of CO<sub>2</sub> and 3.969 mg of H<sub>2</sub>O. In a molar mass determination, 0.205 g of B vaporized at 1.00 bar and 200.0°C and occupied a volume of 89.8 mL. Derive the empirical formula, molar mass, and molecular formula of B, and draw three plausible structures.

- 16.85 Beginning with 3-methyl-1-butyne, show how you would prepare the following compounds:



- 16.86 Indicate the asymmetric carbon atoms in the following compounds:



- 16.87 Suppose benzene contained three distinct single bonds and three distinct double bonds. How many different isomers would there be for dichlorobenzene ( $\text{C}_6\text{H}_4\text{Cl}_2$ )? Draw all your proposed structures.

- 16.88 Write the structural formula of an aldehyde that is a structural isomer of acetone.

- 16.89 Draw structures for the following compounds:  
(a) cyclopentane, (b) *cis*-2-butene, (c) 2-hexanol,  
(d) 1,4-dibromobenzene, and (e) 2-butyne.

- 16.90 Name the classes to which the following compounds belong: (a)  $\text{C}_4\text{H}_9\text{OH}$ , (b)  $\text{CH}_3\text{OC}_2\text{H}_5$ , (c)  $\text{C}_2\text{H}_5\text{CHO}$ ,  
(d)  $\text{C}_6\text{H}_5\text{COOH}$ , and (e)  $\text{CH}_3\text{NH}_2$ .

- 16.91 Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) and dimethyl ether, ( $\text{CH}_3\text{OCH}_3$ ) are structural isomers. Compare their melting points, boiling points, and solubilities in water. Give a molecular explanation of any differences.

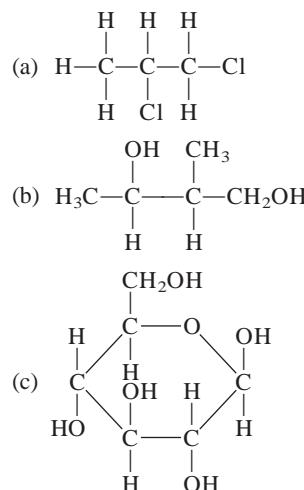
- 16.92 Amines are Brønsted bases. The unpleasant smell of fish is due to the presence of certain amines. Explain why cooks often add lemon juice to suppress the odor of fish (in addition to enhancing the flavor).

- 16.93 You are given two bottles, each containing a colorless liquid. You are told that one liquid is cyclohexane and the other is benzene. Suggest one chemical test that would allow you to distinguish between these two liquids.

- 16.94 Give the chemical names of the following organic compounds, and write their formulas: marsh gas, grain alcohol, wood alcohol, rubbing alcohol, antifreeze, mothballs, and the chief ingredient of vinegar.

- 16.95 The compound  $\text{CH}_3\text{—C}\equiv\text{C—CH}_3$  is hydrogenated to an alkene using platinum as the catalyst. Predict whether the product is the pure *trans* isomer, the pure *cis* isomer, or a mixture of *cis* and *trans* isomers. Based on your prediction, comment on the mechanism of the heterogeneous catalysis.

- 16.96 How many asymmetric carbon atoms are present in each of the following compounds?



- 16.97 2-Propanol (or isopropanol) is prepared by reacting propylene ( $\text{CH}_3\text{CHCH}_2$ ) with sulfuric acid, followed by treatment with water. (a) Show the sequence of steps leading to the product. What is the role of the sulfuric acid? (b) Draw the structure of an alcohol that is an isomer of isopropanol. (c) Is isopropanol a chiral molecule? (d) What property of isopropanol makes it useful as a rubbing alcohol?

- 16.98 When a mixture of methane and bromine vapor is exposed to light, the following reaction occurs slowly:  $\text{CH}_4(g) + \text{Br}_2(g) \longrightarrow \text{CH}_3\text{Br}(g) + \text{HBr}(g)$ . Suggest a mechanism for this reaction. (Hint: Bromine vapor is deep red; methane is colorless.)

- 16.99 What is the field strength (in tesla) needed to generate a  $^1\text{H}$  frequency of 600 MHz. The gyromagnetic ratio for  $^1\text{H}$  is  $26.75 \times 10^7 \text{ T}^{-1} \text{ s}^{-1}$ .

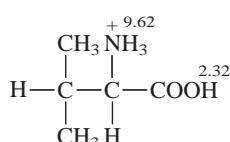
- 16.100 For a 400 MHz NMR spectrometer, what is the difference in resonance frequencies for two protons whose  $\delta$  values differ by 2.5 ppm.

- 16.101 For each of the following molecules, state how many  $^1\text{H}$  NMR peaks occur and whether each peak is a singlet, doublet, triplet, etc. (a)  $\text{CH}_3\text{OCH}_3$ , (b)  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ , (c)  $\text{C}_2\text{H}_6$ , (d)  $\text{CH}_3\text{F}$ , and (e)  $\text{CH}_3\text{COOC}_2\text{H}_5$ .

- 16.102 Sketch the  $^1\text{H}$  NMR spectrum (including splittings) of 2-methylpropanol [isobutyl alcohol— $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$ ], given the following chemical shift data:  $-\text{CH}_3$ : 0.89 ppm,  $-\text{CH}$ : 1.67 ppm,  $-\text{CH}_2$ : 3.27 ppm, and  $-\text{OH}$ : 4.50 ppm.

- 16.103 The  $^1\text{H}$  NMR spectrum of methylbenzene (or toluene) has been recorded at 60 MHz and 1.41 T. It consists of two peaks, one due to the methyl protons and one due to the aromatic protons. (a) What would be the magnetic field at 300 MHz? (b) At 60 MHz, the resonance frequencies are 140 MHz for the methyl protons and 430 MHz for the aromatic protons. What would the frequencies be if the spectrum were recorded on a 300-MHz spectrometer?
- 16.104 2-Butanone can be reduced to 2-butanol by reagents such as lithium aluminum hydroxide ( $\text{LiAlH}_4$ ). (a) Write the formula of the product. Is it chiral? (b) In reality, the product does not exhibit optical activity. Explain.
- 16.105 In Lewis Carroll's tale *Through the Looking Glass*, Alice wonders whether "looking-glass milk" on the other side of the mirror would be fit to drink. Based on your knowledge of chirality and enzyme action, comment on the validity of Alice's concern.
- 16.106 Nylon was designed to be a synthetic silk. (a) The average molar mass of a batch of nylon-66 is 12,000 g mol $^{-1}$ . How many monomer units are there in this sample? (b) Which part of nylon's structure is similar to a polypeptide's structure? (c) How many different tripeptides (made up of three amino acids) can be formed from the amino acids alanine (Ala), glycine (Gly), and serine (Ser), which account for most of the amino acids in silk?
- 16.107 The enthalpy change in the denaturation of a certain protein is 125 kJ mol $^{-1}$ . If the entropy change is 397 J K $^{-1}$  mol $^{-1}$ , calculate the minimum temperature at which the protein would denature spontaneously.
- 16.108 When deoxyhemoglobin crystals are exposed to oxygen, they shatter. On the other hand, deoxymyoglobin crystals are unaffected by oxygen. Explain. (Myoglobin is made up of only one of the four subunits, or polypeptide chains, of hemoglobin.)
- 16.109 Depending on the experimental conditions, the measurement of the molar mass of hemoglobin in an aqueous solution may show that the solution is monodisperse or polydisperse. Explain.
- 16.110 In protein synthesis, the selection of a particular amino acid is determined by the so-called genetic code, or a sequence of three bases in DNA. Could a sequence of only two bases unambiguously determine the selection of 20 amino acids found in proteins? Explain.

- 16.111 Consider the fully protonated amino acid valine:



where the numbers denote the  $pK_a$  values.

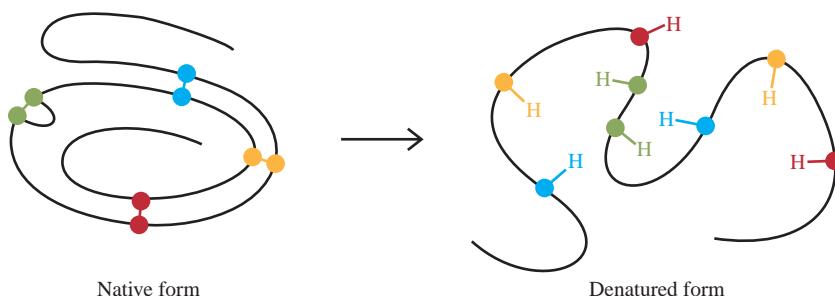
- (a) Which of the two groups ( $-\text{NH}_3^+$  or  $-\text{COOH}$ ) is more acidic? (b) Calculate the predominant form of valine at pH 1.0, 7.0, and 12.0. (c) Calculate the isoelectric point of valine. (Hint: See Problem 12.110).

- 16.112 Consider the formation of a dimeric protein

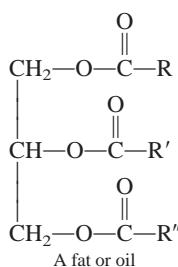


At 25°C, we have  $\Delta H^\circ = 17 \text{ kJ mol}^{-1}$  and  $\Delta S^\circ = 65 \text{ J mol}^{-1} \text{ K}^{-1}$ . Is the dimerization favored at this temperature? Comment on the effect of lowering the temperature. Does your result explain why some enzymes lose their activities under cold conditions?

- 16.113 The left side of the accompanying diagram shows the structure of the enzyme ribonuclease in its native form. The three-dimensional protein structure is maintained in part by the disulfide bond ( $-\text{S}-\text{S}-$ ) between the amino acid residues (each color sphere represents an S atom). Using certain denaturants, the compact structure is destroyed and the disulfide bonds are converted to sulfhydryl group ( $-\text{SH}$ ) shown on the right side of the arrow. (a) Describe the bonding scheme in the disulfide bond in terms of hybridization. (b) Which amino acid in Table 16.6 contains the  $-\text{SH}$  group? (c) Predict the signs of  $\Delta H$  and  $\Delta S$  for the denaturation process. If denaturation is induced by a change in temperature, show why a rise in temperature would favor denaturation. (d) The sulfhydryl groups can be oxidized (i.e., removing the H atoms) to form the disulfide bonds. If the formation of the disulfide bonds is totally random between any two  $-\text{SH}$  groups, what is the fraction of the regenerated protein structures that corresponds to the native form. (e) An effective remedy to deodorize a dog that has been sprayed by a skunk is to rub the affected areas with a solution of an oxidizing agent such as hydrogen peroxide. What is the chemical basis for this action? (Hint: An odiferous component of a skunk's secretion is 2-butene-1-thiol,  $\text{CH}_3\text{CH}=\text{CHCH}_2\text{SH}$ .)

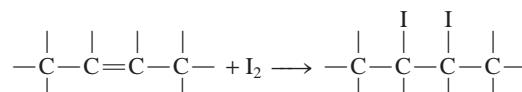


- 16.114 Write the structures of three alkenes that yield 2-methylbutane on hydrogenation.
- 16.115 An alcohol was converted to a carboxylic acid with acidic potassium dichromate. A 4.46-g sample of the acid was added to 50.0 mL of 2.27 M NaOH, and the excess NaOH required 28.7 mL of 1.86 M HCl for neutralization. What is the molecular formula of the alcohol?
- 16.116 Write the skeletal structural formulas of the alcohols with the formula  $C_6H_{13}O$  and indicate those that are chiral.
- 16.117 Fat and oil are names for the same class of compounds, called triglycerides, which contain three ester groups:



where R, R', and R'' represent long hydrocarbon chains. (a) Suggest a reaction that leads to the formation of a triglyceride molecule, starting with glycerol (see page 338 for the structure of glycerol) and carboxylic acids. (b) In the old days, soaps were made by hydrolyzing animal fat with lye (a sodium hydroxide solution). Write an equation for this reaction. (c) The difference between fats and oils is that fats are solids at room temperature, whereas the oils are liquids. Fats are usually produced by

animals, whereas oils are commonly found in plants. The melting points of these substances are determined by the number of C=C bonds (or the extent of unsaturation) present—the larger the number of C=C bonds, the lower the melting point and the more likely that the substance is a liquid. Explain. (d) One way to convert liquid oil to solid fat is to hydrogenate the oil, a process by which some or all of the C=C bonds are converted to C—C bonds. This procedure prolongs the shelf life of the oil by removing the more reactive C=C group and facilitates packaging. How would you carry out such a process (that is, what reagents and catalyst would you employ)? (e) The degree of unsaturation of oil can be determined by reacting the oil with iodine, which reacts with the C=C bond as follows:



The procedure is to add a known amount of iodine to the oil and allow the reaction to go to completion. The amount of excess (unreacted) iodine is determined by titrating the remaining iodine with a standard sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) solution:



The number of grams of iodine that react with 100 g of oil is called the *iodine number*. In one case, 43.8 g of  $\text{I}_2$  was treated with 35.3 g of corn oil. The excess iodine required 20.6 mL of a 0.142 M  $\text{Na}_2\text{S}_2\text{O}_3$  for neutralization. Calculate the iodine number of the corn oil.

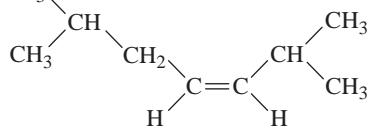
## Answers to Practice Exercises

**16.1** 4,6-diethyl-2-methyloctane

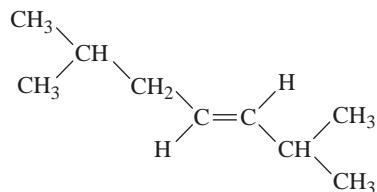


**16.2**  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}(\text{C}_2\text{H}_5)-\text{CH}_2-\text{CH}_3$

**16.3**  $\text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-\text{C}(\text{H})=\text{C}(\text{H})-\text{CH}(\text{CH}_3)-\text{CH}_3$

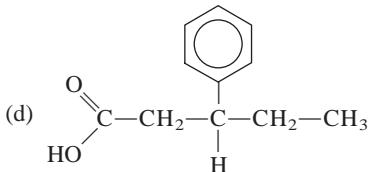
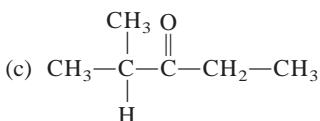
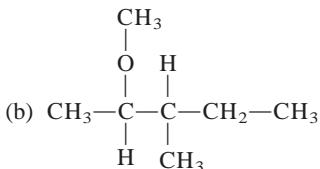
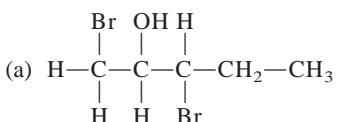


2,6-dimethyl-*cis*-3-heptene



2,6-dimethyl-*trans*-3-heptene

**16.4**



**16.5**  $\text{CH}_3\text{CH}_2\text{COOCH}_3$  and  $\text{H}_2\text{O}$

# 17

Chapter

## Nuclear Chemistry



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## 17.1 | Nuclear Chemistry Is the Study of Changes Involving Atomic Nuclei

### Radioactivity and Nuclear Decay

In 1895, the German physicist Wilhelm Röntgen<sup>1</sup> noticed that cathode rays (Section 0.2) caused glass and metals to emit highly energetic radiation that penetrated matter, darkened covered photographic plates, and caused a variety of substances to fluoresce. Because these rays could not be deflected by a magnet, they could not contain charged particles as cathode rays do. Röntgen called them X-rays because their nature was unknown. Not long after Röntgen's discovery, Antoine Becquerel,<sup>2</sup> a professor of physics in Paris, began to study the fluorescent properties of substances. Purely by accident, he found that exposing thickly wrapped photographic plates to a certain uranium compound caused them to darken, even without the stimulation of cathode rays. Like X-rays, the rays from the uranium compound were highly energetic and could not be deflected by a magnet, but they differed from X-rays because they arose spontaneously. One of Becquerel's students, Marie Curie,<sup>3</sup> suggested the name **radioactivity** to describe this *spontaneous emission of particles and/or radiation*. Since then, any element that spontaneously emits radiation is said to be **radioactive**.

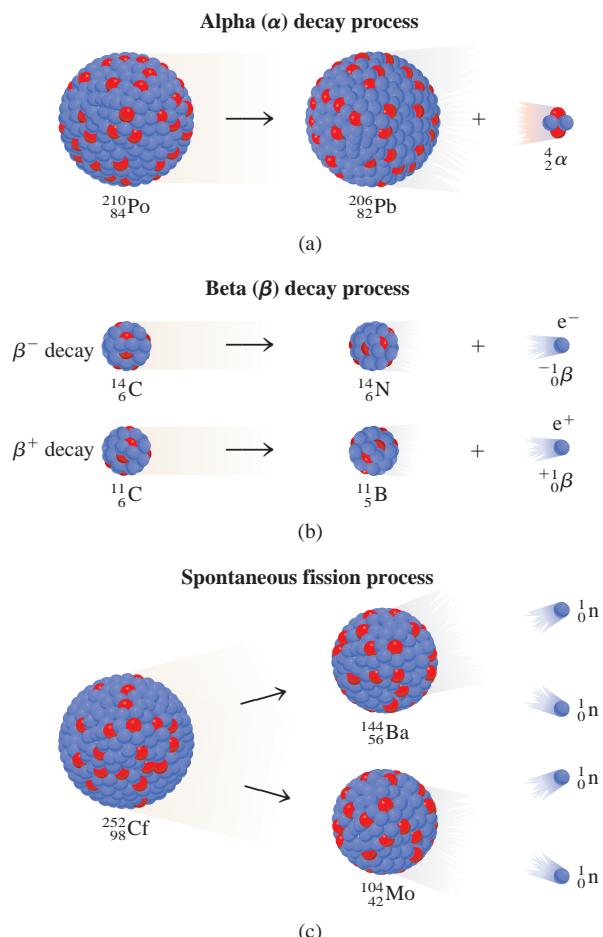
Certain elements are radioactive because their nuclei are unstable and spontaneously decay through the ejection (or capture) of subatomic particles, often accompanied by the emission of high-energy electromagnetic radiation. The principal radioactive decay processes are alpha decay, beta decay, gamma emission, and spontaneous fission.

- ▶ **Alpha ( $\alpha$ ) decay** is the emission by an unstable nucleus of *alpha ( $\alpha$ ) particles*, which are helium-4 nuclei. Alpha decay occurs only in some very heavy nuclei in which the mass number (the total number of neutrons and protons) exceeds about 140. Emission of an  $\alpha$  particle decreases the atomic number ( $Z$ ) of the nucleus by 2 and its atomic mass number ( $A$ ) by 4. Polonium-210 ( $^{210}_{84}\text{Po}$ ), for example, decays spontaneously to lead-206 ( $^{206}_{82}\text{Pb}$ ), through the emission of an  $\alpha$  particle [Figure 17.1(a)].
- ▶ **Beta ( $\beta$ ) decay** can occur in two different ways. In  $\beta^-$  decay, a neutron in the nucleus spontaneously decays into a proton with the simultaneous emission from the nucleus of an electron and a massless, neutral subatomic particle called an *antineutrino ( $\bar{\nu}$ )*. Carbon-14 ( $^{14}_6\text{C}$ ), for example, spontaneously decays into nitrogen-14 ( $^{14}_7\text{N}$ ) through the emission of an electron ( $\beta^-$  particle). In contrast,  $\beta^+$  decay (also called *positron emission*) occurs when a proton in the nucleus spontaneously decays into a neutron with the simultaneous

1. Wilhelm Conrad Röntgen (1845–1923). German physicist. He received the Nobel Prize in Physics in 1901 for the discovery of X rays.

2. Antoine Henri Becquerel (1852–1908). French physicist. He was awarded the Nobel Prize in Physics in 1903 for discovering radioactivity in uranium.

3. Marie (Marya Skłodowska) Curie (1867–1934). Polish-born chemist and physicist. In 1903, she and her French husband, Pierre Curie, were awarded the Nobel Prize in Physics for their work on radioactivity. In 1911, she again received the Nobel Prize, this time in chemistry, for her work on the radioactive elements radium and polonium. She is one of only three people to have received two Nobel prizes in science. Despite her great contribution to science, her nomination to the French Academy of Sciences in 1911 was rejected by one vote because she was a woman! Her daughter Irene and son-in-law Frédéric Joliot-Curie shared the Nobel Prize in Chemistry in 1935.



**Figure 17.1** Examples of nuclear decay processes: (a) alpha decay, (b) beta decay, and (c) spontaneous fission.

ejection from the nucleus of a **positron** (or *antielectron*)<sup>4</sup> and a **neutrino** ( $\nu$ ). Carbon-11 ( $^{11}_6\text{C}$ ), for example, decays to boron-11 ( $^{11}_5\text{B}$ ) through the emission of a positron. Figure 17.1(b) illustrates these two beta decay processes. The process of  $\beta^-$  decay increases the atomic number ( $Z$ ) of the nucleus by 1 (a neutron is converted into a proton) but leaves the mass number ( $N$ ) unchanged. In writing nuclear equations, the  $\beta^-$  particle is denoted by the symbol  $^{-1}_0\beta$ . Likewise, the emission of a positron (denoted by  $^{+1}_0\beta$ ) in  $\beta^+$  decay also leaves the mass number unchanged but *decreases* the atomic number by 1. A decay process closely related to positron emission is

4. In the Standard Model of particle physics, every particle of ordinary matter has an *antimatter* counterpart, called an *antiparticle*. The antiparticle has some properties in common with its matter counterpart and some properties that are exactly opposite. For example, the antiparticles of the proton and electron, the *antiproton* and *positron*, are opposite in charge to their matter counterparts but identical in mass and intrinsic spin. Neutral particles, such as the neutron and the massless neutrino have antimatter counterparts (the antineutron and antineutrino) that are identical in mass and spin but differ in the precise way they interact with other particles. Some neutral particles, such as the *neutral pion*, are their own antiparticle. When a particle and its corresponding antiparticle collide, they annihilate one another and their combined mass-energy is converted to another form—either into a photon of high-energy electromagnetic radiation or into lighter subatomic particles with greater kinetic energy.

**orbital electron capture** in which the nucleus captures an orbital electron. The orbital electron combines with a proton in the nucleus to form a neutron and a neutrino, which is ejected.

- ▶ **Gamma ( $\gamma$ ) emission** is the emission of very high energy electromagnetic radiation by an unstable nucleus during the process of nuclear decay. Like electrons in atoms, nuclei have an energy-shell structure, that is, a nucleus can only exist in certain well-defined quantum states. When a nucleus decays (for example, through an  $\alpha$ - or  $\beta$ -decay process), the transformed nucleus is generally left in an excited quantum state, which then decays to the ground state through the emission of a high-energy photon called *gamma radiation*. Although  $\gamma$  radiation is generally higher in energy and frequency than X-rays, the term refers primarily to its origin from nuclear emission rather than its specific location on the electromagnetic spectrum. Deexcitation of the nucleus can also occur through the related process of **internal conversion** in which the excess energy is transferred to a core orbital electron, which is subsequently ejected from the atom.
- ▶ **Spontaneous fission** is the spontaneous decay of heavy nuclei into two or more smaller nuclei and some neutrons [Figure 17.1(c)]. The smaller nuclei are generally radioactive and decay through a series of  $\beta$ -decay processes until a stable nuclear state is obtained.

These nuclear decay processes describe the *spontaneous decay* of a nucleus, that is, they occur without external input of energy or matter. Radioactive decay can also be induced by the bombardment of nuclei by neutrons, protons, or other nuclei, in a process called **nuclear transmutation**. An important example of nuclear transmutation is the conversion of atmospheric  $^{14}\text{N}$  into  $^{14}\text{C}$  and  $^1\text{H}$ , which results when the nitrogen isotope captures a neutron (from the sun). In some cases, heavier elements are synthesized from lighter elements. This type of transmutation occurs naturally in outer space but can also be achieved artificially, as discussed in Section 17.4.

Spontaneous radioactive decay and nuclear transmutation are *nuclear reactions*, which differ significantly from ordinary chemical reactions. Table 17.1 summarizes the differences.

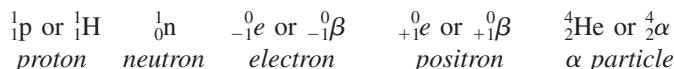
**Table 17.1 Comparison of Chemical Reactions and Nuclear Reactions**

Chemical Reactions	Nuclear Reactions
<ol style="list-style-type: none"> <li>Atoms are rearranged by the breaking and forming of chemical bonds.</li> <li>Only electrons in atomic or molecular orbitals are involved in the breaking and forming of bonds.</li> <li>Reactions are accompanied by absorption or release of relatively small amounts of energy.</li> <li>Rates of reaction are influenced by temperature, pressure, concentration, and catalysts.</li> </ol>	<ol style="list-style-type: none"> <li>Elements (or isotopes of the same elements) are converted from one to another.</li> <li>Protons, neutrons, electrons, and other elementary particles may be involved.</li> <li>Reactions are accompanied by absorption or release of tremendous amounts of energy.</li> <li>Rates of reaction normally are not affected by temperature, pressure, and catalysts.</li> </ol>

## Balancing Nuclear Reactions

To discuss nuclear reactions in any depth, we need to understand how to write and balance the equations. Writing a nuclear equation differs somewhat from writing equations for chemical reactions. In addition to writing the symbols for the various chemical elements, we must also explicitly indicate protons, neutrons, and electrons. In fact, we must show the numbers of protons and neutrons present in *every* species in such an equation.

In writing nuclear reactions, the symbols for the elementary particles are as follows:



In accordance with the notation used in Section 0.2, the superscript in each case denotes the mass number  $A$  (the total number of neutrons and protons present) and the subscript is the atomic number  $Z$  (the number of protons). Thus, the atomic number of a proton is 1, because there is one proton present, and the mass number is also 1, because there is one proton but no neutrons present. On the other hand, the mass number of a neutron is 1, but its atomic number is 0 because there are no protons present. For the electron, the mass number is 0 (there are neither protons nor neutrons present), but the “atomic number” is assigned a value  $-1$ , because the electron possesses a unit negative charge.

The symbol  ${}_{-1}^0e$  represents an electron in or from an atomic orbital. The symbol  ${}_{-1}^0\beta$  is reserved for an electron that, although physically identical to any other electron, is emitted from a nucleus in  $\beta^-$  decay and does not originate from an atomic orbital. Similarly, the symbol  ${}_{+1}^0\beta$  specifically denotes a positron emitted by a nucleus in  $\beta^+$  decay.

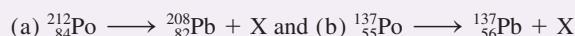
In balancing any nuclear equation, we must observe the following rules:

- ▶ The total number of protons plus neutrons in the products and in the reactants must be the same (conservation of mass number).
- ▶ The total number of nuclear charges in the products and in the reactants must be the same (conservation of atomic number).

If we know the atomic numbers and mass numbers of all the species but one in a nuclear equation, we can identify the unknown species by applying these rules, as shown in Example 17.1, which illustrates how to balance nuclear decay equations.

### Example 17.1

Identify the product X by balancing the following nuclear equations:



**Strategy** In a balanced nuclear equation, the sum of the atomic numbers and the sum of the mass numbers must match on both sides of the equation. To identify X, therefore, subtract the atomic numbers and mass numbers of the known products from those of the reactants.

—Continued

*Continued—*

**Solution** (a) The mass number is 212 and the atomic number is 84 on the left-hand side of the equation, and 208 and 82, respectively, on the right-hand side. Thus, X must have a mass number of  $212 - 208 = 4$  and an atomic number of  $84 - 82 = 2$ , which means that it is an  $\alpha$  particle. The balanced equation is



(b) In this case, the mass number is the same on both sides of the equation, but the atomic number of the product is 1 more than that of the reactant. Thus, X must have a mass number of  $137 - 137 = 0$  and an atomic number of  $55 - 56 = -1$ , which means that it is a  $\beta^-$  particle. Because  $\beta^-$  decay increases the atomic number of the nucleus by 1, the balanced equation is



**Check** The equations in (a) and (b) are balanced for nuclear particles but not for electrical charges. To balance the charges, we would need to add two electrons on the right-hand side of (a) and express barium as a cation ( $\text{Ba}^+$ ) in part (b).

**Practice Exercise** Identify X in the following nuclear equation:



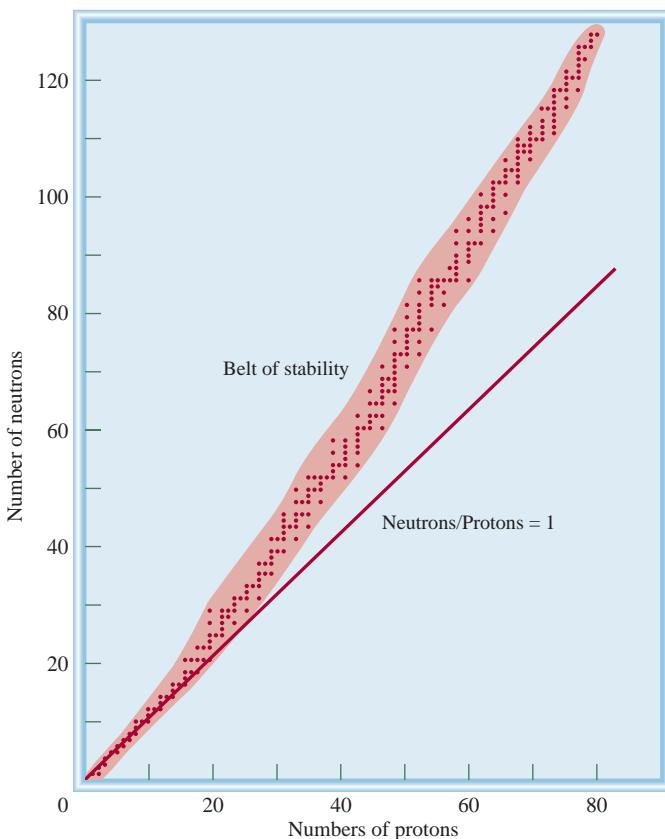
## 17.2 | The Stability of a Nucleus Is Determined Primarily by Its Neutron-to-Proton Ratio

The nucleus occupies a very small portion of the total volume of an atom, but it contains most of the mass of the atom because both the protons and the neutrons reside there. In studying the stability of the atomic nucleus, it is helpful to know something about its density, because it reveals how tightly the particles are packed together. As a sample calculation, assume that a nucleus has a radius of approximately 5 fm (1 femtometer = 1 fm =  $10^{-15}$  m) and a mass of  $1 \times 10^{-22}$  g. These values correspond roughly to a nucleus containing 30 protons and 30 neutrons. Density is mass/volume, and we can calculate the volume from the known radius (the volume of a sphere is  $4\pi r^3/3$ , where  $r$  is the radius of the sphere). First, convert the femtometer units to centimeter (1 fm =  $10^{-13}$  cm), calculate the density in g cm<sup>-3</sup>:

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{1 \times 10^{-22} \text{ g}}{4\pi(5 \times 10^{-13} \text{ cm})^3/3} = 2 \times 10^{13} \text{ g cm}^{-3}$$

This is exceedingly dense. The highest density known for an element is 22.6 g cm<sup>-3</sup>, for osmium (Os). Thus, the average atomic nucleus is roughly  $9 \times 10^{12}$  (or 9 trillion) times more dense than the densest element known!

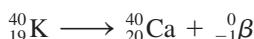
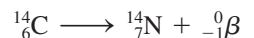
The enormously high density of the nucleus prompts us to wonder what holds the protons and neutrons (collectively called **nucleons**) together so tightly. According to *Coulomb's law*, we know that like charges repel and unlike charges attract one another. We would thus expect the protons to repel one another strongly, particularly when we consider how close they must be to each other. The explanation for this seeming paradox is that, in addition to the repulsive coulomb force, there are also very short-range attractions between nucleons. These short-range attractions are due to the



**Figure 17.2** Plot of the number of neutrons versus the number of protons in the nucleus for various stable isotopes, represented by dots. The straight line represents the points at which the neutron-to-proton ratio equals 1. The shaded area shows the belt of stability.

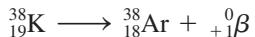
*strong force*—the strongest of the four fundamental forces of nature (see Section 0.1). The stability of any nucleus depends on the relative magnitudes of the coulombic repulsion and the strong force attraction. If repulsion exceeds attraction, the nucleus disintegrates, emitting particles and/or radiation. If strong forces prevail, the nucleus is stable. As in chemical reactions, there is generally a significant activation barrier to nuclear decay, so unstable nuclei do not decay instantaneously, even if the net decay process is energetically favorable.

The graph in Figure 17.2 plots the number of neutrons versus the number of protons in various isotopes. The stable nuclei are located in an area of the graph known as the *belt of stability*. Most radioactive nuclei lie outside this belt. The principal factor in predicting whether a given nucleus is stable is the *neutron-to-proton ratio* (*n/p*), which is the number of neutrons divided by the number of protons in a given nucleus. For stable atoms of elements having low atomic number, the *n/p* values are close to 1. As the atomic number increases, the neutron-to-proton ratios of the stable nuclei become greater than 1. Above the belt of stability, the nuclei have higher neutron-to-proton ratios than those within the belt (for the same number of protons). To lower this ratio (and hence move down toward the belt of stability), these nuclei can undergo beta decay, which leads to an increase in the number of protons in the nucleus and a simultaneous decrease in the number of neutrons. Some examples are

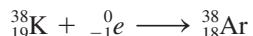


In the beta decay of carbon-14, the *n/p* ratio decreases from  $8/6 = 4/3$  to  $7/7 = 1$ .

Below the belt of stability, the nuclei have lower neutron-to-proton ratios than those in the belt (for the same number of protons). To increase this ratio (and hence move up toward the belt of stability), these nuclei can decay by either positron emission ( $\beta^+$  decay) or orbital electron capture. For example, potassium-38 ( $n/p = 19/19 = 1$ ) decays to argon-38 ( $n/p = 20/18 = 10/9$ ) by positron emission,



or by electron capture,



(We use the symbol  ${}_{-1}^0e$  to denote the electron in the electron capture equation, not  ${}_{-1}^0\beta$ , because  ${}_{-1}^0e$  represents an orbital electron, not the product of beta decay.)

The shape of the belt of stability can be understood by recognizing that the protons and neutrons can, to a good approximation, be described as if they occupy individual quantum energy levels in much the same way that electrons in multielectron atoms are described as occupying individual electron orbitals (Chapter 2). This **shell model** of the nucleus was developed independently by Maria Goeppert-Mayer<sup>5</sup> and by Hans Jensen<sup>6</sup> and coworkers. The shell model has been successful at explaining a number of general trends related to nuclear stability:

- ▶ If the proton-proton interaction is small, the most stable nuclei have nearly equal numbers of protons and neutrons, that is,  $n/p \approx 1$ . This is true for nuclei with small atomic numbers because most of the protons are near the surface of the nucleus and the proton-proton interactions are small compared to the strong-force attractions.<sup>7</sup> The trend is toward larger  $n/p$  ratios at higher atomic numbers because proton-proton interaction is large and a larger number of neutrons are needed to counteract the electrostatic repulsion among the protons and stabilize the nucleus.
- ▶ Nuclei that contain 2, 8, 20, 50, 82, or 126 protons or neutrons are generally more stable than nuclei that do not possess these numbers. For example, there are 10 stable isotopes of tin (Sn) with the atomic number 50 and only 2 stable isotopes of antimony (Sb) with the atomic number 51. The numbers 2, 8, 20, 50, 82, and 126 are called *magic numbers*. The magic numbers for nuclear stability correspond to filled nuclear shells and are analogous to the numbers of electrons associated with the very stable noble gases (that is, 2, 10, 18, 36, 54, and 86 electrons).
- ▶ Nuclei with even numbers of both protons and neutrons are generally more stable than those with odd numbers of these particles (Table 17.2).
- ▶ All isotopes of the elements with  $Z > 83$  are radioactive. Also, all isotopes of technetium (Tc,  $Z = 43$ ) and promethium (Pm,  $Z = 61$ ) are radioactive.

5. Maria Goeppert-Mayer (1906–1972). German-American theoretical physicist. Born in the then-German province of Silesia (now Poland), she received her Ph.D. at the University of Göttingen. She emigrated to the United States in 1930. For her development of the shell model of the nucleus in the late 1940s, she was awarded the Nobel Prize in Physics in 1963 together with Johannes Jensen and Eugene Wigner.

6. Johannes Hans Daniel Jensen (1907–1973). German physicist. While a professor at the University of Heidelberg, he developed the shell model of the nucleus in 1949. For this work, he shared the 1963 Nobel Prize in Physics with Maria Goeppert-Mayer and Eugene Wigner.

7. Nuclei are, to a good approximation, spherical. For small nuclei, a large fraction of the protons will be near the surface. As the size (radius) of the nucleus increases, the fraction of protons in the interior will increase. Because protons in the interior are completely surrounded by other nucleons, they will experience a greater Coulomb repulsion per proton than those at the surface, which are only partially surrounded by other nucleons.

**Table 17.2****Number of Stable Isotopes with Even and Odd Numbers of Protons and Neutrons**

Protons	Neutrons	Number of Stable Isotopes
Odd	Odd	4
Odd	Even	50
Even	Odd	53
Even	Even	164

## Nuclear Binding Energy

A quantitative measure of nuclear stability is the **nuclear binding energy**, which is the *energy required to break up a nucleus into its component protons and neutrons*. This quantity represents the conversion of mass to energy that occurs during an exothermic nuclear reaction. The concept of nuclear binding energy evolved from studies of nuclear properties in which the masses of nuclei were always found to be less than the sum of the masses of the nucleons. The  $^{19}_9\text{F}$  isotope, for example, which consists of 9 protons, 10 neutrons, and 9 electrons has an atomic mass of 18.9984 u. Using the known masses of the  $^1\text{H}$  atom (1.007825 u) and the neutron (1.008665 u), we can carry out the following analysis. The mass of 9  $^1\text{H}$  atoms (that is, the mass of 9 protons and 9 electrons) is  $9 \times 1.007825 \text{ u} = 9.070425 \text{ u}$ , and the mass of 10 neutrons is  $10 \times 1.008665 \text{ u} = 10.08665 \text{ u}$ . Therefore, the atomic mass of an  $^{19}_9\text{F}$  atom calculated from the known numbers of electrons, protons, and neutrons is

$$9.070425 \text{ u} + 10.08665 \text{ u} = 19.15708 \text{ u}$$

This value is larger than 18.9984 u (the measured mass of  $^{19}\text{F}$ ) by 0.1587 u. The difference between the mass of an atom and the sum of the masses of its protons, neutrons, and electrons is called the **mass defect**. According to the theory of special relativity, the loss in mass shows up as energy given off to the surroundings. Thus, the formation of  $^{19}\text{F}$  is exothermic. Using Einstein's mass-energy equivalence relationship

$$E = mc^2$$

where  $E$  is energy,  $m$  is mass, and  $c$  is the velocity of light, we can calculate the amount of energy released. Begin by writing

$$\Delta E = \Delta mc^2 \quad (17.1)$$

where

$$\begin{aligned} \Delta E &= \text{energy of products} - \text{energy of reactants} \\ \Delta m &= \text{mass of products} - \text{mass of reactants} \end{aligned}$$

Thus, the change in mass is

$$\Delta m = 18.9984 \text{ u} - 19.15708 \text{ u} = -0.1587 \text{ u}$$

Because the mass of fluorine-19 is less than the mass calculated from the number of electrons and nucleons present,  $\Delta m$  is a negative quantity. Consequently,  $\Delta E$  is also

negative; that is, energy is released to the surroundings as a result of the formation of the fluorine-19 nucleus. We calculate  $\Delta E$  as follows:

$$\begin{aligned}\Delta E &= (-0.1587 \text{ u}) \left( \frac{1 \text{ kg}}{6.022 \times 10^{26} \text{ u}} \right) (2.998 \times 10^8 \text{ m s}^{-1})^2 \\ &= -2.369 \times 10^{-11} \text{ kg m}^2 \text{ s}^{-2} \\ &= -2.369 \times 10^{-11} \text{ J}\end{aligned}$$

This is the amount of energy released when one fluorine-19 nucleus is formed from 9 protons and 10 neutrons. The nuclear binding energy of this nucleus is  $2.369 \times 10^{-11} \text{ J}$ , which is the amount of energy needed to decompose the nucleus into individual protons and neutrons. For convenience, energies for nuclear processes are generally reported in units of *electron volts* ( $1 \text{ eV} = 1.60218 \times 10^{-19} \text{ J}$ ) or, more commonly, in *million electron volts* (MeV). In MeV, the binding energy of the fluorine nucleus is

$$\begin{aligned}\text{binding energy} &= (2.369 \times 10^{-11} \text{ J}) \left( \frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}} \right) \left( \frac{1 \text{ MeV}}{10^6 \text{ eV}} \right) \\ &= 147.9 \text{ MeV}\end{aligned}$$

The enthalpy changes in ordinary chemical reactions are on the order of  $200 \text{ kJ mol}^{-1}$ . In contrast, the energy released in the formation of 1 mole of fluorine nuclei is

$$\begin{aligned}\Delta E &= (-2.369 \times 10^{-11} \text{ J})(6.022 \times 10^{22} \text{ mol}^{-1}) \\ &= -1.427 \times 10^{13} \text{ J mol}^{-1} \\ &= -1.427 \times 10^{10} \text{ kJ mol}^{-1}\end{aligned}$$

The nuclear binding energy, therefore, is  $1.43 \times 10^{10} \text{ kJ mol}^{-1}$  for fluorine-19 nuclei, which is nearly 100 million ( $10^8$ ) times greater than the typical energy changes in chemical reactions.

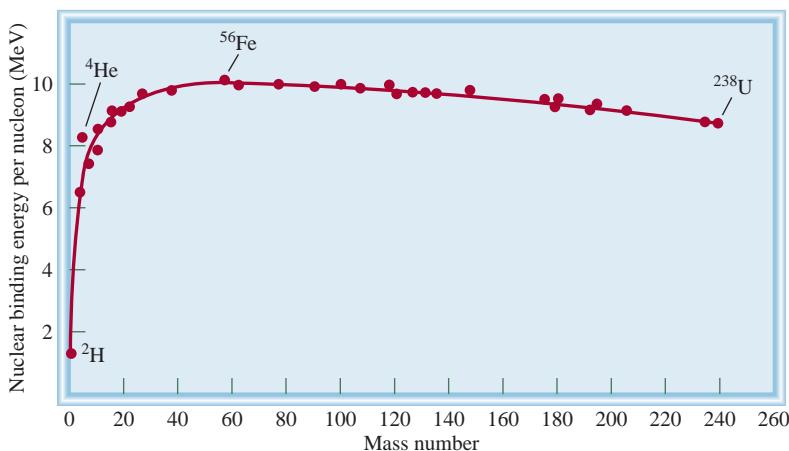
Although the nuclear binding energy is an indication of the stability of a nucleus, we must account for the different numbers of nucleons in two nuclei when comparing their stabilities. For this reason, it is more meaningful to use the *nuclear binding energy per nucleon*, defined as

$$\text{nuclear binding energy per nucleon} = \frac{\text{nuclear binding energy}}{\text{number of nucleons}}$$

For the fluorine-19 nucleus,

$$\begin{aligned}\text{nuclear binding energy per nucleon} &= \frac{147.9 \text{ MeV}}{19 \text{ nucleons}} \\ &= 7.784 \text{ MeV nucleon}^{-1}\end{aligned}$$

The nuclear binding energy per nucleon makes it possible to compare the stability of all nuclei on a common basis. The graph in Figure 17.3 plots the variation of the nuclear binding energy per nucleon versus mass number. The curve rises rather steeply, such that the highest binding energies per nucleon belong to elements with intermediate mass number (between 40 and 100) and are greatest for elements in the iron, cobalt, and nickel region (the Group 8B elements) of the periodic table. Thus, the *net* attractive forces among the particles (protons and neutrons) are greatest for the nuclei of these elements.



**Figure 17.3** Plot of nuclear binding energy per nucleon versus mass number.

The nuclear binding energy and the nuclear binding energy per nucleon are calculated for an iodine nucleus in Example 17.2.

### Example 17.2

The atomic mass of  $^{127}_{53}\text{I}$  is 126.90447 u. Calculate the nuclear binding energy in MeV of this nucleus and the corresponding nuclear binding energy per nucleon.

**Strategy** To calculate the nuclear binding energy, we must first determine the difference between the mass of the nucleus and the mass of the individual protons and neutrons, which gives us the mass deficit. Next, we apply Einstein's mass-energy relationship ( $\Delta E = \Delta mc^2$ ) to calculate  $\Delta E$  in joules, and then convert that value to MeV. Finally, we divide  $\Delta E$  by the number of nucleons to get the corresponding nuclear binding energy per nucleon.

**Solution** There are 53 protons and 74 neutrons in the iodine nucleus. The mass of 53  $^1\text{H}$  atoms is

$$53 \times 1.007825 \text{ u} = 53.41473 \text{ u}$$

and the mass of 74 neutrons is

$$74 \times 1.008665 \text{ u} = 74.64121 \text{ u}$$

Therefore, the predicted mass for  $^{127}_{53}\text{I}$  is  $53.41473 \text{ u} + 74.64121 \text{ u} = 128.05594 \text{ u}$ , and the mass deficit is

$$\Delta m = 126.90447 \text{ u} - 128.05594 \text{ u} = -1.15147 \text{ u}$$

The energy released is

$$\begin{aligned}\Delta E &= \Delta mc^2 \\ &= \left( -1.15147 \text{ u} \times \frac{1 \text{ kg}}{6.022142 \times 10^{26} \text{ u}} \right) (2.99792 \times 10^8 \text{ m s}^{-1})^2 \\ &= -1.71847 \times 10^{-10} \text{ kg m}^2 \text{s}^{-2} \\ &= -1.71847 \times 10^{-10} \text{ J}\end{aligned}$$

—Continued

*Continued—*

Converting to MeV gives

$$\begin{aligned}\Delta E &= -(1.71847 \times 10^{-10} \text{ J}) \left( \frac{1 \text{ eV}}{1.60218 \times 10^{-19} \text{ J}} \right) \left( \frac{1 \text{ MeV}}{10^6 \text{ eV}} \right) \\ &= -1077.26 \text{ MeV}\end{aligned}$$

Thus, the nuclear binding energy is 1077.26 MeV. The nuclear binding energy per nucleon is obtained as follows

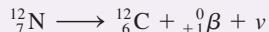
$$\begin{aligned}\text{nuclear binding energy per nucleon} &= \frac{1077 \text{ MeV}}{127 \text{ nucleons}} \\ &= 8.48 \text{ MeV nucleon}^{-1}\end{aligned}$$

**Practice Exercise** Calculate the nuclear binding energy (in MeV) and the nuclear binding energy per nucleon of  $^{209}_{83}\text{Bi}$  (208.9804 u).

The mass-energy relationship can be used to predict the energy release in nuclear decay reactions, as illustrated in Example 17.3.

### Example 17.3

Calculate the energy released (in joules and  $\text{kJ mol}^{-1}$ ) when a nitrogen-12 nucleus undergoes  $\beta^+$  decay (positron emission):



The masses of  $^{12}_7\text{N}$  and  ${}^{12}_6\text{C}$  atoms are 12.018709 u and 12.00000 u, respectively. The mass of the positron is the same as of an electron ( $m_e = 9.1093826 \times 10^{-31} \text{ kg} = 5.485799 \times 10^{-4} \text{ u}$ ) and the neutrino is massless.

**Strategy** Calculate the change in mass,  $\Delta m$ , for the reaction, and convert to energy using Equation 17.1. Note that the masses given are for the neutral atoms not the nuclei, so we have to subtract the mass of the orbital electrons.

**Solution** The change in mass is

$$\begin{aligned}\Delta m &= \text{mass of products} - \text{mass of reactants} \\ &= [m({}^{12}_6\text{C}) - 6m_e] + m_e - [m({}^{12}_7\text{N}) - 7m_e] \\ &= m({}^{12}_6\text{C}) - m({}^{12}_7\text{N}) + 2m_e \\ &= 12.000000 \text{ u} - 12.018709 \text{ u} + 2(5.485799 \times 10^{-4} \text{ u}) \\ &= -0.017611 \text{ u}\end{aligned}$$

Converting to kilograms yields

$$\Delta m = (-0.017611 \text{ u})(1.66053886 \times 10^{-27} \text{ kg u}^{-1}) = -2.9245 \times 10^{-29} \text{ kg}$$

Using Equation 17.1 to convert from mass to energy,

$$\begin{aligned}\Delta E &= \Delta mc^2 \\ &= (-3.01554 \times 10^{-29} \text{ kg})(2.99792458 \times 10^8 \text{ m s}^{-1})^2 \\ &= -2.6284 \times 10^{-12} \text{ J}\end{aligned}$$

—Continued

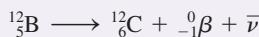
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Thus, the energy released per  $^{12}\text{N}$  atom in this decay is  $2.6284 \times 10^{-12} \text{ J}$ . Multiplying by Avagadro's number and converting to kilojoules gives

$$\Delta E = (2.6284 \times 10^{-15} \text{ kJ})(6.0221367 \times 10^{23} \text{ mol}^{-1}) = 1.5829 \times 10^9 \text{ kJ mol}^{-1}$$

**Comment** The energy released in this reaction goes into the kinetic energies of the positron and the carbon nucleus, as well as into the energy of the neutrino. The exact distribution of this energy among the product particles will vary.

**Practice Exercise** Calculate the energy released (in joules and  $\text{kJ mol}^{-1}$ ) for the beta decay of a  $^{12}\text{B}$  nucleus:

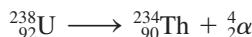


The masses of  $^{12}\text{B}$  and  $^{12}\text{C}$  are 12.014353 u and 12.000000 u, respectively.

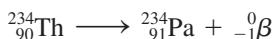
## Radioactive Decay Series

Nuclei outside the belt of stability, as well as all nuclei with  $Z > 83$ , tend to be unstable and will undergo radioactive decay through the emission of particles or radiation. The disintegration of a radioactive nucleus is often the beginning of a **radioactive decay series**, which is *a sequence of nuclear reactions that ultimately form a stable isotope*. Table 17.3 shows the 14-step decay series of naturally occurring uranium-238. This decay scheme is known as the *uranium decay series*. Table 17.3 also shows the *half-lives* (see Chapter 14) of all the products of the decay series.

It is important to be able to balance the nuclear equations for each of the steps in a radioactive decay series. For example, the first step in the uranium decay series is the decay of uranium-238 to thorium-234, with the emission of an  $\alpha$  particle. Hence, the equation for this reaction is



The next step is the  $\beta$  decay of thorium-234 to protactinium-234:



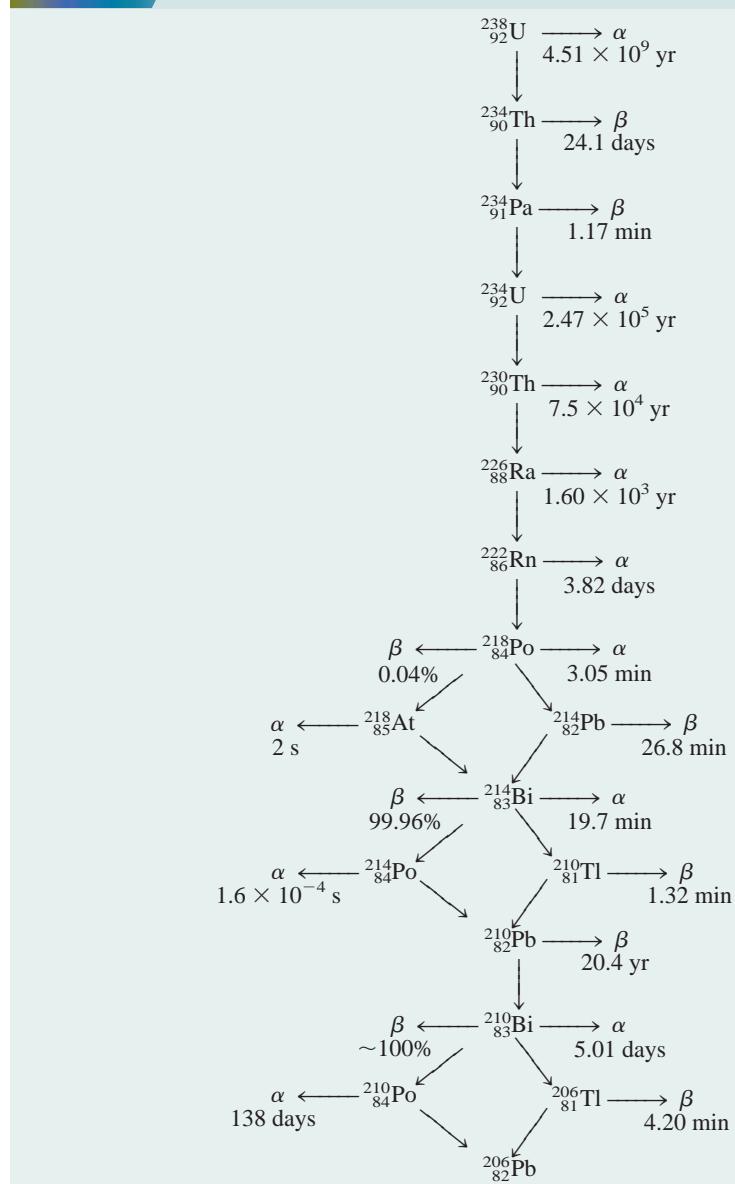
and so on. When discussing radioactive decay steps, the beginning radioactive isotope is called the *parent* and the product is called the *daughter*.

## 17.3 | Radioactive Decay Is a First-Order Kinetic Process

The radioactive decay of an unstable nucleus is a random process. In any given interval of time, there is a well-defined probability that a given nucleus will decay. This probability is independent of time and is the same for all nuclei of a given type, but is different for different isotopes. The number of nuclei decaying per unit time is the rate of nuclear decay (or **activity**), which can be measured using devices, such as the Geiger-Mueller counter (Figure 17.4).

In a collection of  $N$  identical nuclei, the number of nuclei decaying in a short time interval is proportional to the number of nuclei, which defines a first-order decay process (Section 14.2). We have

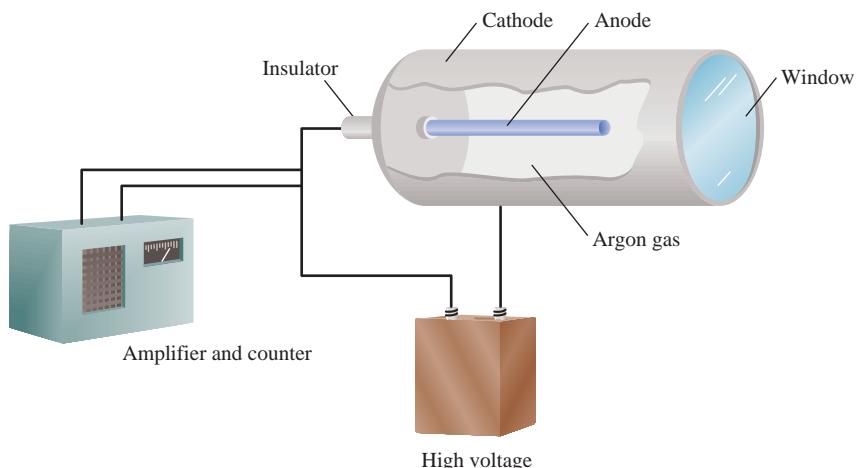
$$\text{activity} = -\frac{dN}{dt} = \lambda N \quad (17.2)$$

**Table 17.3** The Uranium Decay Series\*

\*The times denote the half-lives.

where  $\lambda$  is the nuclear decay rate constant and the negative sign is there to guarantee that activity is a positive quantity. We use  $\lambda$  instead of  $k$  because  $\lambda$  is the notation used by nuclear scientists. The standard SI unit of radioactive activity is the *becquerel* (*Bq*) (named for Henri Becquerel, the discoverer of radioactivity), which is defined as a decay rate of 1 disintegration per second:

$$1 \text{ Bq} \equiv 1 \text{ disintegration s}^{-1}$$



**Figure 17.4** Schematic diagram of a Geiger-Mueller counter. Radiation ( $\alpha$ -,  $\beta$ -, or  $\gamma$ -rays) entering through the window ionizes the argon gas to generate a small current between the electrodes. This current is amplified and is used to flash a light or operate a counter with a clicking sound.

An older unit of activity that is commonly used, especially in the United States, is the *curie* (Ci) (named for Marie Curie), which is defined as  $3.7 \times 10^{10}$  Bq. The curie is the decay rate produced by 1 g of radium-226 (an isotope of one of the elements discovered by Marie Curie).

Equation 17.2 is identical in form to the rate equation describing first-order chemical reaction kinetics (Equation 14.3), and the corresponding solution for  $N(t)$  is given by (see Equation 14.6)

$$N(t) = N_0 e^{-\lambda t} \quad (17.3)$$

where  $N_0$  is the number of nuclei initially present. As in first-order chemical reactions, the half-life of a radioactive material is independent of the amount of material present and is given by (see Equation 14.9)

$$t_{\frac{1}{2}} = \frac{\ln 2}{\lambda} \approx \frac{0.693}{\lambda} \quad (17.4)$$

The half-lives (hence the rate constants) of radioactive isotopes vary greatly from isotope to isotope. Two extreme cases listed in Table 17.3, for example, are uranium-238 and polonium-214:



The half-life of the uranium isotope is about  $1 \times 10^{21}$  times larger than the half-life of the polonium isotope. Unlike the rate constants for chemical reactions, moreover, the rate constants for nuclear decay are unaffected by changes in environmental conditions, such as temperature and pressure (see Table 17.1).

Calculations using Equations 17.3 and 17.4 are similar to those that we encountered in Section 14.3 for first-order chemical reactions. One major difference is that although it is the rate constant that is generally provided for chemical reactions, the half-life is more commonly given for nuclear reactions. In addition, in chemical reactions, we generally measure the concentration as a function of time, whereas in radioactive decay, it is the rate (or activity) that is measured.

Example 17.4 shows a typical nuclear decay calculation.

**Example 17.4**

The isotope  $^{234}_{90}\text{Th}$  undergoes beta decay with a half-life of 24.1 days. Calculate the amount of  $^{234}_{90}\text{Th}$  left after 30.0 days from an initial sample of 0.539 g.

**Strategy** Use Equation 17.4 to find the rate constant, and substitute that into Equation 17.2 to find the amount remaining.

**Solution** Rearranging Equation 17.4 gives an equation for the rate constant in terms of the half-life:

$$\lambda = \frac{\ln 2}{t_{\frac{1}{2}}}$$

so

$$\lambda = \frac{\ln 2}{24.1 \text{ days}} = 0.0288 \text{ days}^{-1}$$

Substituting the calculated value of  $\lambda$  into Equation 17.3 together with the given initial amount of thorium-234 and the elapsed time gives

$$\begin{aligned} N &= N_0 e^{-\lambda t} \\ &= 0.539 \text{ g } e^{-(0.0288 \text{ days}^{-1})(30.0 \text{ days})} \\ &= 0.227 \text{ g} \end{aligned}$$

Thus, 0.227 g of the original 0.539 g of  $^{234}_{90}\text{Th}$  will be left after 30.0 days.

**Check** The result (30.0 days) is longer than one half-life, but shorter than two half-lives, so the calculated amount should be less than one-half of the original amount but greater than one-quarter. This is indeed so.

**Practice Exercise** Iodine-131 undergoes beta decay with a half-life of 8.04 days and is commonly used to test the activity of the thyroid gland. If a patient is given a dose of 0.146 mg of iodine-131, how long would it take for the iodine-131 to decay to 0.001 mg, assuming none is excreted?

**Dating Based on Radioactive Decay**

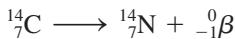
The predictable behavior of radioactive decay as a function of time can in many cases be used as an “atomic clock” to estimate the age of objects. If the initial amount of a radioactive isotope in a sample can be accurately estimated, we can determine the time that has elapsed from that initial time by measuring the current amount of material present and applying Equation 17.3. Some examples of dating by radioactive decay measurements are described here.

**Radiocarbon Dating**

The atmosphere of Earth is constantly being bombarded by cosmic rays of extremely high penetrating power. These rays, which originate in outer space, consist of electrons, neutrons, and atomic nuclei. One of the important reactions between the atmosphere and cosmic rays is the capture of neutrons by atmospheric nitrogen (nitrogen-14 isotope) to produce the radioactive carbon-14 isotope and hydrogen:



The carbon-14 atoms so produced are unstable and decay according to the following equation:



The half-life of carbon-14 is 5730 years, which, according to Equation 17.4, gives a decay rate constant of

$$\lambda = \frac{\ln 2}{t_{\frac{1}{2}}} = \frac{0.693}{5739 \text{ yr}} = 1.21 \times 10^{-4} \text{ yr}^{-1}$$

Using the conversion factor 1 year =  $3.19 \times 10^7$  s gives

$$\lambda = (1.21 \times 10^{-4} \text{ yr}^{-1}) \left( \frac{1 \text{ yr}}{3.19 \times 10^7 \text{ s}} \right) = 3.79 \times 10^{-12} \text{ s}^{-1}$$

The unstable carbon atoms eventually form  ${}^{14}\text{CO}_2$ , which mixes with ordinary  ${}^{12}\text{CO}_2$  in the air. Because carbon-14 in the atmosphere is continually produced (by neutron bombardment) and destroyed (by radioactive decay), a dynamic equilibrium is reached in which the ratio of carbon-14 to carbon-12 in the atmosphere remains constant over time at a value of  $1.3 \times 10^{-12}$ . Thus, in a 1-g sample of carbon from the atmosphere, we should find  $1.3 \times 10^{-12}$  g of carbon-14. Using Equation 17.2 we can calculate the expected activity of one gram of atmospheric carbon:

$$\begin{aligned} \text{activity} &= \lambda N \\ &= (3.79 \times 10^{-12} \text{ s}^{-1}) \left( \frac{1.3 \times 10^{-12} \text{ g}}{12.00 \text{ g mol}^{-1}} \right) (6.022 \times 10^{22} \text{ mol}^{-1}) \\ &= 0.25 \text{ s}^{-1} \\ &= 0.25 \text{ Bq} \end{aligned}$$

The carbon-14 isotopes enter the biosphere when carbon dioxide is taken up in plant photosynthesis. Plants are eaten by animals, which exhale carbon-14 in  $\text{CO}_2$ . Eventually, carbon-14 participates in many aspects of the carbon cycle. The continual exchange between carbon in living tissue and carbon in the atmosphere means that the ratio of carbon-14 to carbon-12 in living matter will be the same as that in the atmosphere. When an individual plant or animal dies, however, the carbon-14 isotope in its cells continues to decay, but is no longer replenished, so the ratio of  ${}^{14}\text{C}$  to  ${}^{12}\text{C}$  decreases. These same processes occur when carbon atoms are trapped in coal, petroleum, or wood preserved underground, and in Egyptian mummies. As the years pass, there are proportionately fewer  ${}^{14}\text{C}$  nuclei in a mummy than in a living person.

In 1955, Willard F. Libby<sup>8</sup> suggested that the  ${}^{14}\text{C}$  to  ${}^{12}\text{C}$  ratio could be used to estimate the length of time the carbon-14 isotope in a particular specimen has been decaying without replenishment. This ingenious technique is based on a remarkably simple idea. By measuring the activity of carbon extracted from the sample, we can calculate the time elapsed since the sample was living tissue by comparing this activity with the equilibrium activity of atmospheric carbon, calculated earlier to be 0.25 Bq  $\text{g}^{-1}$ . Rearranging Equation 17.3 gives

$$t = \frac{1}{\lambda} \ln \frac{N_0}{N} \quad (17.5)$$

8. Willard Frank Libby (1908–1980). American chemist. Libby received the Nobel Prize in Chemistry in 1960 for his work on radiocarbon dating.

Equation 17.4 implies that the ratio  $N_0/N$  is the same as the ratio of the equilibrium atmospheric activity (the activity at  $t = 0$ ) to the current activity of the sample giving

$$t = (8.3 \times 10^3 \text{ yr}) \ln \left( \frac{0.25 \text{ Bq g}^{-1}}{\text{activity per 1-g sample}} \right) \quad (17.6)$$

The success of radiocarbon dating depends on the accuracy with which we can measure the activity. Precision is more difficult with older samples because they contain fewer  $^{14}\text{C}$  nuclei. Nevertheless, radiocarbon dating has become an extremely valuable tool for estimating the age of archaeological artifacts, paintings, and other objects dating back 1000 to 50,000 years. Its predictions have been found to agree very well with other independent measures of age, such as counting the annual rings on trees.

### Dating Using Uranium-238 Isotopes

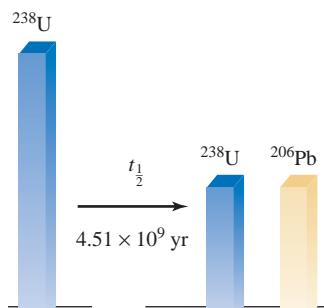
Because some of the intermediate products in the uranium decay series have very long half-lives (see Table 17.3), this series is particularly suitable for estimating the age of rocks in the earth and of extraterrestrial objects. The half-life for the first step ( $^{238}_{92}\text{U}$  to  $^{234}_{90}\text{Th}$ ) is  $4.51 \times 10^9$  years. This is about 20,000 times the second largest value (that is,  $2.47 \times 10^5$  yr), which is the half-life for  $^{234}_{92}\text{U}$  to  $^{230}_{90}\text{Th}$ . As a good approximation, therefore, we can assume that the half-life for the overall process (that is, from  $^{238}_{92}\text{U}$  to  $^{206}_{82}\text{Pb}$ ) is governed solely by the first step:



(In the language of chemical kinetics, the  $^{234}_{92}\text{U}$  to  $^{230}_{90}\text{Th}$  step is *rate limiting*.)

Naturally occurring uranium minerals contain some lead-206 isotopes formed by radioactive decay. Assuming that no lead was present when the mineral was formed and that the mineral has not undergone chemical changes that would allow the lead-206 isotope to be separated from the parent uranium-238, it is possible to estimate the age of the rocks from the mass ratio of  $^{206}_{82}\text{Pb}$  to  $^{238}_{92}\text{U}$ . According to the previous equation, for every mole (238 g) of uranium that undergoes complete decay, 1 mole (206 g) of lead is formed. If only half a mole of uranium-238 has decayed, the mass ratio of  $^{206}_{82}\text{Pb}$  to  $^{238}_{92}\text{U}$  becomes

$$\frac{206 \text{ g}/2}{238 \text{ g}/2} = 0.866$$



**Figure 17.5** After one half-life, half of the original uranium-238 is converted to lead-206.

and the process would have taken a half-life of  $4.51 \times 10^9$  years to complete (Figure 17.5). Ratios lower than 0.866 mean that the rocks are less than  $4.51 \times 10^9$  years old, and higher ratios suggest a greater age. Studies based on the uranium series (as well as other decay series) put the age of the oldest rocks and, therefore, probably the age of Earth itself, at  $4.5 \times 10^9$ , or 4.5 billion, years.

### Dating Using Potassium-40 Isotopes

Radioactive dating using potassium-40 is one of the most important techniques in geochemistry. The radioactive potassium-40 isotope decays by several different modes, but the one most relevant for dating is electron capture:



The accumulation of gaseous argon-40 is used to gauge the age of a specimen. When a potassium-40 atom in a mineral decays, argon-40 is trapped in the lattice of the mineral and can escape only if the material is melted. Melting, therefore, is the procedure for analyzing a mineral sample in the laboratory. The amount of argon-40 present can be conveniently measured with a mass spectrometer (see page 46). Knowing the ratio of argon-40 to potassium-40 in the mineral and the half-life of decay makes it possible to establish the ages of rocks ranging from millions to billions of years old.

Example 17.5 gives an illustration of a radioisotope calculation of age.

### Example 17.5

The activity of a 0.126-g sample of carbon taken from a piece of linen cloth from an archeological dig was measured to be  $1.87 \times 10^{-2}$  Bq. Estimate the age of the sample.

**Strategy** Find the activity of a 1-g sample of carbon and use Equation 17.6 to estimate the age.

**Solution** The activity per gram of the carbon sample is  $(1.87 \times 10^{-2} \text{ Bq})/(0.126 \text{ g})$  or  $0.148 \text{ Bq g}^{-1}$ . Using Equation 17.6 gives

$$\begin{aligned} t &= (8.3 \times 10^3 \text{ yr}) \ln\left(\frac{0.25 \text{ Bq g}^{-1}}{\text{activity per 1-g sample}}\right) \\ &= (8.3 \times 10^3 \text{ yr}) \ln\left(\frac{0.25 \text{ Bq g}^{-1}}{0.148 \text{ Bq g}^{-1}}\right) \\ &= 4400 \text{ yr} \end{aligned}$$

**Practice Exercise** Estimate the age of a rock for which the  $^{206}_{82}\text{Pb}$  to  $^{238}_{92}\text{U}$  mass ratio is 0.390. What assumptions do you have to make to perform this calculation?

## 17.4 | New Isotopes Can Be Produced Through the Process of Nuclear Transmutation

The scope of nuclear chemistry would be rather narrow if it were limited to natural radioactive elements. An experiment performed by Rutherford in 1919, however, suggested the possibility of producing radioactivity artificially. He bombarded a sample of nitrogen-14 with  $\alpha$  particles yielding oxygen-17 and protons:



This reaction demonstrated for the first time that it was feasible to convert one element into another, by the process of *nuclear transmutation*. Nuclear transmutation differs from radioactive decay in that the transmutation is brought about by the collision of two particles, not by the inherent instability of an isotope.

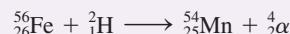
The reaction of nitrogen-14 with an  $\alpha$  particle to yield oxygen-17 and a proton can be abbreviated as  ${}_{7}^{14}\text{N}(\alpha, \text{p}) {}_{8}^{17}\text{O}$ . Note that in the parentheses the bombarding particle is written first, followed by the ejected particle. Example 17.6 shows how to use this notation to represent nuclear transmutations.

**Example 17.6**

Write the balanced equation for the nuclear reaction  ${}_{26}^{56}\text{Fe}(\text{d},\alpha){}_{25}^{54}\text{Mn}$ , where d represents the deuterium nucleus (i.e.,  ${}_{1}^2\text{H}$ ).

**Strategy** To write the balanced nuclear equation, remember that the first isotope ( ${}_{26}^{56}\text{Fe}$ ) is the reactant and the second isotope ( ${}_{25}^{54}\text{Mn}$ ) is the product. Furthermore, the first symbol in the parentheses (d) is the bombarding particle, and the second ( $\alpha$ ) is the particle emitted as a result of nuclear transmutation.

**Solution** According to the abbreviated nuclear equation, iron-56 is bombarded with a deuterium nucleus, producing manganese-54 nucleus plus an  $\alpha$  particle ( ${}_{2}^4\text{He}$ ):



**Check** Make sure that the sum of the mass numbers and the sum of the atomic numbers are the same on both sides of the equation.

**Practice Exercise** Write the balanced equation for  ${}_{46}^{106}\text{Pd}(\alpha,\text{p}){}_{47}^{109}\text{Ag}$ .

Particle accelerators have made it possible to synthesize **transuranium elements**—elements with atomic numbers greater than 92. Neptunium ( $Z = 93$ ) was first prepared in 1940. Since then, 23 other transuranium elements have been synthesized. All isotopes of these elements are radioactive. Table 17.4 lists the transuranium elements up to  $Z = 111$  and the reactions by which they are formed.

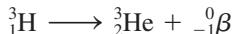
**Table 17.4 The Transuranium Elements**

Atomic Number	Name	Symbol	Preparation
93	Neptunium	Np	${}_{92}^{238}\text{U} + {}_0^1\text{n} \longrightarrow {}_{93}^{239}\text{Np} + {}_{-1}^0\beta$
94	Plutonium	Pu	${}_{93}^{239}\text{Np} \longrightarrow {}_{94}^{239}\text{Pu} + {}_{-1}^0\beta$
95	Americium	Am	${}_{94}^{239}\text{Pu} + {}_0^1\text{n} \longrightarrow {}_{95}^{240}\text{Am} + {}_{-1}^0\beta$
96	Curium	Cm	${}_{94}^{239}\text{Pu} + {}_2^4\alpha \longrightarrow {}_{96}^{242}\text{Cm} + {}_0^1\text{n}$
97	Berkelium	Bk	${}_{95}^{241}\text{Am} + {}_2^4\alpha \longrightarrow {}_{97}^{243}\text{Bk} + {}_0^1\text{n}$
98	Californium	Cf	${}_{96}^{242}\text{Cm} + {}_2^4\alpha \longrightarrow {}_{98}^{245}\text{Cf} + {}_0^1\text{n}$
99	Einsteinium	Es	${}_{92}^{238}\text{U} + {}_{15}^1\text{n} \longrightarrow {}_{99}^{253}\text{Es} + {}_{-1}^0\beta$
100	Fermium	Fm	${}_{92}^{238}\text{U} + {}_{17}^1\text{n} \longrightarrow {}_{100}^{255}\text{Fm} + {}_{-1}^0\beta$
101	Mendelevium	Md	${}_{99}^{253}\text{Es} + {}_2^4\alpha \longrightarrow {}_{101}^{256}\text{Md} + {}_0^1\text{n}$
102	Nobelium	No	${}_{96}^{246}\text{Cm} + {}_{12}^6\text{C} \longrightarrow {}_{102}^{254}\text{No} + {}_0^1\text{n}$
103	Lawrencium	Lr	${}_{98}^{252}\text{Cf} + {}_{10}^5\text{B} \longrightarrow {}_{103}^{257}\text{Lr} + {}_0^1\text{n}$
104	Rutherfordium	Rf	${}_{98}^{249}\text{Cf} + {}_{12}^6\text{C} \longrightarrow {}_{104}^{257}\text{Rf} + {}_0^1\text{n}$
105	Dubnium	Db	${}_{98}^{249}\text{Cf} + {}_{15}^7\text{N} \longrightarrow {}_{105}^{260}\text{Db} + {}_0^1\text{n}$
106	Seaborgium	Sg	${}_{98}^{249}\text{Cf} + {}_{18}^8\text{O} \longrightarrow {}_{106}^{263}\text{Sg} + {}_0^1\text{n}$
107	Bohrium	Bh	${}_{83}^{209}\text{Bi} + {}_{24}^{54}\text{Cr} \longrightarrow {}_{107}^{262}\text{Bh} + {}_0^1\text{n}$
108	Hassium	Hs	${}_{82}^{208}\text{Pb} + {}_{26}^{58}\text{Fe} \longrightarrow {}_{108}^{265}\text{Hs} + {}_0^1\text{n}$
109	Meitnerium	Mt	${}_{83}^{209}\text{Bi} + {}_{26}^{58}\text{Fe} \longrightarrow {}_{109}^{266}\text{Mt} + {}_0^1\text{n}$
110	Darmstadtium	Ds	${}_{82}^{208}\text{Pb} + {}_{28}^{62}\text{Ni} \longrightarrow {}_{110}^{269}\text{Ds} + {}_0^1\text{n}$
111	Roentgenium	Rg	${}_{82}^{209}\text{Bi} + {}_{28}^{64}\text{Ni} \longrightarrow {}_{111}^{272}\text{Rg} + {}_0^1\text{n}$

Although light elements are generally not radioactive, they can be made so by bombarding their nuclei with appropriate particles. As we saw earlier, the radioactive carbon-14 isotope can be prepared by bombarding nitrogen-14 with neutrons. Tritium,  ${}^3_1\text{H}$ , is prepared by bombarding lithium-6 with neutrons:



Tritium then decays to helium-3 with the emission of  ${}^{-1}_1\beta$  particles:

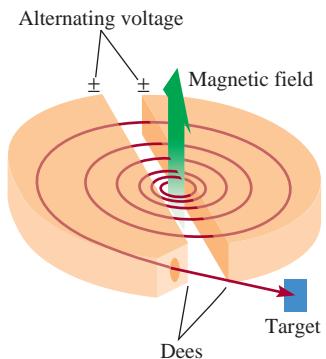


Many synthetic isotopes are prepared by using neutrons as projectiles. This approach is particularly convenient because neutrons carry no charges and therefore are not repelled by the targets—the nuclei. In contrast, when the projectiles are positively charged particles (such as, protons or  $\alpha$  particles), they must have considerable kinetic energy to overcome the electrostatic repulsion between themselves and the target nuclei. The synthesis of phosphorus from aluminum is one example:



A *particle accelerator* uses electric and magnetic fields to increase the kinetic energy of charged species so that a reaction will occur (Figure 17.6). Alternating the polarity (that is, + and −) on specially constructed plates causes the particles to accelerate along a spiral path. When they have the energy necessary to initiate the desired nuclear reaction, they are guided out of the accelerator into a collision with a target substance.

Various designs have been developed for particle accelerators, one of which accelerates particles along a linear path of about 3 km (Figure 17.7). It is now possible to accelerate particles to a speed well above 90 percent of the speed of light. (According to Einstein's theory of relativity, it is impossible for a particle with nonzero rest mass to move *at* the speed of light.) Physicists use the extremely energetic particles produced in accelerators to smash atomic nuclei to fragments. Studying the debris from such disintegrations provides valuable information about nuclear structure and binding forces.



**Figure 17.6** Schematic diagram of a cyclotron particle accelerator. The particle (an ion) to be accelerated starts out at the center and is forced to move in a spiral path through the influence of electric and magnetic fields until it emerges at high velocity. The magnetic fields are perpendicular to the plane of the “dees” (so called because of their shape), which are hollow and serve as electrodes.

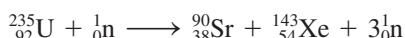


**Figure 17.7** A section of a particle accelerator.

## 17.5 | In Nuclear Fission, a Large Nucleus Is Split into Smaller Nuclei

**Nuclear fission** occurs when a heavy nucleus ( $A > 200$ ) divides to form smaller nuclei of intermediate mass and one or more neutrons. Because the heavy nucleus is less stable than its products (see Figure 17.2), fission releases a large amount of energy.

The first nuclear fission reaction to be studied was that of uranium-235 bombarded with slow neutrons, whose speed was comparable to that of air molecules at room temperature. Under these conditions, uranium-235 undergoes fission (Figure 17.8), yielding more than 30 different elements among the possible fission products (Figure 17.9). A representative reaction is



Although many heavy nuclei can be made to undergo fission, only the fission of naturally occurring uranium-235 and of the artificial isotope plutonium-239 have any practical importance.

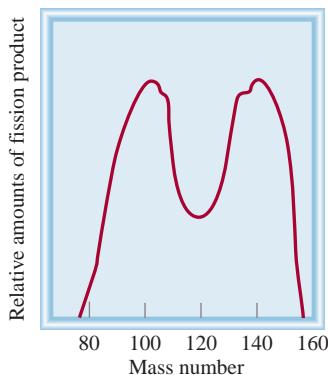
Table 17.5 lists the nuclear binding energies of uranium-235 and its fission products in the preceding reaction. As the table shows, the binding energy per nucleon for uranium-235 is less than the sum of the binding energies for strontium-90 and xenon-143. As a result, energy is released when a uranium-235 nucleus is split into two smaller nuclei. The difference between the binding energies of the reactants and products is  $(768 + 1200) \text{ MeV} - 1760 \text{ MeV} = 208 \text{ MeV}$  per uranium-235 nucleus. For 1 mole of uranium-235, the energy released would be

$$(208 \text{ MeV})(1.602 \times 10^{-13} \text{ J MeV}^{-1})(6.02 \times 10^{23} \text{ mol}^{-1}) = 2.0 \times 10^{13} \text{ J mol}^{-1}$$

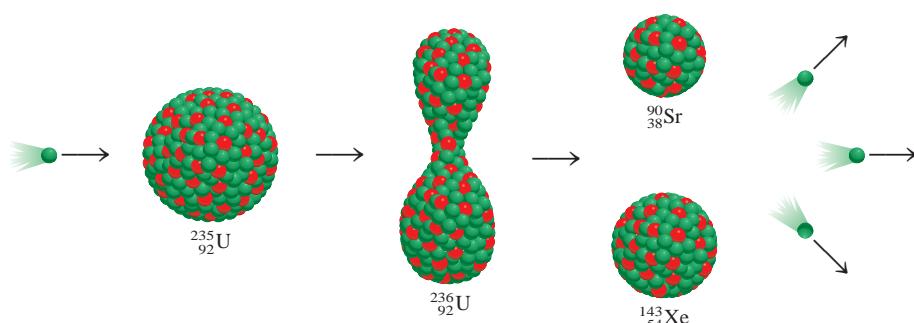
This is an extremely exothermic reaction, considering that the heat of combustion of 1 ton of coal is only about  $5 \times 10^7 \text{ J}$ .

Uranium-235 fission not only releases an enormous amount of energy, but it also produces more neutrons than were originally captured in the process. This feature makes possible a **nuclear chain reaction**, which is a self-sustaining sequence of nuclear fission reactions. The neutrons generated during the initial stages of fission can induce fission in other uranium-235 nuclei, which in turn produce more neutrons, and so on. In less than a second, the reaction can become uncontrollable, liberating a tremendous amount of heat to the surroundings.

Figure 17.10 shows two types of fission reactions. For a chain reaction to occur, enough uranium-235 must be present in the sample to capture the neutrons. Otherwise,



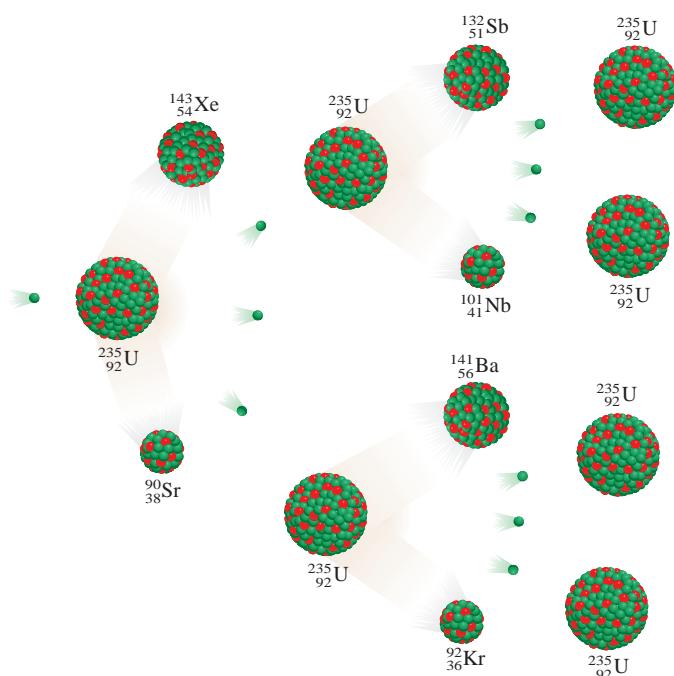
**Figure 17.9** Relative yields of the products resulting from the fission of U-235, as a function of mass number.



**Figure 17.8** Nuclear fission of U-235. When a U-235 nucleus captures a neutron (red dot), it undergoes fission to yield two smaller nuclei. On average, 2.4 neutrons are emitted for every U-235 nucleus that divides.

**Table 17.5** Nuclear Binding Energies of  $^{235}\text{U}$  and Two Typical Fission Products

Nuclear Binding Energy		
	$J$	$\text{MeV}$
$^{235}\text{U}$	$2.82 \times 10^{-10}$	$1.76 \times 10^3$
$^{90}\text{Sr}$	$1.23 \times 10^{-10}$	$7.68 \times 10^2$
$^{143}\text{Xe}$	$1.92 \times 10^{-10}$	$1.20 \times 10^3$



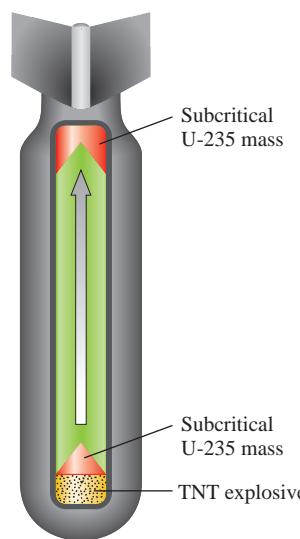
**Figure 17.10** If a critical mass is present, many of the neutrons emitted during the fission process will be captured by other  $^{235}\text{U}$  nuclei and a chain reaction will occur.

many of the neutrons will escape from the sample and the chain reaction will not occur. In this situation, the mass of the sample is said to be *subcritical*. Figure 17.10 shows what happens when the amount of the fissionable material is equal to or greater than the *critical mass*, the minimum mass of fissionable material required to generate a self-sustaining nuclear chain reaction. In this case, most of the neutrons will be captured by uranium-235 nuclei, and a chain reaction will occur.

## The Atomic Bomb

The first application of nuclear fission was in the development of the atomic bomb in 1945. How is such a bomb made and detonated? The crucial factor in the design of the bomb is determining the critical mass necessary. A small atomic bomb is equivalent to 20,000 tons of TNT (trinitrotoluene). Because 1 ton of TNT releases about  $4 \times 10^9$  J of energy, 20,000 tons (or 20 kilotons) produces  $8 \times 10^{13}$  J. Recall that 1 mole, (235 g) of uranium-235 liberates  $2.0 \times 10^{13}$  J of energy when it undergoes fission. Thus, the mass of the isotope present in a small bomb must be at least

$$(235 \text{ g}) \left( \frac{8 \times 10^{13} \text{ J}}{2.0 \times 10^{13} \text{ J}} \right) \approx 1 \text{ kg}$$



**Figure 17.11** Schematic cross section of an atomic bomb. The TNT explosives are set off first. The explosion forces the subcritical sections of fissionable material together to form an amount considerably larger than the critical mass.

An atomic bomb is never assembled with the critical mass already in place. Instead, the critical mass is formed by using a conventional explosive, such as TNT, to force the fissionable sections together, as shown in Figure 17.11. Neutrons from a source at the center of the device trigger the nuclear chain reaction. Uranium-235 was the fissionable material in the bomb dropped on Hiroshima, Japan, on August 6, 1945. Plutonium-239 was used in the bomb exploded over Nagasaki, Japan, 3 days later. The fission reactions generated were similar in these two cases, as was the extent of the destruction.

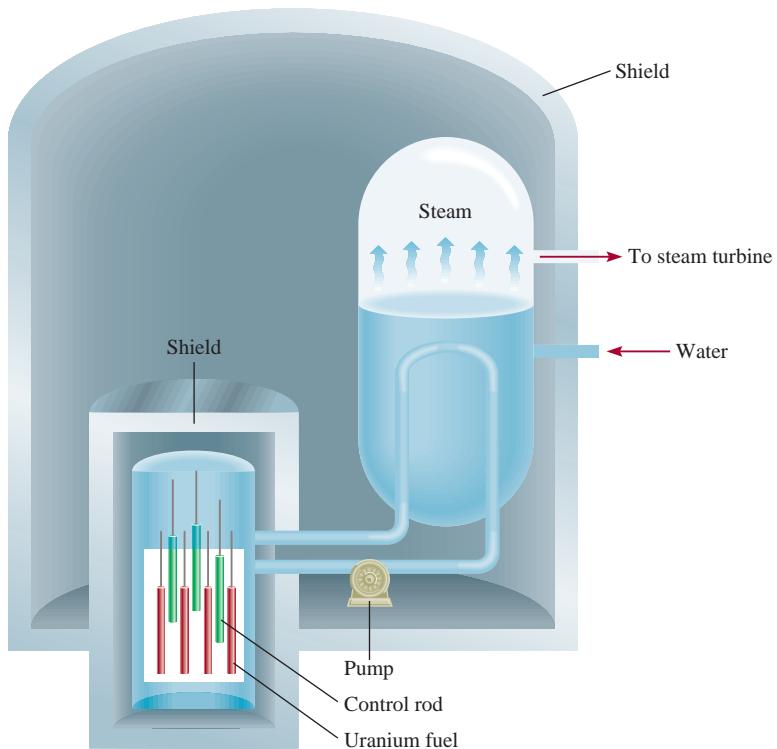
### Nuclear Reactors

A peaceful, but controversial, application of nuclear fission is the generation of electricity using heat from a controlled chain reaction in a nuclear reactor. Currently, nuclear reactors provide about 20 percent of the electric energy in the United States. This is a small but by no means negligible contribution to the nation's energy production. Several different types of nuclear reactors are in operation; we will briefly discuss the main features of three of them—namely, light water reactors, heavy water reactors, and breeder reactors—along with their advantages and disadvantages.

Most of the nuclear reactors in the United States are **light water reactors**, an example of which is shown schematically in Figure 17.12. Figure 17.13 shows the refueling process in the core of such a nuclear reactor.

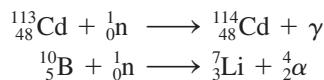
The speed of the neutrons is a crucial aspect of the fission reaction. Slow neutrons split uranium-235 nuclei more efficiently than do fast ones. Because fission reactions are highly exothermic, the neutrons produced usually move at high velocities. To improve the efficiency of the reaction, therefore, the neutrons must be slowed down with **moderators** (*substances that can reduce the kinetic energy of neutrons*) before they can be used to induce nuclear disintegration. A good moderator must be nontoxic

**Figure 17.12** Schematic diagram of a nuclear fission reactor. The fission reaction is controlled by cadmium or boron rods. The heat generated by the reaction is used to produce steam for the generation of electricity.



and inexpensive (because very large quantities of it are needed), and it should resist conversion into a radioactive substance by neutron bombardment. Furthermore, it is helpful if the moderator is a liquid so that it can also be used as a coolant. No substance fulfills all these requirements, although water comes closer than many others that have been considered. Nuclear reactors that use  ${}^1\text{H}_2\text{O}$  as a moderator are called light water reactors because  ${}^1\text{H}$  is the lightest isotope of the element hydrogen.

The nuclear fuel consists of uranium, usually in the form of its oxide ( $\text{U}_3\text{O}_8$ ) (Figure 17.14). Naturally occurring uranium contains about 0.7 percent of the uranium-235 isotope, which is too low a concentration to sustain a small-scale chain reaction. For effective operation of a light water reactor, uranium-235 must be enriched to a concentration of 3 or 4 percent. In principle, the main difference between an atomic bomb and a nuclear reactor is that the chain reaction that takes place in a nuclear reactor is kept under control at all times. The factor limiting the rate of the reaction is the number of neutrons present. This can be controlled by lowering cadmium or boron control rods between the fuel elements. These rods capture neutrons according to the following equations:



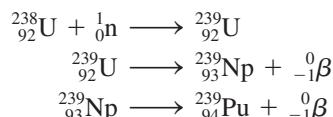
where  $\gamma$  denotes gamma emission. Without the control rods, the reaction could not be controlled and the reactor core would melt from the heat generated and release radioactive materials into the environment.

Nuclear reactors have rather elaborate cooling systems that absorb the heat given off by the nuclear reaction and transfer it outside the reactor core, where it is used to produce enough steam to drive an electric generator. In this respect, a nuclear power plant is similar to a conventional power plant that burns fossil fuel. In both cases, large quantities of cooling water are needed to condense steam for reuse. Thus, most nuclear power plants are built near a river or a lake. Unfortunately, this method of cooling causes thermal pollution.

A **heavy water reactor** uses  $\text{D}_2\text{O}$  ( ${}^2\text{H}_2\text{O}$  or *heavy water*) as the moderator rather than  $\text{H}_2\text{O}$ . Deuterium absorbs neutrons much less efficiently than ordinary hydrogen. Because fewer neutrons are absorbed, the reactor is more efficient and does not require enriched uranium. On the other hand, more neutrons leak out of the reactor, too, though this is not a serious disadvantage.

The main advantage of a heavy water reactor is that it eliminates the need for building expensive uranium enrichment facilities. However,  $\text{D}_2\text{O}$  must be prepared by either fractional distillation or electrolysis of ordinary water, which can be very expensive considering the amount of water used in a nuclear reactor. In countries where hydroelectric power is abundant, the cost of producing  $\text{D}_2\text{O}$  by electrolysis can be reasonably low. At present, Canada is the only nation successfully using heavy water nuclear reactors. Because no enriched uranium is required in a heavy water reactor, Canada enjoys the benefits of nuclear power without undertaking work that is closely associated with weapons technology.

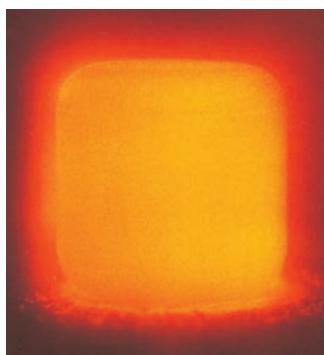
A **breeder reactor** uses uranium fuel, but unlike a conventional nuclear reactor, it *produces more fissionable materials than it uses*. Recall from Table 17.3 that uranium-238, when bombarded with fast neutrons, undergoes the following reactions:



**Figure 17.13** Refueling the core of a nuclear reactor.



**Figure 17.14** Uranium oxide ( $\text{U}_3\text{O}_8$ ).

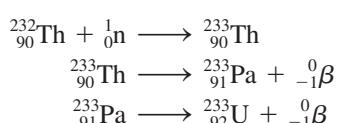


**Figure 17.15** The red glow of the radioactive plutonium oxide, ( $\text{PuO}_2$ ).

In this manner, the nonfissionable uranium-238 is transmuted into the fissionable isotope plutonium-239 (Figure 17.15).

In a typical breeder reactor, nuclear fuel containing uranium-235 or plutonium-239 is mixed with uranium-238 so that breeding takes place within the core. For every uranium-235 (or plutonium-239) nucleus undergoing fission, more than one neutron is captured by uranium-238 to generate plutonium-239. Thus, the stockpile of fissionable material can be steadily increased as the starting nuclear fuels are consumed. It takes about 7 to 10 years to regenerate the sizable amount of material needed to refuel the original reactor and to fuel another reactor of comparable size. This interval is called the *doubling time*.

Another fertile isotope is  $^{232}_{90}\text{Th}$ . Upon capturing slow neutrons, thorium is transmuted to uranium-233, which, like uranium-235, is a fissionable isotope:



Uranium-233 ( $t_{\frac{1}{2}} = 1.6 \times 10^5$  yr) is stable enough for long-term storage.

Although the amounts of uranium-238 and thorium-232 in the Earth's crust are relatively plentiful (4 ppm and 12 ppm by mass, respectively), the development of breeder reactors has been very slow. To date, the United States does not have a single operating breeder reactor, and only a few have been built in other countries, such as France and Russia. One problem is economics; breeder reactors are more expensive to build than conventional reactors. There are also more technical difficulties associated with the construction of such reactors. As a result, the future of breeder reactors, in the United States at least, is rather uncertain.

### The Hazards of Nuclear Energy

Many people, not just environmentalists, regard nuclear fission as a highly undesirable method of energy production. Many fission products such as strontium-90 are dangerous radioactive isotopes with long half-lives. Plutonium-239, used as a nuclear fuel and produced in breeder reactors, is one of the most toxic substances known. It is an  $\alpha$ -emitter with a half-life of 24,400 years.

Accidents, too, can present many dangers. An accident at the Three Mile Island reactor near Harrisburg, Pennsylvania, on March 28, 1979, first brought the potential hazards of nuclear plants to public attention. In this instance, very little radiation escaped the reactor, but the plant remained closed for more than a decade while repairs were made and safety issues addressed. Several years later, on April 26, 1986, a reactor at the Chernobyl nuclear plant in Ukraine surged out of control. The fire and explosion that followed released large amounts of radioactive material into the environment. People working near the plant died within weeks as a result of the exposure to the intense radiation. The long-term effects of the radioactive fallout from this incident have not yet been clearly assessed, although agriculture and dairy farming were affected by it. The number of potential cancer cases attributable to the radiation contamination is estimated to be between a few thousand and more than 100,000.

In addition to the risk of accidents, the problem of radioactive waste disposal has not been satisfactorily resolved even for safely operated nuclear plants. Many suggestions have been made as to where to store or dispose of nuclear waste, including burial underground, burial beneath the ocean floor, and storage in deep geologic formations. None

## Nature's Own Fission Reactor

It all started with a routine analysis in May 1972 at the nuclear fuel processing plant in Pierrelatte, France. A staff member was checking the isotope ratio of U-235 to U-238 in a uranium ore and obtained a puzzling result. It had long been known that the relative natural occurrence of U-235 and U-238 is 0.7202 percent and 99.2798 percent, respectively. In this case, however, the amount of U-235 present was only 0.7171 percent. This may seem like a very small deviation, but the measurements were so precise that this difference was considered highly significant. The ore had come from the Oklo mine in the Gabon Republic, a small country on the west coast of Africa. Subsequent analyses of other samples showed that some contained even less U-235, in some cases as little as 0.44 percent.

The logical explanation for the low percentages of U-235 was that a nuclear fission reaction at the mine must have consumed some of the U-235 isotopes. But how did this happen? There are several conditions under which such a nuclear fission reaction could take place. In the presence of heavy water, for example, a chain reaction is possible with unenriched uranium. Without heavy water, such a fission reaction could still occur if the uranium ore and the moderator were arranged according to some specific geometric constraints at the site of the reaction. Both of the possibilities seem rather farfetched. The most plausible explanation was that the uranium ore originally present in the mine was enriched with U-235 and that a nuclear fission reaction took place with light water, as in a conventional nuclear reactor.

As mentioned earlier, the natural abundance of U-235 is 0.7202 percent, but it has not always been that low. The half-lives of U-235 and U-238 are 700 million and 4.51 billion years, respectively. This means that U-235 must have been *more* abundant in the past, because it has a shorter half-life. In fact, at the time Earth was formed, the natural abundance of U-235 was as high as 17 percent! Because the lowest concentration of U-235 required for the operation of a fission reactor is 1 percent, a nuclear chain reaction could have taken place as recently as 400 million years ago. By analyzing the amounts of radioactive fission products left in the ore, scientists concluded that the Gabon "reactor" operated about 2 billion years ago.

Having an enriched uranium sample is only one of the requirements for starting a controlled chain reaction. There must also have been a sufficient amount of the ore and an appropriate moderator present. It appears that as a result of a geologic transformation, uranium ore was continually being washed into the Oklo region to yield concentrated deposits. The moderator needed for the fission process was largely water, present as water of crystallization in the sedimentary ore.

Thus, in a series of extraordinary events, a natural nuclear fission reactor operated at the time when the first life forms appeared on Earth. As is often the case in scientific endeavors, humans are not necessarily the innovators but merely the imitators of nature.



Photo showing the natural nuclear reactor site (lower right-hand corner) at Oklo, Gabon Republic.

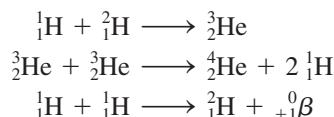
of these sites, however, has proved absolutely safe in the long run. Radioactive wastes could leak into underground water, for example, thus endangering nearby communities.

The ideal disposal site would seem to be the sun, where a bit more radiation would make little difference, but this kind of operation would be enormously expensive and complicated and would require space technology that was 100 percent reliable (so that the waste did not accidentally return to Earth).

## 17.6 | In Nuclear Fusion, Energy Is Produced When Light Nuclei Combine to Form Heavier Ones

Recall from Figure 17.2 that for the lightest elements, nuclear stability increases with increasing mass number. Thus, if two light nuclei combine or fuse together to form a larger, more stable nucleus, an appreciable amount of energy should be released in the process. *The combining of light nuclei to form a heavier one is called nuclear fusion.*

Although nuclear fusion is not yet feasible for producing energy on Earth, it occurs constantly in the sun. The sun is made up mostly of hydrogen and helium. In its interior, where temperatures reach about 15 million degrees Celsius, the following fusion reactions are believed to take place:



Because *fusion reactions take place only at very high temperatures*, they are often called *thermonuclear reactions*.

### Fusion Reactors

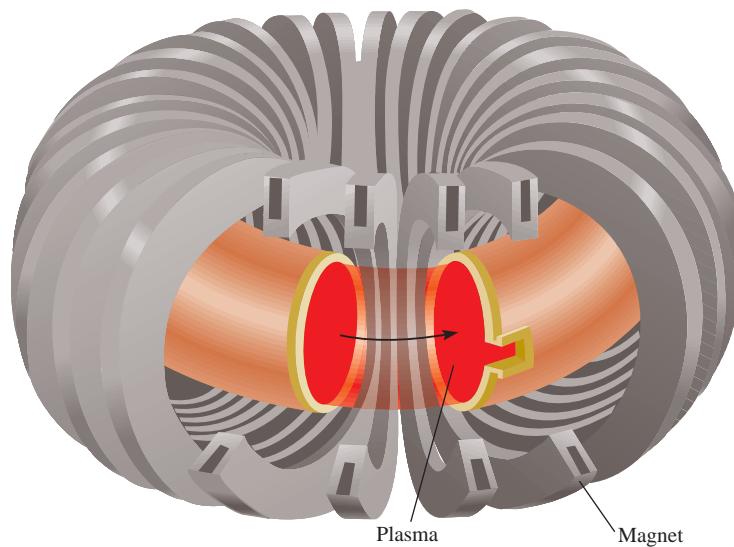
A major concern in choosing the proper nuclear fusion process for energy production is the temperature necessary to carry out the process. Some promising reactions are

Reaction	Energy Released
${}^2_1\text{H} + {}^2_1\text{H} \longrightarrow {}^3_1\text{H} + {}^1_1\text{H}$	3.9 MeV ( $6.3 \times 10^{-13}$ J)
${}^2_1\text{H} + {}^3_1\text{H} \longrightarrow {}^4_2\text{He} + {}^1_0\text{n}$	17 MeV ( $2.8 \times 10^{-12}$ J)
${}^6_3\text{Li} + {}^2_1\text{H} \longrightarrow 2 {}^4_2\text{He}$	22 MeV ( $3.6 \times 10^{-12}$ J)

These reactions take place at extremely high temperatures—on the order of 100 million degrees Celsius—to overcome the repulsive forces between the nuclei. The first reaction is particularly attractive because the world's supply of deuterium is virtually inexhaustible. The total volume of water on Earth is about  $1.5 \times 10^{21}$  L. Because the natural abundance of deuterium is  $1.5 \times 10^{-2}$  percent, the total amount of deuterium present is roughly  $4.5 \times 10^{21}$  g, or  $5.0 \times 10^{15}$  tons. The cost of preparing deuterium is minimal compared with the value of the energy released by the reaction.

In contrast to the nuclear fission, nuclear fusion seems very promising as an energy source, at least “on paper.” Although thermal pollution would be a problem, fusion fuels are cheap and almost inexhaustible and the fusion process produces little radioactive waste. If a fusion generator were turned off, it would shut down completely and instantly, without any danger of a meltdown.

If nuclear fusion is so advantageous, why isn't there even one fusion reactor producing energy? Although we command the scientific knowledge to design such a reactor, the technical difficulties have not yet been solved. The basic problem is finding a way to hold the nuclei together long enough, and at the appropriate temperature, for fusion to occur. At temperatures of about 100 million degrees Celsius, molecules cannot exist, and most or all of the atoms are stripped of their electrons. This *state of matter, a gaseous mixture of positive ions and electrons*, is called *plasma*. The problem of containing this plasma is formidable. What solid container can exist at such temperatures? None, unless the amount of plasma is small, but then the solid surface would immediately cool the sample and quench the fusion reaction. One approach to solving this problem is to use *magnetic confinement*. Because a plasma consists of charged particles moving at high



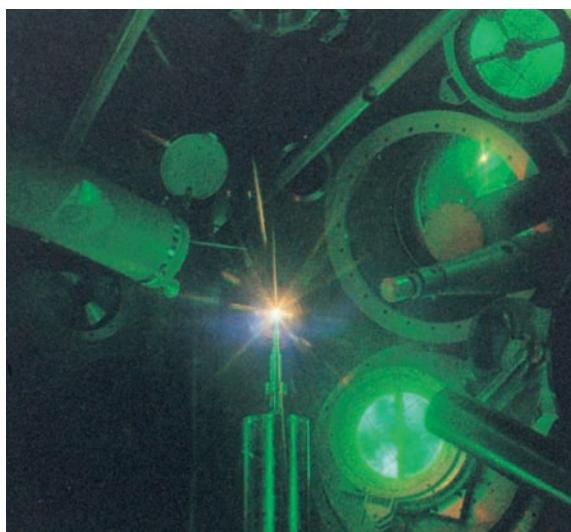
**Figure 17.16** A magnetic plasma containment design called a tokamak.

speeds, a magnetic field will exert a force on it. As shown in Figure 17.16, the plasma moves through a doughnut-shaped tunnel, confined by a complex magnetic field, so the plasma never comes in contact with the walls of the container.

Another promising design employs high-powered lasers to initiate the fusion reaction. In test runs, a number of laser beams transfer energy to a small fuel pellet, heating it and causing it to *implode*, that is, to collapse inward from all sides and compress into a small volume (Figure 17.17), thus causing fusion to occur. Like the magnetic confinement approach, though, laser fusion presents a number of technical difficulties that still need to be overcome before it can be put to practical use on a large scale.

### The Hydrogen Bomb

Nuclear fusion is the main source of power in a hydrogen bomb (also called a *thermonuclear bomb*), but the technical problems inherent in the design of a nuclear fusion reactor do not hinder the production of hydrogen bombs. This is because, unlike a



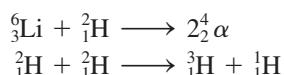
**Figure 17.17** A small-scale fusion reaction was created at Lawrence Livermore National Laboratory using Nova, the world's most powerful laser.



**Figure 17.18** The explosion of a thermonuclear bomb.

reactor, which must release power in a controlled fashion, the objective of a bomb is to unleash as much power as possible with very little control, so containing the reaction is unnecessary (or even counterproductive).

Hydrogen bombs do not contain gaseous hydrogen or gaseous deuterium; instead, they contain solid lithium deuteride ( $\text{LiD}$ ), which can be packed very tightly. Thus, the detonation of a hydrogen bomb occurs in two stages—first a fission reaction and then a fusion reaction. The required temperature for fusion is achieved with a fission reaction generated by an atomic bomb. Immediately after the atomic bomb explodes, the following fusion reactions occur, releasing vast amounts of energy (Figure 17.18):



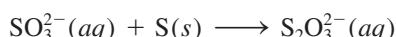
There is no critical mass in a fusion bomb, and the force of the explosion is limited only by the quantity of reactants present. Thermonuclear bombs are described as being “cleaner” than atomic bombs because the only radioactive isotopes they produce are tritium, which is a weak  $\beta$ -particle emitter ( $t_{1/2} = 12.5$  years), and the products of the fission starter. Their damaging effects on the environment can be aggravated, however, by incorporating in the construction some nonfissionable material such as cobalt. Upon bombardment by neutrons, cobalt-59 is converted to cobalt-60, which is a very strong  $\gamma$ -ray emitter with a half-life of 5.2 years. The presence of radioactive cobalt isotopes in the debris or fallout from a thermonuclear explosion would be fatal to those who survived the initial blast.

## 17.7 | Radioactive and Stable Isotopes Alike Have Many Applications in Science and Medicine

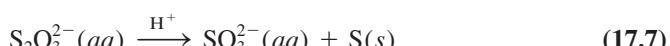
We have previously described the use of isotopes in the study of reaction mechanisms (see Section 14.5) and in dating artifacts (see Section 17.3). In this section, we will describe the use of isotopes in determining chemical structures, in unraveling the reactions in photosynthesis, and in diagnosing diseases.

### Structural Determination

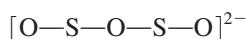
The formula of the thiosulfate ion is  $\text{S}_2\text{O}_3^{2-}$ , but for many years chemists were uncertain whether the two sulfur atoms occupied equivalent positions in the ion. The thiosulfate ion is prepared by treatment of the sulfite ion with elemental sulfur:



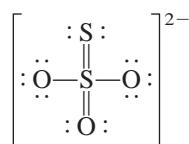
When thiosulfate is treated with dilute acid, the reaction is reversed. The sulfite ion is reformed, and elemental sulfur precipitates:



If  $\text{SO}_3^{2-}(aq)$  is treated with elemental sulfur enriched with the radioactive sulfur-35 isotope, the isotope acts as a “label” for the S atoms in  $\text{S}_2\text{O}_3^{2-}(aq)$ . When  $\text{S}_2\text{O}_3^{2-}(aq)$  is subsequently treated with dilute acid (Equation 17.7), all the labels are found in the sulfur precipitate; none of them appears in the  $\text{SO}_3^{2-}(aq)$ . As a result, the two atoms of sulfur in  $\text{S}_2\text{O}_3^{2-}$  cannot be structurally equivalent, as would be the case if the structure were

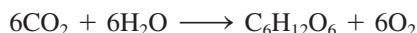


Otherwise, the radioactive isotope would be present in both the elemental sulfur precipitate and the sulfite ion. Based on spectroscopic studies, we now know that the structure of the thiosulfate ion is



### Study of Photosynthesis

The study of photosynthesis is also rich with isotope applications. The overall photosynthesis reaction can be represented as

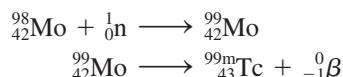


Recall from Section 14.5 that the  $^{18}\text{O}$  isotope was used to determine the source of  $\text{O}_2$  in this reaction. The radioactive  $^{14}\text{C}$  isotope helped to determine the path of carbon in photosynthesis. Starting with  $^{14}\text{CO}_2$ , it was possible to isolate the intermediate products during photosynthesis and measure the amount of radioactivity of each carbon-containing compound. In this manner, the path from  $\text{CO}_2$  through various intermediate compounds to carbohydrate could be clearly charted. *Isotopes, especially radioactive isotopes that are used to trace the path of the atoms of an element in a chemical or biological process are called tracers.*

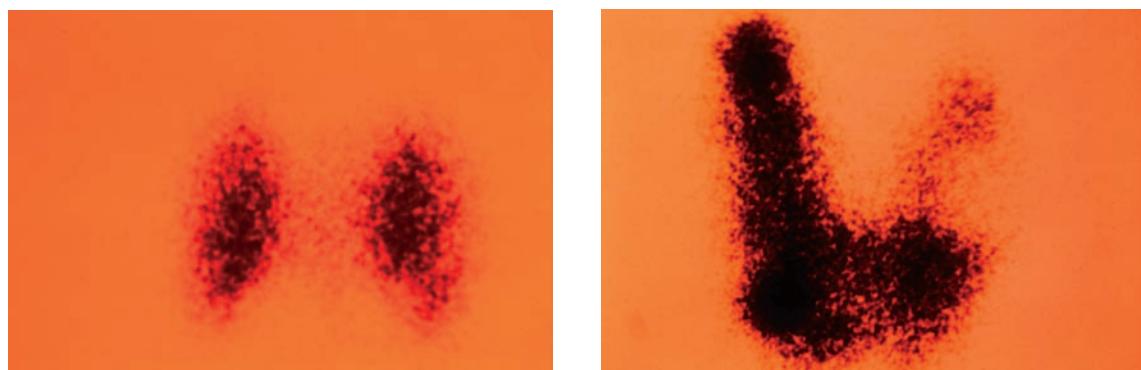
### Isotopes in Medicine

Tracers are used also for diagnosis in medicine. Sodium-24 (a  $\beta$ -emitter with a half-life of 14.8 h) can be injected into the bloodstream as a salt solution and can be then monitored to trace the flow of blood and detect possible constrictions or obstructions in the circulatory system. Iodine-131 (a  $\beta$ -emitter with a half-life of 8 days) is commonly used to test the activity of the thyroid gland. A malfunctioning thyroid can be detected by giving the patient a drink of a solution containing a known amount of  $\text{Na}^{131}\text{I}$  and measuring the radioactivity just above the thyroid to see if the iodine is absorbed at the normal rate. The amounts of radioisotope used to diagnose diseases in the human body must always be kept small; otherwise, the patient might suffer permanent damage from the high-energy radiation. Another radioactive isotope of iodine, iodine-123 (a  $\gamma$ -ray emitter), is used to image the thyroid gland (Figure 17.19).

Technetium, the first artificially prepared element, is one of the most useful elements in nuclear medicine. Although technetium is a transition metal, all its isotopes are radioactive. In the laboratory, it is prepared by the following nuclear reactions:



where the superscript “m” denotes that the technetium-99 isotope is produced in its excited nuclear state. This isotope has a half-life of about 6 h, decaying by  $\gamma$  radiation to technetium-99 in its nuclear ground state. To use technetium as a diagnostic tool, the patient either drinks or is injected with a solution containing  ${}^{99m}\text{Tc}$ . By detecting the  $\gamma$  rays emitted by  ${}^{99m}\text{Tc}$ , doctors can obtain images of organs such as the heart, liver, and lungs.



**Figure 17.19** After ingesting  $\text{Na}^{131}\text{I}$ , the uptake of the radioactive iodine by the thyroid gland in a patient is monitored with a scanner. The photos show a normal thyroid gland (left) and an enlarged thyroid gland (right).

A major advantage of using radioactive isotopes as tracers is that they are easy to detect. Their presence even in very small amounts can be detected by photographic techniques or by devices known as counters, such as the Geiger-Mueller counter pictured in Figure 17.4.

## 17.8 | The Biological Effects of Radiation Can Be Quite Dramatic

In this section, we will examine briefly the effects of radiation on biological systems. But first we need to define quantitative measures of radiation relevant to biological systems. As discussed in Section 17.3, the fundamental unit of radioactivity is the becquerel (Bq), which corresponds to 1 disintegration per second. This unit only measures the quantity of radiation, whereas the intensity of radiation depends on the energy and type of radiation being emitted as well. One common unit for the absorbed dose of radiation is the *rad* (*radiation absorbed dose*), which is the amount of radiation that results in the absorption of  $1 \times 10^{-5}$  J per gram of irradiated material. The biological effect of radiation depends on the part of the body irradiated and the type of radiation. For this reason, the rad is often multiplied by a factor called the *RBE* (*relative biological effectiveness*). The product is called a *rem* (*roentgen equivalent for man*):

$$1 \text{ rem} = 1 \text{ rad} \times 1 \text{ RBE}$$

Of the three types of nuclear radiation,  $\alpha$  particles usually have the least penetrating power. Beta particles are more penetrating than  $\alpha$  particles but less so than  $\gamma$  rays. Gamma rays have very short wavelengths and high energies. Furthermore, because they carry no charge, they cannot be stopped by shielding materials as easily as  $\alpha$  and  $\beta$  particles. If  $\alpha$ - or  $\beta$ -emitters are ingested, however, their damaging effects are greatly aggravated because the organs will be constantly subjected to damaging radiation at close range. For example, strontium-90 (a  $\beta$ -emitter) can replace calcium in bones, where it does the greatest damage.

Table 17.6 lists the average amounts of radiation an American receives every year. For short-term exposures to radiation, a dosage of 50–200 rem will cause a decrease in white blood cell counts and other complications, while a dosage of 500 rem or

**Table 17.6** Average Yearly Radiation Doses for Americans

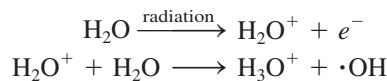
Source	Dose (mrem/yr)*
Cosmic rays	20–50
Ground and surroundings	25
Human body <sup>†</sup>	26
Medical and dental X rays	50–75
Air travel	5
Fallout from weapons tests	5
Nuclear waste	2
Total	<u>133–188</u>

\*1 mrem = 1 millirem =  $1 \times 10^{-3}$  rem.

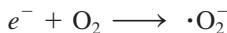
<sup>†</sup>The radioactivity in the body comes from food and air.

greater may result in death within weeks. Current safety standards permit nuclear workers to be exposed to no more than 5 rem per year and specify a maximum of 0.5 rem of human-made radiation per year for the general public.

The chemical basis of radiation damage is ionizing radiation. Radiation by either  $\alpha$  or  $\beta$  particles or  $\gamma$  rays can remove electrons from atoms and molecules in its path, leading to the formation of ions and radicals. **Radicals** (also called *free radicals*) are *molecular fragments having one or more unpaired electrons; they are usually short-lived and highly reactive*. When water is irradiated with  $\gamma$  rays, for example, the following reactions take place:



The electron (in the hydrated form) can subsequently react with water or with a hydrogen ion to form atomic hydrogen, and with oxygen to produce the superoxide ion,  $\text{O}_2^-$  (a radical):



In tissues, the superoxide ions and other free radicals attack cell membranes and a host of organic compounds, such as enzymes and DNA molecules. Organic compounds can themselves be directly ionized and destroyed by high-energy radiation.

Exposure to high-energy radiation can induce cancer in humans and other animals. Cancer is characterized by uncontrolled cellular growth. On the other hand, cancer cells also can be destroyed by proper radiation treatment. In radiation therapy, a compromise is sought. The radiation to which the patient is exposed must be sufficient to destroy cancer cells without killing too many normal cells and, it is hoped, without inducing another form of cancer.

Radiation damage to living systems is generally classified as *somatic* or *genetic*. Somatic injuries are those that affect the organism during its own lifetime. Sunburn, skin rash, cancer, and cataracts are examples of somatic damage. Genetic damage is inheritable changes or gene mutations. For example, a person whose chromosomes have been damaged or altered by radiation may have deformed offspring.

## Food Irradiation

If you eat processed food, you have probably eaten ingredients exposed to radiation. In the United States, up to 10 percent of herbs and spices are irradiated with X-rays to control mold. A typical dose is equivalent to 60 million chest X-rays. Although food irradiation has been used in one way or another for more than 40 years, it faces an uncertain future in this country.

Back in 1953, the U.S. Army started an experimental program of food irradiation so that deployed troops could have fresh food without refrigeration. The procedure is a simple one. Food is exposed to high levels of radiation to kill insects and harmful bacteria. It is then packaged in airtight containers, in which it can be stored for months without deterioration. The radiation sources for most food preservation are cobalt-60 and cesium-137, both of which are  $\gamma$ -emitters, although X-rays and electron beams can also be used to irradiate food.

Food irradiation reduces energy demand by eliminating the need for refrigeration, and it prolongs the shelf life of various foods, which is of vital importance for poor countries. Nevertheless, there is considerable opposition to this procedure. There is a concern, for example, that irradiated food may itself become radioactive. So far, no such evidence has been found. A more serious objection is that irradiation can destroy the nutrients in food, such as vitamins and amino



Strawberries irradiated at 200 kilorads (right) are still fresh after 15 days storage at 4°C; those not irradiated are moldy.

acids. Additionally, the ionizing radiation used to irradiate food produces reactive species, such as the hydroxyl radical, which then react with the organic molecules in food to produce potentially harmful substances. The same effects, however, are produced when food is cooked by heat.

### Food Irradiation Dosages and Their Effects\*

Dosage	Effect
Low dose (up to 100 kilorad)	Inhibits sprouting of potatoes, onions, garlic. Inactivates trichiniae in pork. Kills or prevents insects from reproducing in grains, fruits, and vegetables after harvest.
Medium dose (100–1000 kilorads)	Delays spoilage of meat, poultry, and fish by killing spoilage microorganisms. Reduces salmonella and other food-borne pathogens in meat, fish, and poultry. Extends shelf life by delaying mold growth on strawberries and some other fruits.
High dose (1000–10,000 kilorads)	Sterilizes meat, poultry, fish, and some other foods. Kills microorganisms and insects in spices and seasonings.

\*Source: *Chemical & Engineering News*, May 5, 1986.

## Summary of Facts and Concepts

### Section 17.1

- Certain elements are radioactive because their nuclei are unstable and spontaneously decay through the ejection (or capture) of subatomic particles, often accompanied by the emission of high-energy electromagnetic radiation.

- The principal radioactive decay processes are alpha decay, beta decay, gamma emission, and spontaneous fission. Beta decay can occur through the emission of an electron ( $\beta^-$  decay) or a positron ( $\beta^+$  decay) from the nucleus. Closely related to positron emission is orbital electron capture.

- The equation for a nuclear reaction includes the particles emitted, and both the mass numbers and the atomic numbers must balance.

### Section 17.2

- For stable nuclei of low atomic number, the neutron-to-proton ratio is close to 1. For heavier stable nuclei, the ratio becomes greater than 1. All nuclei with 84 or more protons are unstable and radioactive. Nuclei with even atomic numbers tend to have a greater number of stable isotopes than those with odd atomic numbers.
- Nuclear binding energy is a quantitative measure of nuclear stability. It can be calculated from a knowledge of the mass defect of the nucleus.
- Uranium-238 is the parent of a natural radioactive decay series.

### Section 17.3

- Radioactive decay is a first-order kinetic process that can be used to determine the age of objects.

### Section 17.4

- Artificial radioactive elements can be created by bombarding other elements with accelerated neutrons, protons, or  $\alpha$  particles.

## Key Words

activity, p. 867  
 alpha ( $\alpha$ ) decay, p. 856  
 beta ( $\beta$ ) decay, p. 856  
 breeder reactor, p. 879  
 critical mass, p. 877  
 gamma ( $\gamma$ ) emission, p. 858  
 heavy water reactor, p. 879

internal conversion, p. 858  
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## Problems

### Nuclear Chemistry Is the Study of Changes Involving Atomic Nuclei

17.1 Balance the following nuclear equations by identifying X in each case:

- $^{26}_{12}\text{Mg} + ^1_1\text{p} \longrightarrow ^4_2\alpha + \text{X}$
- $^{59}_{27}\text{Co} + ^2_1\text{H} \longrightarrow ^{60}_{27}\text{Co} + \text{X}$
- $^{235}_{92}\text{U} + ^1_0\text{n} \longrightarrow ^{94}_{36}\text{Kr} + ^{139}_{56}\text{Ba} + 3\text{X}$
- $^{53}_{24}\text{Cr} + ^4_2\alpha \longrightarrow ^1_0\text{n} + \text{X}$
- $^{20}_8\text{O} \longrightarrow ^{20}_9\text{F} + \text{X}$

17.2 Balance the following nuclear equations by identifying X in each case:

- $^{135}_{53}\text{I} \longrightarrow ^{135}_{54}\text{Xe} + \text{X}$

### Section 17.5

- Nuclear fission is the splitting of a large nucleus into two smaller nuclei and one or more neutrons. When the free neutrons are captured efficiently by other nuclei, a chain reaction can occur.
- Nuclear reactors use the heat from a controlled nuclear fission reaction to produce power. The three important types of reactors are light water reactors, heavy water reactors, and breeder reactors.

### Section 17.6

- Nuclear fusion, the type of reaction that occurs in the sun, is the combination of two light nuclei to form one heavy nucleus. Fusion takes place only at very high temperatures, so high that controlled large-scale nuclear fusion has so far not been achieved.

### Section 17.7

- Radioactive isotopes are easy to detect and thus make excellent tracers in chemical reactions and in medical practice.

### Section 17.8

- High-energy radiation damages living systems by causing ionization and the formation of free radicals.

- $^{40}_{19}\text{K} \longrightarrow ^0_{-1}\beta + \text{X}$
- $^{59}_{27}\text{Co} + ^1_0\text{n} \longrightarrow ^{56}_{25}\text{Mn} + \text{X}$
- $^{235}_{92}\text{U} + ^1_0\text{n} \longrightarrow ^{99}_{40}\text{Zr} + ^{135}_{52}\text{Sr} + 2\text{X}$

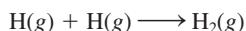
17.3 Write balanced nuclear equations for the following processes:

- Positron emission of  $^{13}_{7}\text{N}$
- $\beta^-$  decay of  $^{20}_{9}\text{F}$
- Electron capture by  $^{37}_{18}\text{Ar}$
- $\alpha$  decay of  $^{148}_{64}\text{Gd}$

- 17.4 Write balanced nuclear equations for the following processes:
- $\alpha$  decay of  $^{235}_{92}\text{U}$
  - $\beta^+$  decay of  $^{15}_{8}\text{O}$
  - $\beta^-$  decay of  $^{11}_{4}\text{Be}$
  - $\beta^-$  decay of  $^{238}_{92}\text{U}$

### The Stability of a Nucleus Is Determined Primarily by Its Neutron-to-Proton Ratio

- 17.5 The radius of a uranium-235 nucleus is about  $7.0 \times 10^{-3}$  pm. Calculate the density of the nucleus in  $\text{g cm}^{-3}$ . (Assume the atomic mass is 235 u.)
- 17.6 For each of the following pairs of isotopes, predict which one is least stable: (a)  $^6_3\text{Li}$  or  $^9_3\text{Li}$ , (b)  $^{23}_{11}\text{Na}$  or  $^{25}_{11}\text{Na}$ , and (c)  $^{48}_{20}\text{Ca}$  or  $^{48}_{21}\text{Sc}$ .
- 17.7 For each of the following pairs of elements, predict which one has more stable isotopes: (a) Co or Ni, (b) F or Se, and (c) Ag or Cd.
- 17.8 For each of the following pairs of isotopes, indicate which one you think would be radioactive: (a)  $^{20}_{10}\text{Ne}$  or  $^{17}_{10}\text{Ne}$ , (b)  $^{40}_{20}\text{Ca}$  or  $^{45}_{20}\text{Ca}$ , (c)  $^{95}_{42}\text{Mo}$  or  $^{92}_{43}\text{Tc}$ , (d)  $^{195}_{80}\text{Hg}$  or  $^{196}_{80}\text{Hg}$ , and (e)  $^{209}_{83}\text{Bi}$  or  $^{242}_{96}\text{Cm}$ .
- 17.9 Given that  $\Delta H^\circ = -436.4 \text{ kJ mol}^{-1}$  for



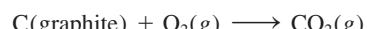
calculate the change in mass (in kg) per mole of  $\text{H}_2$  formed.

- 17.10 The total energy output of the sun is estimated to be  $5 \times 10^{26} \text{ J s}^{-1}$ . What is the corresponding mass loss in  $\text{kg s}^{-1}$  of the sun?
- 17.11 Calculate the nuclear binding energy (in joules and MeV) and the binding energy per nucleon of the following isotopes: (a)  $^7_3\text{Li}$  (7.01600 u) and (b)  $^{35}_{17}\text{Cl}$  (34.95952 u).
- 17.12 Calculate the nuclear binding energy (in joules and MeV) and the binding energy per nucleon of the following isotopes: (a)  $^4_2\text{He}$  (4.0026 u) and (b)  $^{184}_{74}\text{W}$  (183.9510 u).
- 17.13 Carbon-11 and carbon-14 are both unstable isotopes of carbon. Which would be more likely to undergo positron emission? Explain.
- 17.14 Neon-23 and neon-19 are both unstable isotopes of neon. Which would be more likely to undergo  $\beta^-$  decay? Explain.
- 17.15 Calculate the energy released (in J and  $\text{J mol}^{-1}$ ) when a fluorine-17 nucleus undergoes positron emission ( $\beta^+$  decay) to form oxygen-17. The masses of  $^{17}\text{F}$  and  $^{17}\text{O}$  are 17.002098 and 16.999133 u, respectively.
- 17.16 Polonium-210 (mass = 209.98286 u) undergoes alpha decay to form lead-206 (mass = 205.97444 u):



This nuclear reaction is sometimes used as an atomic heat source to power thermoelectric generators in satellites and unmanned space probes.

- (a) Calculate the total energy (in kJ) available from the decay of 1.0 g of Po-210. The mass of the alpha particle is 4.001507 u. (b) What mass of coal would have to be burned to generate the same amount of energy? Assume that the reaction for the burning of coal is



### Radioactive Decay Is a First-Order Kinetic Process

- 17.17 A radioactive substance undergoes decay as follows:

Time (Days)	Mass (g)
0	500
1	389
2	303
3	236
4	184
5	143
6	112

Calculate the first-order decay constant and the half-life of the reaction.

- 17.18 The radioactive decay of Tl-206 to Pb-206 has a half-life of 4.20 min. Starting with  $5.00 \times 10^{22}$  atoms of Tl-206, calculate the number of such atoms left after 42.0 min.
- 17.19 A freshly isolated sample of  $^{90}\text{Y}$  was found to have an activity of  $9.8 \times 10^5$  disintegrations per minute (dpm) at 1:00 P.M. on December 3, 2003. At 2:15 P.M. on December 17, 2003, its activity was redetermined and found to be  $2.6 \times 10^4$  dpm. Calculate the half-life of  $^{90}\text{Y}$ .
- 17.20 Why do radioactive decay series obey first-order kinetics?
- 17.21 In the thorium decay series, thorium-232 loses a total of six  $\alpha$  particles and four  $\beta^-$  particles in a 10-stage process. What is the final isotope produced?
- 17.22 Strontium-90 is one of the products of the fission of uranium-235. This strontium isotope is radioactive, with a half-life of 28.1 years. Calculate how long (in years) it will take for 1.00 g of the isotope to be reduced to 0.200 g by decay.
- 17.23 Consider the decay series



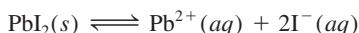
where A, B, and C are radioactive isotopes with half-lives of 4.50 s, 15.0 days, and 1.00 s, respectively, and D is nonradioactive. Starting with 1.00 mole of A, and none of B, C, or D, calculate the number of moles of A, B, C, and D present after 30 days.

## New Isotopes Can Be Produced Through the Process of Nuclear Transmutation

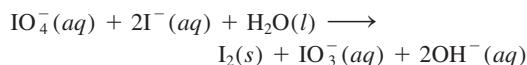
- 17.24 Write balanced nuclear equations for the following reactions and identify X:  
 (a)  $X(p,\alpha)^{12}_6C$ , (b)  $^{27}_{13}Al(d,\alpha)X$ , and (c)  $^{55}_{25}Mn(n,\gamma)X$ .
- 17.25 Write balanced nuclear equations for the following reactions and identify X:  
 (a)  $^{80}_{34}Se(d,p)X$ , (b)  $X(d,2p)^{9}_3Li$ , and (c)  $^{10}_{5}B(n,\alpha)X$ .
- 17.26 Describe how you would prepare astatine-211, starting with bismuth-209.
- 17.27 A long-cherished dream of alchemists was to produce gold from cheaper and more abundant elements. This dream was finally realized when  $^{198}_{80}Hg$  was converted into gold by neutron bombardment. Write a balanced equation for this reaction.

## Radioactive and Stable Isotopes Alike Have Many Applications in Science and Medicine

- 17.28 Describe how you would use a radioactive iodine isotope to demonstrate that the following process is in dynamic equilibrium:



- 17.29 Consider the following oxidation-reduction reaction:



When  $KIO_4$  is added to a solution containing iodide ions labeled with radioactive iodine-128, all the radioactivity appears in  $I_2$  and none in the  $IO_3^-$  ion. What can you deduce about the mechanism for the reaction?

- 17.30 Explain how you might use a radioactive tracer to show that ions diffuse even in crystals.
- 17.31 Each molecule of hemoglobin, the oxygen carrier in blood, contains four Fe atoms. Explain how you would use the radioactive isotope  $^{59}_{26}Fe$  ( $t_{\frac{1}{2}} = 46$  days) to show that the iron in a certain food is converted into hemoglobin.

## Additional Problems

- 17.32 How does a Geiger-Mueller counter work?
- 17.33 Nuclei with an even number of protons and an even number of neutrons are more stable than those with an odd number of protons and/or an odd number of neutrons. What is the significance of the even numbers of protons and neutrons in this case?
- 17.34 Tritium ( $^3_1H$ ) is radioactive and decays by  $\beta^-$  emission with a half-life of 12.5 years. In ordinary water, the ratio of  $^1H$  to  $^3H$  atoms is  $1.0 \times 10^{17}$  to 1. (a) Write a balanced nuclear equation for tritium decay. (b) How many disintegrations will be observed per minute in a 1.00-kg sample of water?
- 17.35 (a) What is the activity, in millicuries, of a 0.500-g sample of  $^{237}_{93}Np$ ? (This isotope decays by  $\alpha$ -particle emission and has a half-life of  $2.20 \times 10^6$  yr.)  
 (b) Write a balanced nuclear equation for the decay of  $^{237}_{93}Np$ .
- 17.36 The following equations are for nuclear reactions that are known to occur in the explosion of an atomic bomb. Identify X in each case.  
 (a)  $^{235}_{92}U + ^1_0n \longrightarrow ^{140}_{56}Ba + ^3_0n + X$   
 (b)  $^{235}_{92}U + ^1_0n \longrightarrow ^{144}_{55}Cs + ^{90}_{37}Rb + 2X$   
 (c)  $^{235}_{92}U + ^1_0n \longrightarrow ^{87}_{35}Br + ^3_0n + X$   
 (d)  $^{235}_{92}U + ^1_0n \longrightarrow ^{160}_{62}Cs + ^{72}_{30}Zn + 4X$
- 17.37 Calculate the nuclear binding energies (in joules per nucleon) for the following species: (a)  $^{10}_3B$  (10.0129 u), (b)  $^{11}_5B$  (11.00931 u), (c)  $^{14}_7N$  (14.00307 u), and (d)  $^{56}_{26}Fe$  (55.9349 u).
- 17.38 Write complete nuclear equations for the following processes: (a) tritium,  $^3_1H$ , undergoes  $\beta^-$  decay, (b)  $^{242}_{92}Pu$  undergoes  $\alpha$ -particle emission, (c)  $^{131}_5I$  undergoes  $\beta^-$  decay, (d)  $^{251}_{96}Cf$  emits an  $\alpha$  particle, and (e)  $^8_3B$  undergoes positron decay.
- 17.39 The nucleus of nitrogen-18 lies above the stability belt. Write an equation for a nuclear reaction by which nitrogen-18 can achieve stability.
- 17.40 Why is strontium-90 a particularly dangerous isotope for humans?
- 17.41 How are scientists able to tell the age of a fossil?
- 17.42 After the Chernobyl accident, people living close to the nuclear reactor site were urged to take large amounts of potassium iodide as a safety precaution. What is the chemical basis for this action?
- 17.43 Astatine, the last known member of Group 7A, can be prepared by bombarding bismuth-209 with  $\alpha$  particles. (a) Write an equation for the reaction. (b) Represent the equation in the abbreviated form introduced in Section 17.4.
- 17.44 To detect bombs that may be smuggled onto airplanes, the Federal Aviation Administration (FAA) requires all major airports in the United States to install thermal neutron analyzers. The thermal neutron analyzer bombards baggage with low-energy neutrons, converting some of the nitrogen-14 nuclei to nitrogen-15, with simultaneous emission of  $\gamma$  rays. Because nitrogen content is usually high in explosives, detection of a high dosage of  $\gamma$  rays will suggest that a bomb may be present. (a) Write an equation for the nuclear process. (b) Compare this technique with the conventional X-ray detection method.
- 17.45 Explain why achieving nuclear fusion in the laboratory requires a temperature of about 100 million degrees Celsius, which is much higher

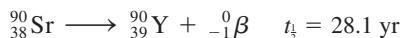
than that in the interior of the sun (15 million degrees Celsius).

- 17.46 Tritium contains one proton and two neutrons. There is no proton-proton repulsion present in the nucleus. Why, then, is tritium radioactive?
- 17.47 The carbon-14 decay rate of a sample obtained from a young tree is 0.260 disintegrations per second per gram of the sample. Another wood sample prepared from an object recovered at an archaeological excavation gives a decay rate of 0.186 disintegrations per second per gram of the sample. What is the age of the object?
- 17.48 The usefulness of radiocarbon dating is limited to objects no older than 50,000 years. What percent of the carbon-14, originally present in the sample, remains after this period of time?

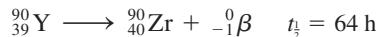
- 17.49 The radioactive potassium-40 isotope decays to argon-40 with a half-life of  $1.2 \times 10^9$  years. (a) Write a balanced equation for the reaction. (b) A sample of moon rock is found to contain 18 percent potassium-40 and 82 percent argon by mass. Calculate the age of the rock in years.

- 17.50 Both barium (Ba) and radium (Ra) are members of Group 2A and are expected to exhibit similar chemical properties. Ra, however, is not found in barium ores. Instead, it is found in uranium ores. Explain.

- 17.51 Nuclear waste disposal is one of the major concerns of the nuclear industry. In choosing a safe and stable environment to store nuclear wastes, consideration must be given to the heat released during nuclear decay. As an example, consider the  $\beta$  decay of  $^{90}\text{Sr}$  (89.907738 u):



The  $^{90}\text{Y}$  (89.907152 u) further decays as follows:



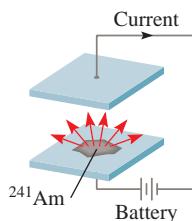
Zirconium-90 (89.904703 u) is a stable isotope. (a) Use the mass defect to calculate the energy released (in joules) in each of the decays of  $^{90}\text{Sr}$  and  $^{90}\text{Y}$ . (The mass of the electron is  $5.4857 \times 10^{-4}$  u.) (b) Starting with 1 mole of  $^{90}\text{Sr}$ , calculate the number of moles of  $^{90}\text{Sr}$  that will decay in a year. (c) Calculate the amount of heat released (in kJ) corresponding to the number of moles of  $^{90}\text{Sr}$  that decayed to  $^{90}\text{Zr}$  in part (b).

- 17.52 Which of the following poses a greater health hazard: a radioactive isotope with a short half-life or a radioactive isotope with a long half-life? Explain. [Assume the isotopes have the same type of radiation ( $\alpha$  or  $\beta^-$ ) and comparable energetics per particle emitted.]
- 17.53 As a result of being exposed to the radiation released during the Chernobyl nuclear accident, the dose of

iodine-131 in a person's body is 7.4 mCi (1 mCi =  $1 \times 10^3$  Ci). Use the relationship  $\text{rate} = \lambda N$  to calculate the number of atoms of iodine-131 to which this radioactivity corresponds. (The half-life of  $^{131}\text{I}$  is 8.1 d.)

- 17.54 Referring to the Food Irradiation inset on page 888, why is it highly unlikely that irradiated food would become radioactive?
- 17.55 From the definition of a curie, calculate Avogadro's number, given that the molar mass of  $^{226}\text{Ra}$  is 226.03 g mol $^{-1}$  and that it decays with a half-life of  $1.6 \times 10^3$  years.
- 17.56 Since 1994, elements 110 (darmstadtium, Ds), 111 (roentgenium, Rg), 112 (ununbium, Uub), and 114 (ununquadium, Uuq) have been synthesized. Element 110 was created by bombarding  $^{208}\text{Pb}$  with  $^{62}\text{Ni}$ ; element 111 was created by bombarding  $^{209}\text{Bi}$  with  $^{64}\text{Ni}$ ; element 112 was created by bombarding  $^{208}\text{Pb}$  with  $^{66}\text{Zn}$ , and element 114 was created by bombarding  $^{244}\text{Pu}$  with  $^{48}\text{Ca}$ . Write an equation for each synthesis. Predict the chemical properties of these elements.
- 17.57 Sources of energy on Earth include fossil fuels, geothermal, gravitational, hydroelectric, nuclear fission, nuclear fusion, solar, and wind. Which of these have a "nuclear origin," either directly or indirectly?
- 17.58 A person received an anonymous gift of a decorative cube, which he placed on his desk. A few months later he became ill and died shortly afterward. After investigation, the cause of his death was linked to the box. The box was airtight and had no toxic chemicals on it. What might have killed the man?
- 17.59 Identify two of the most abundant radioactive elements that exist on Earth. Explain why they are still present? (You may need to consult a handbook of chemistry.)
- 17.60 (a) Calculate the energy released (in MeV and joules) when a U-238 isotope decays to Th-234. The atomic masses are 238.0508 u for U-238, 234.0436 u for Th-234, and 4.0026 u for He-4. (b) The energy released in (a) is transformed into the kinetic energy of the recoiling Th-234 nucleus and the  $\alpha$  particle. Which of the two will move away faster? Explain.
- 17.61 Cobalt-60 is an isotope used in diagnostic medicine and cancer treatment. It decays with  $\gamma$ -ray emission. Calculate the wavelength of the radiation in nanometers if the energy of the  $\gamma$  ray is  $2.4 \times 10^{-13}$  J per photon.
- 17.62 Americium-241 is used in smoke detectors because it has a long half-life (458 years) and because the  $\alpha$  particles it emits are energetic enough to ionize

air molecules. Given the following schematic diagram of a smoke detector, explain how it works.



- 17.63 The constituents of wine contain carbon, hydrogen, and oxygen atoms, among others. A bottle of wine was sealed about 6 years ago. To confirm its age, which of the isotopes would you choose in a radioactive dating study? The half-lives of the isotopes are 5730 years for  $^{13}\text{C}$ , 124 s for  $^5\text{O}$ , and 12.5 years for  $^3\text{H}$ . Assume that the activities of the isotopes were known at the time the bottle was sealed.

- 17.64 Name two advantages of a nuclear-powered submarine over a conventional submarine.

- 17.65 In 1997, a scientist at a nuclear research center in Russia placed a thin shell of copper on a sphere of highly enriched uranium-235. Suddenly, there was a huge burst of radiation, which turned the air blue. Three days later, the scientist died of radiation poisoning. Explain what caused the accident. (*Hint:* Copper is an effective metal for reflecting neutrons.)

- 17.66 A radioactive isotope of copper decays as follows:



Starting with 84.0 g of  $^{64}\text{Cu}$ , calculate the quantity of  $^{64}\text{Zn}$  produced after 18.4 h.

- 17.67 A 0.0100-g sample of a radioactive isotope with a half-life of  $1.3 \times 10^9$  years decays at the rate of  $2.9 \times 10^4$  dpm. Calculate the molar mass of the isotope.

- 17.68 An isolated neutron will undergo spontaneous  $\beta^-$  decay ( ${}_{0}^1n \longrightarrow {}_{+1}^1p + {}_{-1}^0\beta + \bar{\nu}$ ) with a half-life

of about 10.5 min; however, spontaneous  $\beta^+$  decay of an isolated proton ( ${}_{+1}^1p \longrightarrow {}_{0}^1n + {}_{-1}^0\beta + \nu$ ) is not observed. (a) Give an explanation for this observation. (*Hint:* What are the masses of protons and neutrons?) (b) Why is  $\beta^+$  (positron emission) from a nucleus possible even though it does not occur for an isolated proton.

- 17.69 The half-life of  $^{27}\text{Mg}$  is 9.50 min. (a) Initially there were  $4.20 \times 10^{12}$   $^{27}\text{Mg}$  nuclei present. How many  $^{27}\text{Mg}$  are left 30.0 min later? (b) Calculate the  $^{27}\text{Mg}$  activities (in Ci) at  $t = 0$  and  $t = 30.0$  min. (c) What is the probability that any one  $^{27}\text{Mg}$  nucleus decays during a 1-s interval? What assumption is made in this calculation?

- 17.70 The radioactive isotope  $^{238}\text{Pu}$ , used in pacemakers, decays by emitting an  $\alpha$  particle with a half-life of 86 years. (a) Write an equation for the decay process. (b) The energy of the emitted  $\alpha$  particle is  $9.0 \times 10^{-13}$  J, which is the energy per decay. Assume that all the  $\alpha$  particle energy is used to run the pacemaker, calculate the power output at  $t = 0$  and  $t = 10$  yr. Initially 1.0 mg of  $^{238}\text{Pu}$  was present in the pacemaker. (*Hint:* after 10 years, the activity of the isotope decreases by 8.0 percent. Power is measured in watts or  $\text{J s}^{-1}$ .)

- 17.71 (a) Assume nuclei are spherical in shape, show that the radius ( $r$ ) of a nucleus is proportional to the cube root of mass number ( $A$ ). (b) In general, the radius of a nucleus is given by  $r = r_0 A^{1/3}$ , where  $r_0$ , the proportionality constant, is given by  $1.2 \times 10^{-15}$  m. Calculate the volume of the  $^{238}\text{U}$  nucleus.

- 17.72 The quantity of a radioactive material is often measured by its activity (measured in curies or millicuries) rather than by its mass. In a brain scan procedure, a 70-kg patient is injected with 15.0 mCi of  $^{99m}\text{Tc}$ , which decays by emitting  $\gamma$ -ray photons with a half-life of 6.0 h. Given that the RBE of these photons is 0.98 and only two-third of the photons are absorbed by the body, calculate the rem dose received by the patient. Assume all the  $^{99m}\text{Tc}$  nuclei decay while in the body.

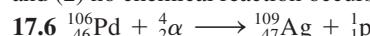
## Answers to Practice Exercises

**17.1**  ${}_{10}^{22}\text{Ne}$  **17.2** 1640.4 MeV,  $7.8488 \text{ MeV nucleon}^{-1}$

**17.3**  $2.1421 \times 10^{-12} \text{ J}$ ,  $1.2900 \times 10^9 \text{ kJ mol}^{-1}$  **17.4** 57.8 days

**17.5**  $2.41 \times 10^9 \text{ yr}$ ; assumptions: (1) no lead initially present,

and (2) no chemical reaction occurs.





# Appendix 1

## Measurement and Mathematical Background

### A1.1 | Measurement

The measurements chemists make are often used in calculations to obtain other related quantities. Different instruments enable us to measure a substance's properties: The meter stick measures length or scale; the buret, the pipet, the graduated cylinder, and the volumetric flask measure volume; the balance measures mass; and the thermometer measures temperature. Any measured quantity should always be written as a number with an appropriate unit. To say that the distance between New York and San Francisco by car along a certain route is 5166 is meaningless. We must specify that the distance is 5166 kilometers. The same is true in chemistry; units are essential to stating measurements correctly.

### Units

For many years, scientists recorded measurements in *metric units*, which are related decimalily, that is, by powers of 10. In 1960, however, the General Conference of Weights and Measures, the international authority on units, proposed a revised metric system called the *International System of Units* (abbreviated *SI*, from the French *Système Internationale d'Unités*). The SI system of units consists of seven basic units:

- ▶ **Time:** The SI unit of time is the *second* (symbol: s), defined as the length of time required for 9,192,631,770 periods of the radiation corresponding to the transition between two specific electronic states of a cesium-133 atom at 0 K.
- ▶ **Length:** The SI unit of length is the *meter* (symbol: m). A meter is defined such that the speed of light in a vacuum is  $299,792,458 \text{ m s}^{-1}$  exactly.
- ▶ **Mass:** The unit of mass in the SI system is the *kilogram* (symbol: kg). The kilogram is defined as the mass of a platinum-iridium alloy cylinder called the *International Prototype Kilogram* (IPK) that is stored in a vault near Paris.
- ▶ **Electric Current:** The SI unit of current is the *ampere* (symbol: A). The ampere is defined as the current carried by two parallel, straight wires of infinite length and negligible cross section that yields a force of  $2 \times 10^{-7}$  newtons (or  $2 \times 10^{-7} \text{ kg m s}^{-1}$ ) when the wires are held exactly 1 m apart.
- ▶ **Thermodynamic temperature:** The SI unit of temperature is the *kelvin* (symbol: K), defined such that the triple point of water is exactly 273.16 K.
- ▶ **Amount of substance:** The *mole* (symbol: mol) is the SI unit for the amount of a substance and is equal to the number of atoms in 0.012 kg of carbon-12 atoms.
- ▶ **Luminous intensity:** The SI unit for the intensity of light is the *candela* (symbol: cd). The candela is the luminous intensity, in a given direction, of a light source that emits monochromatic light of frequency  $540 \times 10^{12} \text{ s}^{-1}$  with a radiant intensity of 1/683 watts per steradian.

All other units of measurement can be derived from these seven base units. SI units are modified in decimal fashion by a series of prefixes, as shown in Table A1.1. Table A1.2 lists the definitions of a number of common units derived from the SI system.

In addition to the SI units listed in Tables A1.1 and A1.2, a number of non-SI units are utilized commonly in scientific work. Table A1.3 lists those non-SI units that are used in this text.

**Table A1.1** Prefixes Used with SI Units

Prefix	Symbol	Meaning	Example
tera-	T	1,000,000,000,000, or $10^{12}$	1 terameter (Tm) = $1 \times 10^{12}$ m
giga-	G	1,000,000,000, or $10^9$	1 gigameter (Gm) = $1 \times 10^9$ m
mega-	M	1,000,000, or $10^6$	1 megameter (Mm) = $1 \times 10^6$ m
kilo-	k	1,000, or $10^3$	1 kilometer (km) = $1 \times 10^3$ m
hecto-	h	100 or $10^2$	1 hectometer (hm) = 100 m
deca-	da	10 or $10^1$	1 decameter (dam) = 10 m
deci-	d	1/10, or $10^{-1}$	1 decimeter (dm) = 0.1 m
centi-	c	1/100, or $10^{-2}$	1 centimeter (cm) = 0.01 m
milli-	m	1/1,000, or $10^{-3}$	1 millimeter (mm) = 0.001 m
micro-	$\mu$	1/1,000,000, or $10^{-6}$	1 micrometer ( $\mu$ m) = $1 \times 10^{-6}$ m
nano-	n	1/1,000,000,000, or $10^{-9}$	1 nanometer (nm) = $1 \times 10^{-9}$ m
pico-	p	1/1,000,000,000,000, or $10^{-12}$	1 picometer (pm) = $1 \times 10^{-12}$ m
femto-	f	$10^{-15}$	1 femtometer (fm) = $1 \times 10^{-15}$ m
atto-	a	$10^{-18}$	1 attometer (am) = $1 \times 10^{-18}$ m
zepto-	z	$10^{-21}$	1 zeptometer (zm) = $10^{-21}$ m

**Table A1.2** Common SI Derived Units

Quantity	Unit	Symbol	Definition
Energy	joule	J	$1 \text{ kg m}^2 \text{ s}^{-2}$
Force	newton	N	$1 \text{ kg m s}^{-1}$
Volume	cubic meter	$\text{m}^3$	$1 \text{ m}^3$
Temperature (T)	degree celsius	$^{\circ}\text{C}$	$T(^{\circ}\text{C}) = T(\text{K}) - 273.15$
Power	watt	W	$1 \text{ J s}^{-1}$
Electric charge	coulomb	C	$1 \text{ A s}$
Pressure	pascal	Pa	$1 \text{ N m}^{-2}$
Frequency	hertz	Hz	$1 \text{ s}^{-1}$
Electromotive force	volt	V	$1 \text{ W A}^{-1}$
Electric conductance	siemens	S	$1 \text{ A V}^{-1}$
Magnetic flux density	tesla	T	$1 \text{ kg s}^{-2} \text{ A}^{-1}$

## Scientific Notation

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

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

hydrogen atoms. Each hydrogen atom has a mass of only

0.0000000000000000000000000000166 g

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

$$0.000000056 \times 0.0000000048 = 0.0000000000000002688$$

**Table A1.3 Common Non-SI Derived Units Used in Scientific Work**

Quantity	Unit	Symbol	Definition
Volume	liter	L	$1 \text{ L} = 1 \text{ dm}^3 = 10^{-3} \text{ m}^3$
Mass	atomic mass unit	u	$1 \text{ u} = 1.66053886 \times 10^{-27} \text{ kg}$
Concentration	molar	M	$1 \text{ M} = 1 \text{ mol (L of solution)}^{-1}$
	molal	m	$1 \text{ m} = 1 \text{ mol (kg of solute)}^{-1}$
Length	Ångstrom	Å	$1 \text{ Å} = 10^{-10} \text{ m}$
Energy	electron volt	eV	$1 \text{ eV} = 1.60217646 \times 10^{-19} \text{ J}$
	erg	erg	$1 \text{ erg} = 1 \text{ g cm}^2 \text{ s}^{-2}$
	calorie	cal	$1 \text{ cal} = 4.184 \text{ J}$
Pressure	bar	bar	$1 \text{ bar} = 10^5 \text{ Pa}$
	atmosphere	atm	$1 \text{ atm} = 1.01325 \text{ bar}$
	torr	torr	$1 \text{ torr} = 101325/760 \text{ Pa}$ $\approx 133.3223684 \text{ Pa}$
	mm of mercury	mmHg	$1 \text{ mmHg} = 133.3223874 \text{ Pa}$ $\approx 1 \text{ torr}$

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

$$N \times 10^n$$

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

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

- Express 568.762 in scientific notation:

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

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

- Express 0.00000772 in scientific notation:

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

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

Next, we consider how scientific notation is handled in arithmetic operations.

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

$$(7.4 \times 10^3) + (2.1 \times 10^3) = 9.5 \times 10^3$$

$$(4.31 \times 10^4) + (3.9 \times 10^3) = (4.31 \times 10^4) + (0.39 \times 10^4) = 4.70 \times 10^4$$

$$(2.22 \times 10^{-2}) - (4.10 \times 10^{-3}) = (2.22 \times 10^{-2}) - (0.410 \times 10^{-2}) = 1.81 \times 10^{-2}$$

**Multiplication and Division:** To multiply numbers expressed in scientific notation, we multiply  $N_1$  and  $N_2$  in the usual way, but *add* the exponents together. To divide using scientific notation, we divide  $N_1$  and  $N_2$  as usual and subtract the exponents.

The following examples show how these operations are performed:

$$(8.0 \times 10^4) \times (5.0 \times 10^2) = (8.0 \times 5.0)(10^{4+2}) = 40 \times 10^6 \\ = 4.0 \times 10^7$$

$$(4.0 \times 10^{-5}) \times (7.0 \times 10^2) = (4.0 \times 7.0)(10^{-5+2}) = 28 \times 10^{-2} \\ = 2.8 \times 10^{-1}$$

$$\frac{6.9 \times 10^7}{3.0 \times 10^{-5}} = \frac{6.9}{3.0} \times 10^{7-(-5)} = 2.3 \times 10^{12}$$

$$\frac{2.8 \times 10^4}{5.6 \times 10^9} = \frac{2.8}{5.6} \times 10^{4-9} = 0.50 \times 10^{-5} \\ = 5.0 \times 10^{-6}$$

## Significant Figures

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

### Guidelines for Using Significant Figures

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

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

as  $4 \times 10^2$  for one significant figure,  $4.0 \times 10^2$  for two significant figures, or  $4.00 \times 10^2$  for three significant figures.

Example A1.1 shows the determination of significant figures.

### Example A1.1

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

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

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

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

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

$$\begin{array}{r}
 89.332 \\
 + 1.1 \\
 \hline
 90.432
 \end{array}
 \quad \begin{array}{l}
 \leftarrow \text{one digit after the decimal point} \\
 \leftarrow \text{round off to } 90.4
 \end{array}$$
  

$$\begin{array}{r}
 2.097 \\
 - 0.12 \\
 \hline
 1.977
 \end{array}
 \quad \begin{array}{l}
 \leftarrow \text{two digits after the decimal point} \\
 \leftarrow \text{round off to } 1.98
 \end{array}$$

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

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

$$2.8 \times 4.5039 = 12.62092 \quad \leftarrow \text{round off to } 1.3$$

$$\begin{array}{r}
 6.85 \\
 \hline
 112.04
 \end{array}
 = 0.0611388789 \quad \leftarrow \text{round off to } 0.0611$$

3. When taking the natural or base-10 logarithm of a measured value, the number of significant figures to the right of the decimal point in the result is the same as the number of significant figures in the original measurement. For example,

$$\log_{10}(29.23) = 1.465828815 \quad \leftarrow \text{round to } 1.4658$$

$$\ln(7.9 \times 10^{17}) = 41.21080934 \quad \leftarrow \text{round to } 41.21$$

4. When taking the natural or base-10 antilogarithm (exponentiation), the number of significant figures in the result is the same as the number of significant figures to the right of the decimal point in the original measurement. For example,

$$\begin{aligned} e^{5.875} &= 356.02466 && \leftarrow \text{round to } 3.56 \times 10^2 \\ 10^{3.3} &= 1995.26231 && \leftarrow \text{round to } 2 \times 10^3 \end{aligned}$$

5. Keep in mind that exact numbers obtained from definitions or by counting numbers of objects can be considered to have an infinite number of significant figures. If an object has a mass of 0.2786 g, then the mass of eight such objects is

$$0.2786 \text{ g} \times 8 = 2.229 \text{ g}$$

We do *not* round off this product to one significant figure because the number 8 is 8.00000 . . . by definition. Similarly, to take the average of two measured lengths 6.64 cm and 6.68 cm, we write

$$\text{average} = \frac{6.68 \text{ cm} + 6.64 \text{ cm}}{2} = 6.66 \text{ cm}$$

because the number 2 is 2.00000 . . ., by definition.

Example A1.2 shows how significant figures are handled in arithmetic operations.

### Example A1.2

Carry out the following arithmetic operations to the correct number of significant figures: (a) 11,254.1 g + 0.1983 g, (b) 66.59 L – 3.113 L, (c) 8.16 m × 5.1355, (d) (0.0154 kg)/(88.3 mL), (e)  $\log_{10}(3.485 \times 10^7)$ , and (f)  $e^{2.34}$ .

#### Solution

- (a) 
$$\begin{array}{r} 11,245.1 \text{ g} \\ + 0.1983 \text{ g} \\ \hline 11,254.2983 \text{ g} \end{array} \quad \leftarrow \text{round off to } 11,254.3$$
- (b) 
$$\begin{array}{r} 66.59 \text{ L} \\ - 3.113 \text{ L} \\ \hline 63.477 \text{ L} \end{array} \quad \leftarrow \text{round off to } 63.58 \text{ L}$$
- (c)  $8.16 \text{ m} \times 5.1355 = 41.90568 \text{ m} \quad \leftarrow \text{round off to } 41.9 \text{ m}$
- (d) 
$$\begin{array}{r} (0.0154 \text{ kg})/(88.3 \text{ mL}) = 1.7440544 \times 10^{-4} \text{ kg mL}^{-1} \\ \qquad \qquad \qquad \leftarrow \text{round off to } 1.74 \times 10^{-4} \text{ kg mL}^{-1} \end{array}$$
- (e)  $\log_{10}(3.485 \times 10^7) = 7.542202782 \quad \leftarrow \text{round off to } 7.5422$
- (f)  $e^{2.34} = 10.38123656 \quad \leftarrow \text{round to } 1.0 \times 10^1$

**Practice Exercise** Carry out the following arithmetic operations to the correct number of significant figures: (a) 26.5862 L + 0.17 L, (b) 9.1 g – 4.682 g, (c)  $7.1 \times 10^4 \text{ dm} \times 2.2654 \times 10^2 \text{ dm}$ , (d)  $(6.54 \text{ g})/(86.5542 \text{ mL})$ , (e)  $\ln(109.3)$ , and (f)  $10^{17.234}$ .

The preceding rounding-off procedure applies to one-step calculations. In *chain calculations*, that is, calculations involving more than one step, we use a modified procedure. Consider the following two-step calculation:

$$\begin{array}{l} \text{first step: } A \times B = C \\ \text{second step: } C \times D = E \end{array}$$

Let us suppose that A = 3.66, B = 8.45, and D = 2.11. Depending on whether we round off C to three or four significant figures, we obtain a different number for E:

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

However, if we had carried out the calculation as  $3.66 \times 8.45 \times 2.11$  on a calculator without rounding off the intermediate result, we would have obtained 65.3 as the answer for E. In general, in this text we will show the correct number of significant figures in each step of a multistep calculation.

### Accuracy and Precision

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

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

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

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

## A1.2 | Mathematical Background

### Differential Calculus

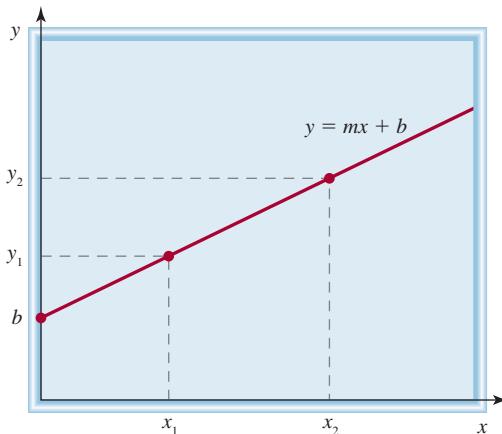
In the physical sciences, we are often interested in understanding how a physical property changes when another property of the system is varied. For example, in Section 10.4, we discuss how the equilibrium constant for a reaction changes when the temperature is changed. This analysis is especially simple if the relationship between the property of interest ( $y$ ) and the property to be varied ( $x$ ) is a straight line (Figure A1.1):

$$y = mx + b$$

where  $m$  is the *slope* and  $b$  is the *intercept* of the line. Because the slope of this line is independent of  $x$ , we can obtain both  $m$  and  $b$  (and thus the value of  $y$  at any  $x$ ) from a measurement of  $y$  at two points  $x_1$  and  $x_2$ :

$$m = \frac{y_2 - y_1}{x_2 - x_1} \quad \text{and} \quad b = y_2 - mx_2$$

**Figure A1.1** The slope of a line  $y = mx + b$  can be found if two points  $(x_1, y_1)$  and  $(x_2, y_2)$  are known.



However, if the relationship between  $y$  and  $x$  is not a straight line, the slope of the curve will not be constant (i.e., independent of  $x$ ). For example, consider the curve

$$y = f(x)$$

The rate of change of this function is not necessarily constant, but is in general a function of  $x$ . We define the *first derivative* ( $df/dx$ ) of a function  $f$  as the slope of the line tangent to the curve  $y = f(x)$  at point  $x$ . This slope can be found by the following procedure (Figure A1.2)

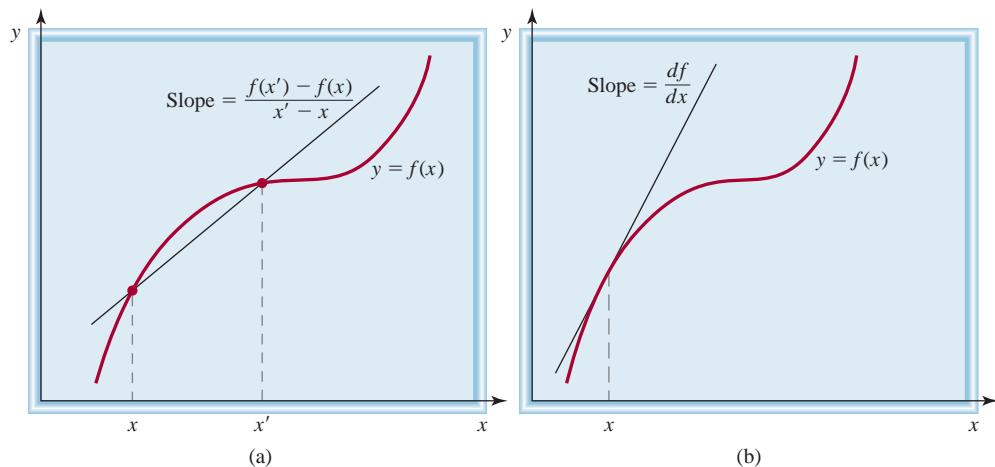
1. Choose a nearby point  $x'$ .
2. Calculate the slope of the line connecting the points  $f(x)$  and  $f(x')$

$$\text{slope} = \frac{f(x') - f(x)}{x' - x}$$

3. The first derivative is found as the value of this slope in the limit that  $x'$  approaches  $x$ :

$$\frac{df}{dx} = \lim_{x' \rightarrow x} \frac{f(x') - f(x)}{x' - x} \quad (\text{A1.1})$$

The first derivative of a function  $f(x)$  at point  $x$  gives the instantaneous rate of change of the function with respect to variations in  $x$  and represents a generalization of the slope for



**Figure A1.2** (a) The slope between two points  $x$  and  $x'$  on a curve  $f(x)$  separated by a finite distance ( $x' - x$ ) is determined using Equation A1.1. (b) In the limit that  $x'$  approaches  $x$ , the slope defined by Equation A1.1 approaches the first derivative of  $f(x)$  at the point  $x$ .

**Table A1.4 Derivatives of Some Common Functions**

$f(x)$	$\frac{df}{dx}$	$f(x)$	$\frac{df}{dx}$
$c$ (a constant)	0	$\ln x$	$1/x$
$x$	1	$\sin x$	$\cos x$
$x^n$	$n x^{n-1}$	$\cos x$	$-\sin x$
$e^x$	$e^x$		

curves that are not straight lines. Use of the derivative (Equation A1.1) in describing the rate of change of functions is called *differential calculus*. The values of the derivative for a number of functions used in this text are listed in Table A1.4.

For more complicated expressions involving the functions above, the following rules can be used to evaluate the first derivative.

$$1. \text{ } \mathbf{Additivity:} \frac{d(f+g)}{dx} = \frac{df}{dx} + \frac{dg}{dx} \quad (\text{A1.2})$$

$$\text{Example: } \frac{d(x^3 + x^2 + 5)}{dx} = \frac{d(x^3)}{dx} + \frac{d(x^2)}{dx} + \frac{d(5)}{dx} = 3x^2 + 2x$$

$$2. \text{ } \mathbf{Product\ Rule:} \frac{d(f \times g)}{dx} = \frac{df}{dx} \times g + f \times \frac{dg}{dx} \quad (\text{A1.3})$$

$$\text{Example: } \frac{d(x^2 e^x)}{dx} = \frac{d(x^2)}{dx} e^x + x^2 \frac{d(e^x)}{dx} = 2x e^x + x^2 e^x$$

$$3. \text{ } \mathbf{Chain\ Rule:} \frac{d[f(g)]}{dx} = \frac{df}{dg} \times \frac{dg}{dx} \quad (\text{A1.4})$$

*Example:* If  $f(x) = \ln(x)$  and  $g(x) = \sin x$ , then

$$\frac{d[\ln(\sin x)]}{dx} = \frac{d(\ln g)}{dg} \times \frac{d(\sin x)}{dx} = \frac{1}{g} \times \cos x = \frac{\cos x}{\sin x}$$

### Partial Derivatives

Often a function of interest will depend upon more than one variable. For example, the function

$$f(x,y) = 3x^2y + 3y^3$$

is a function of both  $x$  and  $y$ . We can differentiate this function two ways:

- We can differentiate with respect to  $x$  and hold  $y$  constant.

$$\left( \frac{\partial f}{\partial x} \right)_y = \left( \frac{\partial [3x^2y + 3y^3]}{\partial x} \right)_y = 6xy$$

- We can differentiate with respect to  $y$  and hold  $x$  constant.

$$\left( \frac{\partial f}{\partial y} \right)_x = \left( \frac{\partial [3x^2y + 3y^3]}{\partial y} \right)_x = 3x^2 + 6y$$

Such derivatives are called *partial derivatives* because we are differentiating with respect to only one of the dependent variables. To distinguish partial derivatives from ordinary derivatives, we use the “ $\partial$ ” symbol instead of “ $d$ .” The variables that are held constant are indicated as subscripts. For example, suppose we have the function

$$g(x,y,z) = 3x^2yz^3$$

The partial derivative of  $g$  with respect to  $x$  (with  $y$  and  $z$  held constant) is

$$\left(\frac{\partial g}{\partial x}\right)_{y,z} = \left(\frac{\partial[3x^2yz^3]}{\partial x}\right)_{y,z} = 3xyz^3$$

## Integral Calculus

In scientific work, it is often more convenient to measure the rate of change of a quantity rather than the quantity itself. For example, a Geiger counter directly measures the rate of decay of a radioactive material, not the amount of material present. In another example, the speedometer on a car measures the rate of change of the car's position (that is, its velocity) and not its absolute position. The central problem of *integral calculus* is to determine the value of a particular property given that its derivative (rate of change) is known.

### Indefinite Integration

We define the *indefinite integral* (or *antiderivative*) of a function  $f(x)$  as the function  $F(x)$  that, when differentiated, yields the original function  $f(x)$ . That is,

$$f(x) = \frac{dF(x)}{dx}$$

The process of integration is denoted symbolically by

$$\int f(x) dx = F(x) + C \quad (\text{A1.5})$$

where the constant  $C$  is necessary because adding a constant to any function does not change the value of its derivative, which is why Equation A1.5 is called an indefinite integral. The symbol “ $dx$ ” indicates that the integration is carried out over the variable  $x$ . Table A1.5 lists the indefinite integrals of some common functions used in this text.

## Definite Integration

Because the indefinite integral  $F(x)$  is only defined with an arbitrary constant  $C$  (Equation A1.5), it is not possible to fix the exact value of a  $F(x)$  given only its rate of change  $f(x)$ . However, if, in addition to  $f(x)$ , the value of  $F(x)$  at some initial value  $x = a$  is known, it is then possible to determine the definite value of  $F(x)$  at any other point  $x = b$ . This is because the constant  $C$

**Table A1.5** Indefinite Integrals of Common Functions

$f(x)$	$F(x) = \int f(x)dx$	$f(x)$	$F(x) = \int f(x)dx$
$c$ (a constant)	$cx$	$\sin x$	$-\cos x$
$x$	$\frac{x^2}{2}$	$\cos x$	$\sin x$
$x^n$	$\frac{x^{n+1}}{n+1}$	$e^x$	$e^x$

cancels when we calculate the difference between  $F(b)$  and  $F(a)$ . To do this we define the *definite integral* of  $f(x)$  between  $x = a$  and  $x = b$  as

$$\int_a^b f(x) dx = F(x)|_a^b = F(b) - F(a) \quad (\text{A1.6})$$

where we used the notation  $F(x)|_a^b$  to denote  $F(b) - F(a)$ .

As an example, suppose that we are given that the rate of change of a function  $F$  with respect to  $x$  is equal to the square of  $x$ :

$$\frac{dF(x)}{dx} = f(x) = x^2$$

and that the value of  $F$  at  $x = 1$  is equal to 5. We can then calculate the value of  $F$  at  $x = 2$  using Equation A1.6:

$$\begin{aligned} F(2) &= F(1) + \int_1^2 x^2 dx \\ &= 5 + \left. \frac{x^3}{3} \right|_1^2 = 5 + \left( \frac{2^3}{3} - \frac{1^3}{3} \right) = \frac{22}{3} \end{aligned}$$

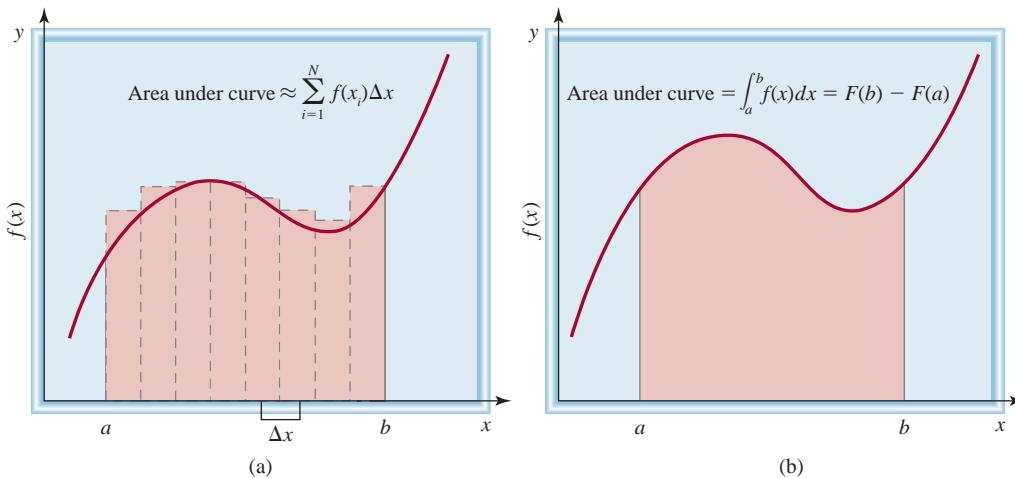
where we have used Table A1.5 to determine the indefinite integral of  $x^2$  to be  $x^3/3$ .

The definite integral also has a geometrical interpretation. If we divide the interval between  $x = a$  and  $x = b$  into  $N$  equal segments of length  $\Delta x = (b - a)/N$ , we can approximate the area under a curve  $f(x)$  by summing up the areas of  $N$  rectangles of height  $f(x_i)$  and width  $\Delta x$ , where  $i = 1, \dots, N$  [Figure A1.3(a)]:

$$\text{area under curve} \approx \sum_{i=1}^N f(x_i) \Delta x \quad (\text{A1.7})$$

This approximation will become exact in the limit that the segment spacing  $\Delta x$  approaches zero. In this limit, the sum in Equation A1.7 approaches the definite integral of  $f(x)$  between  $x = a$  and  $x = b$  [Figure A1.3(b)]:

$$\text{area under curve} = \lim_{\Delta x \rightarrow 0} \sum_{i=1}^N f(x_i) \Delta x = \int_a^b f(x) dx = F(b) - F(a) \quad (\text{A1.8})$$



**Figure A1.3** (a) The area under the curve  $f(x)$  can be approximated by the sum of rectangular areas of width  $\Delta x$  and height  $f(x_i)$ . (b) In the limit that  $\Delta x \rightarrow 0$ , the area under the rectangles approaches the exact area under the curve given by the definite integral  $\int_a^b f(x) dx$ .

## Linear Regression

Relationships between physical properties can, in many cases, be described by a straight line

$$y = mx + b \quad (\text{A1.9})$$

One example is the van't Hoff equation (Equation 10.16), which expresses the linear relationship between the logarithm of an equilibrium constant and inverse temperature ( $1/T$ ), with a slope proportional to the enthalpy of reaction  $\Delta H^\circ$ :

$$\ln \frac{K}{K_1} = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T} \right)$$

By plotting experimental data for the equilibrium constant versus  $1/T$ , the enthalpy of reaction can be found from the slope, which according to the van't Hoff equation is equal to  $-\Delta H^\circ/R$ , where  $R$  is the gas constant. However, expressions, such as the van't Hoff equation, are often approximate, so experimental data will not conform exactly to a straight line. Also, experimental measurements always have a certain level of uncertainty that depends upon the precision of the experimental technique. As a result, we often desire to determine the best straight line through a set of data points. The standard method for accomplishing this is known as *least-squares linear regression*.

To see how least-squares linear regression works, consider that we are given a set of  $N$  experimental data values  $\{(x_i, y_i), i = 1, \dots, N\}$ . We wish to find the best straight line (Equation A1.9) that fits this data. The deviation of each data point from a line of slope  $m$  and intercept  $b$  is given by

$$\Delta y_i = [y_i - (mx_i + b)]$$

In least-squares linear regression, the best line fit is determined by finding the values of  $m$  and  $b$  for which the sum of the squared deviations is as small as possible, that is, we wish to minimize the quantity

$$F(m, b) = \sum_{i=1}^N [y_i - (mx_i + b)]^2$$

Using differential calculus, the values of  $m$  and  $b$  for the best line through the data points are found to be

$$m = \frac{N \sum_{i=1}^N x_i y_i - \left( \sum_{i=1}^N x_i \right) \left( \sum_{i=1}^N y_i \right)}{N \sum_{i=1}^N x_i^2 - \left( \sum_{i=1}^N x_i \right)^2} \quad (\text{A1.10})$$

$$b = \frac{\sum_{i=1}^N y_i - m \sum_{i=1}^N x_i}{N} \quad (\text{A1.11})$$

The quality of the fit can be determined by calculating the correlation coefficient

$$r = \frac{N \sum_{i=1}^N x_i y_i - \left( \sum_{i=1}^N x_i \right) \left( \sum_{i=1}^N y_i \right)}{\sqrt{\left[ N \sum_{i=1}^N x_i^2 - \left( \sum_{i=1}^N x_i \right)^2 \right] \left[ N \sum_{i=1}^N y_i^2 - \left( \sum_{i=1}^N y_i \right)^2 \right]}} \quad (\text{A1.12})$$

A value of  $r$  that is close to 1.0 indicates that the data is well fitted by a straight line, whereas a value near 0.0 tells us that a straight line does not describe the data very well.

Evaluating Equations A1.10 to A1.12 by hand can be tedious, especially for large data sets. Fortunately, most scientific calculators and spreadsheet programs have built-in least-squares linear regression functions that can do most of the work for you.

## Solving Polynomial Equations

A polynomial equation is any equation of the form

$$a_n x^n + a_{n-1} x^{n-1} + \cdots + a_2 x^2 + a_1 x + a_0 = 0$$

where the coefficients  $\{a_i; i = 0, 1, \dots, n\}$  are real numbers.

### Quadratic Equations ( $n = 2$ )

A significant fraction of polynomial equations that we encounter in chemistry have  $n = 2$ . Such equations are called *quadratic equations* and are of the form

$$ax^2 + mx + b = 0$$

The two roots of this equation are computed using the *quadratic formula*:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad (\text{A1.13})$$

In most physical problems, a single answer is required. In such cases, one can generally exclude one of the two roots in Equation A1.13 as unphysical. For example, if we are calculating a molarity and Equation A1.13 gives values of 0.534 and  $-0.287$ , then we can eliminate the latter value ( $-0.287$ ) because molarities must be positive.

### Higher-Order Polynomial Equations

For polynomial equations with  $n = 3$  or higher, analytical solutions analogous to the quadratic equation for  $n = 2$  either do not exist ( $n \geq 5$ ) or are quite complex ( $n = 3$  or 4). For such equations, the roots are found numerically using a computer program or spreadsheet or a graphing calculator.

# Appendix 2

## Thermodynamic Data at 1 Bar and 25°C\*

Inorganic Substances				
Substance	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	$\Delta G_f^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\bar{C}_P^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
Ag(s)	0	0	42.6	27.2
Ag <sup>+</sup> (aq)	105.6	77.1	72.7	21.8
AgCl( <i>s</i> )	-127.0	-109.7	96.1	50.8
AgBr( <i>s</i> )	-100.4	-96.9	107.1	52.4
Agl( <i>s</i> )	-61.8	-66.3	115.5	56.8
AgNO <sub>3</sub> ( <i>s</i> )	-124.4	-33.4	140.9	93.1
Al( <i>s</i> )	0	0	28.3	24.2
Al <sup>3+</sup> ( <i>aq</i> )	-531.0	-485.0	-321.7	—
Al <sub>2</sub> O <sub>3</sub> ( <i>s</i> )	-1675.7	-1582.3	50.9	79
As( <i>s</i> )	0	0	35.15	24.6
AsO <sub>4</sub> <sup>3-</sup> ( <i>aq</i> )	-888.1	-648.4	-162.8	—
AsH <sub>3</sub> ( <i>g</i> )	66.4	68.9	222.8	38.1
H <sub>2</sub> AsO <sub>4</sub> ( <i>s</i> )	-906.3	—	—	—
Au( <i>s</i> )	0	0	47.4	25.4
Au <sub>2</sub> O <sub>3</sub> ( <i>s</i> )	80.8	163.2	125.5	—
AuCl( <i>s</i> )	-34.7	—	—	—
AuCl <sub>3</sub> ( <i>s</i> )	-117.6	—	—	—
B( <i>s</i> )	0	0	5.9	11.1
B <sub>2</sub> O <sub>3</sub> ( <i>s</i> )	-1273.5	-1194.3	54.0	62.8
H <sub>3</sub> BO <sub>3</sub> ( <i>s</i> )	-1094.3	-968.9	90	86.1
H <sub>3</sub> BO <sub>3</sub> ( <i>aq</i> )	-1067.8	-963.3	159.8	—
Ba( <i>s</i> )	0	0	62.5	28.1
Ba <sup>2+</sup> ( <i>aq</i> )	-537.6	-560.8	9.6	—
BaO( <i>s</i> )	-558.2	-528.4	70.3	—
BaCl <sub>2</sub> ( <i>s</i> )	-855	-806.7	123.7	75.1
BaSO <sub>4</sub> ( <i>s</i> )	-1464.4	-1353.1	132.2	—
BaCO <sub>3</sub> ( <i>s</i> )	-1213	-1134.4	112.1	86
Be( <i>s</i> )	0	0	9.5	16.4
BeO( <i>s</i> )	-609.4	-580.1	13.8	25.6
Br <sub>2</sub> ( <i>l</i> )	0	0	152.3	75.7
Br <sup>-</sup> ( <i>aq</i> )	-121.6	-104.0	82.4	-141.8
HBr( <i>g</i> )	-36.2	-53.2	198.70	29.1
C(graphite)	0	0	5.69	8.5
C(diamond)	1.90	2.87	2.4	6.1
CO( <i>g</i> )	-110.5	-137.3	197.9	29.1

\*The thermodynamic quantities of ions are based on the reference states that  $\Delta H_f^\circ[\text{H}^+(\text{aq}) = 0]$ ,  $\Delta G_f^\circ[\text{H}^+(\text{aq}) = 0]$ , and  $S^\circ[\text{H}^+(\text{aq})] = 0$ .

(Continued)

Substance	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	$\Delta G_f^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\bar{C}_P^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
CO <sub>2</sub> (g)	-393.5	-394.4	213.6	37.1
CO <sub>2</sub> (aq)	-412.9	-386.2	121.3	—
CO <sub>3</sub> <sup>2-</sup> (aq)	-677.1	-527.8	-56.9	—
HCO <sub>3</sub> <sup>-</sup> (aq)	-691.1	-587.1	94.98	—
H <sub>2</sub> CO <sub>3</sub> (aq)	-699.7	-623.2	187.4	—
CS <sub>2</sub> (g)	116.7	67.1	237.8	45.1
CS <sub>2</sub> (l)	89	64.6	151.3	76.4
HCN(aq)	105.4	112.1	128.9	—
CN <sup>-</sup> (aq)	150.6	172.4	94.1	—
(NH <sub>2</sub> ) <sub>2</sub> CO(s)	-333.19	-197.15	104.6	—
(NH <sub>2</sub> ) <sub>2</sub> CO(aq)	-319.2	-203.84	173.85	—
Ca(s)	0	0	41.6	25.9
Ca <sup>2+</sup> (aq)	-542.8	-553.6	-55.3	—
CaO(s)	-634.9	-603.3	38.1	42
Ca(OH) <sub>2</sub> (s)	-985.2	-897.5	83.4	87.5
CaF <sub>2</sub> (s)	-1228.1	-1175.1	68.5	67
CaCl <sub>2</sub> (s)	-795.4	-748.8	108.4	72.9
CaSO <sub>4</sub> (s)	-1434.5	-1322	106.5	99.7
CaCO <sub>3</sub> (s)	-1207.6	-1129.1	91.7	83.5
Cd(s)	0	0	51.8	26
Cd <sup>2+</sup> (aq)	-75.9	-77.6	-73.2	—
CaO(s)	-258.4	-228.6	43.4	—
CdCl <sub>2</sub> (s)	-391.5	-343.9	115.3	74.7
CdSO <sub>4</sub> (s)	-933.3	-822.7	123	99.6
Cl <sub>2</sub> (g)	0	0	223.0	33.9
Cl <sup>-</sup> (aq)	-167.2	-131.2	56.5	-136.4
HCl(g)	-92.3	-95.27	187.0	29.1
Co(s)	0	0	30	24.8
Co <sup>2+</sup> (aq)	-58.2	-54.4	-113.0	—
CoO(s)	-237.9	-214.2	53	55.2
Cr(s)	0	0	23.8	23.4
Cr <sup>2+</sup> (aq)	-143.5	—	—	—
Cr <sub>2</sub> O <sub>3</sub> (s)	-1139.7	-1058.1	81.2	118.7
CrO <sub>4</sub> <sup>2-</sup> (aq)	-881.2	-727.8	50.2	—
Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> (aq)	-1460.6	-1257.29	213.8	—
Cs(s)	0	0	85.2	32.2
Cs <sup>+</sup> (aq)	-258.3	-292.2	133.1	-10.5
Cu(s)	0	0	33.2	24.4
Cu <sup>+</sup> (aq)	71.7	50.0	40.6	—
Cu <sup>2+</sup> (aq)	64.8	65.5	-99.6	—
CuO(s)	-157.3	-129.7	42.6	42.3
Cu <sub>2</sub> O(s)	-168.6	-146	93.1	63.6

(Continued)

Substance	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	$\Delta G_f^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\bar{C}_P^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
CuCl(s)	-137.2	-119.9	86.2	48.5
CuCl <sub>2</sub> (s)	-220.1	-175.7	108.1	71.9
CuS(s)	-53.1	-53.6	66.5	47.8
CuSO <sub>4</sub> (s)	-771.4	-662.2	109.2	—
F <sub>2</sub> (g)	0	0	202.8	31.3
F <sup>-</sup> (aq)	-332.6	-278.8	-13.8	—
HF(g)	-273.3	-275.4	173.8	—
Fe(s)	0	0	27.3	25.1
Fe <sup>2+</sup> (aq)	-87.86	-84.9	-113.39	—
Fe <sup>3+</sup> (aq)	-47.7	-10.5	-293.3	—
FeO(s)	-272.0	-255.2	60.8	—
Fe <sub>2</sub> O <sub>3</sub> (s)	-824.2	-742.2	87.4	103.9
Fe(OH) <sub>2</sub> (s)	-568.19	-483.55	79.5	—
Fe(OH) <sub>3</sub> (s)	-824.25	—	—	—
H(g)	218.2	203.2	114.6	20.8
H <sub>2</sub> (g)	0	0	130.7	28.8
H <sup>+</sup> (aq)	0	0	0	—
OH <sup>-</sup> (aq)	-229.94	-157.30	-10.5	—
H <sub>2</sub> O(g)	-241.83	-228.6	188.8	33.6
H <sub>2</sub> O(l)	-285.8	-237.1	69.95	75.3
H <sub>2</sub> O <sub>2</sub> (l)	-187.8	-120.4	109.6	89.1
Hg(l)	0	0	75.9	28
Hg <sup>2+</sup> (aq)	—	-164.38	—	—
HgO(s)	-90.7	-58.5	72.0	44.1
HgCl <sub>2</sub> (s)	-224.3	-178.6	144.5	—
Hg <sub>2</sub> Cl <sub>2</sub> (s)	-265.4	-210.7	191.6	—
HgS(s)	-58.16	-48.8	77.8	48.8
HgSO <sub>4</sub> (s)	-704.17	—	—	—
Hg <sub>2</sub> SO <sub>4</sub> (s)	-741.99	-623.92	200.75	132
I <sub>2</sub> (s)	0	0	116.7	54.4
I <sup>-</sup> (aq)	-55.9	-51.67	109.37	—
HI(g)	25.9	1.30	206.3	29.2
K(s)	0	0	64.7	29.6
K <sup>+</sup> (aq)	-251.2	-282.28	102.5	—
KOH(s)	-424.6	-379.4	81.2	68.9
KCl(s)	-436.5	-408.5	82.6	51.3
KClO <sub>3</sub> (s)	-391.20	-289.9	142.97	100.3
KClO <sub>4</sub> (s)	-432.8	-304.18	151.0	112.4
KBr(s)	-392.17	-379.2	96.4	52.3
KI(s)	-327.65	-322.29	104.35	52.9
KNO <sub>3</sub> (s)	-492.7	-393.1	132.9	96.4
Li(s)	0	0	29.1	24.8
Li <sup>+</sup> (aq)	-278.46	-293.8	14.2	68.6

(Continued)

Substance	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	$\Delta G_f^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\bar{C}_P^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
Li <sub>2</sub> O( <i>s</i> )	-595.8	-561.2	37.6	54.1
LiOH( <i>s</i> )	-487.5	-441.5	42.8	49.6
Mg( <i>s</i> )	0	0	32.7	24.9
Mg <sup>2+</sup> ( <i>aq</i> )	-461.96	-456.0	-117.99	—
MgO( <i>s</i> )	-601.8	-569.6	26.78	—
Mg(OH) <sub>2</sub> ( <i>s</i> )	-924.5	-833.5	63.2	77
MgCl <sub>2</sub> ( <i>s</i> )	-641.8	-592.3	89.5	71.4
MgSO <sub>4</sub> ( <i>s</i> )	-1278.2	-1173.6	91.6	96.5
MgCO <sub>3</sub> ( <i>s</i> )	-1112.9	-1029.3	65.69	75.5
Mn( <i>s</i> )	0	0	31.76	26.3
Mn <sup>2+</sup> ( <i>aq</i> )	-218.8	-223.4	-83.68	50.0
MnO <sub>2</sub> ( <i>s</i> )	-520.9	-466.1	53.1	54.1
N <sub>2</sub> ( <i>g</i> )	0	0	191.6	29.1
N <sub>3</sub> <sup>-</sup> ( <i>aq</i> )	245.18	—	—	—
NH <sub>3</sub> ( <i>g</i> )	-45.9	-16.4	192.8	35.1
NH <sub>4</sub> <sup>+</sup> ( <i>aq</i> )	-132.80	-79.5	112.8	—
NH <sub>4</sub> Cl( <i>s</i> )	-314.4	-202.9	94.6	84.1
NH <sub>3</sub> ( <i>aq</i> )	-80.3	-26.5	111.3	—
N <sub>2</sub> H <sub>4</sub> ( <i>l</i> )	50.6	149.3	121.2	98.9
NO( <i>g</i> )	91.3	87.6	210.8	29.9
NO <sub>2</sub> ( <i>g</i> )	33.85	51.8	240.46	37.2
N <sub>2</sub> O <sub>4</sub> ( <i>g</i> )	9.66	98.29	304.3	79.2
N <sub>2</sub> O( <i>g</i> )	81.56	103.6	219.99	38.6
HNO <sub>2</sub> ( <i>aq</i> )	-118.8	-53.6	—	—
HNO <sub>3</sub> ( <i>l</i> )	-174.1	-80.7	155.6	109.9
NO <sub>3</sub> <sup>-</sup> ( <i>aq</i> )	-207.4	-111.3	146.4	—
Na( <i>s</i> )	0	0	51.3	28.2
Na <sup>+</sup> ( <i>aq</i> )	-240.1	-261.9	59.0	46.4
Na <sub>2</sub> O( <i>s</i> )	-414.2	-375.5	75.1	69.1
NaCl( <i>s</i> )	-411.2	-384.1	72.1	50.5
NaI( <i>s</i> )	-287.8	-286.1	98.5	52.1
Na <sub>2</sub> SO <sub>4</sub> ( <i>s</i> )	-1387.1	-1270.2	149.6	128.2
NaNO <sub>3</sub> ( <i>s</i> )	-467.9	-367	116.5	92.9
Na <sub>2</sub> CO <sub>3</sub> ( <i>s</i> )	-1130.7	-1044.4	135	112.3
NaHCO <sub>3</sub> ( <i>s</i> )	-950.8	-851	101.7	87.6
Ni( <i>s</i> )	0	0	29.9	26.1
Ni <sup>2+</sup> ( <i>aq</i> )	-54.0	-45.6	-128.9	—
NiO( <i>s</i> )	-244.35	-216.3	38.58	—
Ni(OH) <sub>2</sub> ( <i>s</i> )	-529.7	-447.2	88	—
O( <i>g</i> )	249.2	231.7	161.1	21.9
O <sub>2</sub> ( <i>g</i> )	0	0	205.0	29.4
O <sub>3</sub> ( <i>aq</i> )	-12.09	16.3	110.88	—
O <sub>3</sub> ( <i>g</i> )	142.7	163.2	238.9	39.2

(Continued)

Substance	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	$\Delta G_f^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$C_p^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
P(white)	0	0	41.1	23.8
P(red)	-18.4	13.8	29.3	21.2
PO <sub>4</sub> <sup>3-</sup> (aq)	-1277.4	-1018.7	-220.5	—
P <sub>4</sub> O <sub>10</sub> (s)	-3012.48	—	—	—
PH <sub>3</sub> (g)	5.4	13.5	210.2	37.1
HPO <sub>4</sub> <sup>2-</sup> (aq)	-1292.1	-1089.2	-33.5	—
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> (aq)	-1296.3	-1130.2	90.4	—
Pb(s)	0	0	64.89	26.4
Pb <sup>2+</sup> (aq)	-1.7	-24.4	10.5	—
PbO(s)	-217.3	-187.9	68.5	45.8
PbO <sub>2</sub> (s)	-277.4	-217.3	68.6	64.6
PbCl <sub>2</sub> (s)	-359.4	-314.1	136	—
PbS(s)	-100.4	-98.7	91.2	49.5
PbSO <sub>4</sub> (s)	-920	-813	148.5	103.2
Pt(s)	0	0	41.6	25.9
PtCl <sub>4</sub> <sup>2-</sup> (aq)	-516.3	-384.5	175.7	—
Rb(s)	0	0	76.8	31.1
Rb <sup>+</sup> (aq)	-251.2	-284.0	121.5	—
S(rhombic)	0	0	32.1	22.6
S(monoclinic)	0.30	0.10	32.55	—
SO <sub>2</sub> (g)	-296.8	-300.1	248.2	39.9
SO <sub>3</sub> (g)	-395.7	-371.1	256.8	50.7
SO <sub>3</sub> <sup>2-</sup> (aq)	-635.5	-486.5	-29.0	—
SO <sub>4</sub> <sup>2-</sup> (aq)	-909.3	-744.5	20.1	-293.0
H <sub>2</sub> S(g)	-20.6	-33.4	205.8	34.2
HSO <sub>3</sub> <sup>-</sup> (aq)	-626.2	-527.7	139.7	—
HSO <sub>4</sub> <sup>-</sup> (aq)	-887.3	-755.9	131.8	-84.0
H <sub>2</sub> SO <sub>4</sub> (I)	-814	-690	156.9	138.9
SF <sub>6</sub> (g)	-1220.5	-1116.5	291.5	97
Si(s)	0	0	18.8	20
SiO <sub>2</sub> (s)	-910.7	-856.3	41.5	44.4
Sr(s)	0	0	55	26.8
Sr <sup>2+</sup> (aq)	-545.8	-559.5	-32.6	—
SrCl <sub>2</sub> (s)	-828.9	-781.1	114.9	75.6
SrSO <sub>4</sub> (s)	-1453.1	-1340.9	117	—
SrCO <sub>3</sub> (s)	-1220.1	-1140.1	97.1	81.4
Zn(s)	0	0	41.6	25.4
Zn <sup>2+</sup> (aq)	-153.9	-147.1	-112.1	46.0
ZnO(s)	-350.5	-320.5	43.7	40.3
ZnCl <sub>2</sub> (s)	-415.1	-369.4	111.5	71.3
ZnS(s)	-206	-201.3	57.7	46
ZnSO <sub>4</sub> (s)	-982.8	-871.5	110.5	99.2

Organic Substances					
Substance	Formula	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	$\Delta G_f^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$C_P$ (J mol <sup>-1</sup> K <sup>-1</sup> )
Ethanoic acid (acetic acid)( <i>l</i> )	CH <sub>3</sub> COOH	-484.3	-389.9	159.8	123.3
Ethanal (acetaldehyde)( <i>g</i> )	CH <sub>3</sub> CHO	-166.2	-133	263.8	55.3
2-Propanone (acetone)( <i>l</i> )	CH <sub>3</sub> COCH <sub>3</sub>	-246.8	-153.55	198.7	126.3
Ethyne (acetylene)( <i>g</i> )	C <sub>2</sub> H <sub>2</sub>	227.4	209.9	200.9	44
Benzene( <i>l</i> )	C <sub>6</sub> H <sub>6</sub>	49.1	124.5	173.4	136
Butane( <i>g</i> )	C <sub>4</sub> H <sub>10</sub>	-124.7	-15.7	310.0	140.9
Ethanol( <i>l</i> )	C <sub>2</sub> H <sub>5</sub> OH	-277.6	-174.8	160.7	112.3
Ethane( <i>g</i> )	C <sub>2</sub> H <sub>6</sub>	-84	-32	229.2	52.5
Ethene (ethylene)( <i>g</i> )	C <sub>2</sub> H <sub>4</sub>	52.4	68.4	219.3	42.9
Methanoic acid (formic acid)( <i>l</i> )	HCOOH	-425	-361.4	129.0	99
Glucose( <i>s</i> )	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	-1274.5	-910.56	212.1	—
Methane( <i>g</i> )	CH <sub>4</sub>	-74.6	-50.8	186.3	35.7
Methanol( <i>l</i> )	CH <sub>3</sub> OH	-239.2	-166.6	126.8	81.1
Propane( <i>g</i> )	C <sub>3</sub> H <sub>8</sub>	-103.8	-23.4	270.3	73.6
Sucrose( <i>s</i> )	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	-2221.7	-1544.3	360.2	—

# Appendix 3

## *Derivation of the Names of Elements\**

Element	Symbol	Atomic No.	Atomic Mass <sup>†</sup>	Date of Discovery	Discoverer and Nationality <sup>‡</sup>	Derivation
Actinium	Ac	89	(227)	1899	A. Debierne (Fr.)	Gr. <i>aktis</i> , beam or ray
Aluminum	Al	13	26.98	1827	F. Woehler (Ge.)	Alum, the aluminum compound in which it was discovered; derived from L. <i>alumen</i> , astringent taste
Americium	Am	95	(243)	1944	A. Ghiorso (USA) R. A. James (USA) G. T. Seaborg (USA) S. G. Thompson (USA)	The Americas
Antimony	Sb	51	121.8	Ancient		L. <i>antimonium</i> ( <i>anti</i> , opposite of; <i>monium</i> , isolated condition), so named because it is a tangible (metallic) substance which combines readily; symbol L. <i>stibium</i> , mark
Argon	Ar	18	39.95	1894	Lord Raleigh (GB) Sir William Ramsay (GB)	Gr. <i>argos</i> , inactive
Arsenic	As	33	74.92	1250	Albertus Magnus (Ge.)	Gr. <i>aksenikon</i> , yellow pigment; L. <i>arsenicum</i> , orpiment; the Greeks once used arsenic trisulfide as a pigment
Astatine	At	85	(210)	1940	D. R. Corson (USA) K. R. MacKenzie (USA) E. Segré (USA)	Gr. <i>astatos</i> , unstable
Barium	Ba	56	137.3	1808	Sir Humphry Davy (GB)	Barite, a heavy spar, derived from Gr. <i>barys</i> , heavy
Berkelium	Bk	97	(247)	1950	G. T. Seaborg (USA) S. G. Thompson (USA) A. Ghiorso (USA)	Berkeley, Calif.
Beryllium	Be	4	9.012	1828	F. Woehler (Ge.) A. A. B. Bussy (Fr.)	Fr. L. <i>beryl</i> , sweet

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\*At the time this table was drawn up, only 103 elements were known to exist.

<sup>†</sup>The atomic masses given here correspond to the 1961 values of the Commission on Atomic Weights. Masses in parentheses are those of the most stable or most common isotopes.

<sup>‡</sup>The abbreviations are (Ar.) Arabic; (Au.) Austrian; (Du.) Dutch; (Fr.) French; (Ge.) German; (GB) British; (Gr.) Greek; (H.) Hungarian; (I.) Italian; (L.) Latin; (P.) Polish; (R.) Russian; (Sp.) Spanish; (Swe.) Swedish; (USA) American.

(Continued)

Element	Symbol	Atomic No.	Atomic Mass <sup>†</sup>	Date of Discovery	Discoverer and Nationality <sup>‡</sup>	Derivation
Bismuth	Bi	83	209.0	1753	Claude Geoffroy (Fr.)	Ge. <i>bismuth</i> , probably a distortion of <i>weisse masse</i> (white mass) in which it was found
Boron	B	5	10.81	1808	Sir Humphry Davy (GB) J. L. Gay-Lussac (Fr.) L. J. Thenard (Fr.)	The compound borax, derived from Ar. <i>buraq</i> , white
Bromine	Br	35	79.90	1826	A. J. Balard (Fr.)	Gr. <i>bromos</i> , stench
Cadmium	Cd	48	112.4	1817	Fr. Stromeyer (Ge.)	Gr. <i>kadmia</i> , earth; L. <i>cadmia</i> , calamine (because it is found along with calamine)
Calcium	Ca	20	40.08	1808	Sir Humphry Davy (GB)	L. <i>calx</i> , lime
Californium	Cf	98	(249)	1950	G. T. Seaborg (USA) S. G. Thompson (USA) A. Ghiorso (USA) K. Street, Jr. (USA)	California
Carbon	C	6	12.01	Ancient		L. <i>carbo</i> , charcoal
Cerium	Ce	58	140.1	1803	J. J. Berzelius (Swe.) William Hisinger (Swe.) M. H. Klaproth (Ge.)	Asteroid Ceres
Cesium	Cs	55	132.9	1860	R. Bunsen (Ge.) G. R. Kirchhoff (Ge.)	L. <i>caesium</i> , blue (cesium was discovered by its spectral lines, which are blue)
Chlorine	Cl	17	35.45	1774	K. W. Scheele (Swe.)	Gr. <i>chloros</i> , light green
Chromium	Cr	24	52.00	1797	L. N. Vauquelin (Fr.)	Gr. <i>chroma</i> , color (because it is used in pigments)
Cobalt	Co	27	58.93	1735	G. Brandt (Ge.)	Ge. <i>Kobold</i> , goblin (because the ore yielded cobalt instead of the expected metal, copper, it was attributed to goblins)
Copper	Cu	29	63.55	Ancient		L. <i>cuprum</i> , copper, derived from <i>cyprium</i> , Island of Cyprus, the main source of ancient copper
Curium	Cm	96	(247)	1944	G. T. Seaborg (USA) R. A. James (USA) A. Ghiorso (USA)	Pierre and Marie Curie
Dysprosium	Dy	66	162.5	1886	Lecoq de Boisbaudran (Fr.)	Gr. <i>dysprositos</i> , hard to get at
Einsteinium	Es	99	(254)	1952	A. Ghiorso (USA)	Albert Einstein

(Continued)

Element	Symbol	Atomic No.	Atomic Mass <sup>†</sup>	Date of Discovery	Discoverer and Nationality <sup>‡</sup>	Derivation
Erbium	Er	68	167.3	1843	C. G. Mosander (Swe.)	Ytterby, Sweden, where many rare earths were discovered
Europium	Eu	63	152.0	1896	E. Demarcay (Fr.)	Europe
Fermium	Fm	100	(253)	1953	A. Ghiorso (USA)	Enrico Fermi
Fluorine	F	9	19.00	1886	H. Moissan (Fr.)	Mineral fluorspar, from <i>L. fluere</i> , flow (because fluorspar was used as a flux)
Francium	Fr	87	(223)	1939	Marguerite Perey (Fr.)	France
Gadolinium	Gd	64	157.3	1880	J. C. Marignac (Fr.)	Johan Gadolin, Finnish rare earth chemist
Gallium	Ga	31	69.72	1875	Lecoq de Boisbaudran (Fr.)	<i>L. Gallia</i> , France
Germanium	Ge	32	72.59	1886	Clemens Winkler (Ge.)	<i>L. Germania</i> , Germany
Gold	Au	79	197.0	Ancient		<i>L. aurum</i> , shining dawn
Hafnium	Hf	72	178.5	1923	D. Coster (Du.) G. von Hevesey (H.)	<i>L. Hafnia</i> , Copenhagen
Helium	He	2	4.003	1868	P. Janssen (spectr) (Fr.) Sir William Ramsay (isolated) (GB)	Gr. <i>helios</i> , sun (because it was first discovered in the sun's spectrum)
Holmium	Ho	67	164.9	1879	P. T. Cleve (Swe.)	<i>L. Holmia</i> , Stockholm
Hydrogen	H	1	1.008	1766	Sir Henry Cavendish (GB)	Gr. <i>hydro</i> , water; <i>genes</i> , forming (because it produces water when burned with oxygen)
Indium	In	49	114.8	1863	F. Reich (Ge.) T. Richter (Ge.)	Indigo, because of its indigo blue lines in the spectrum
Iodine	I	53	126.9	1811	B. Courtois (Fr.)	Gr. <i>iodes</i> , violet
Iridium	Ir	77	192.2	1803	S. Tennant (GB)	<i>L. iris</i> , rainbow
Iron	Fe	26	55.85	Ancient		<i>L. ferrum</i> , iron
Krypton	Kr	36	83.80	1898	Sir William Ramsay (GB) M. W. Travers (GB)	Gr. <i>kryptos</i> , hidden
Lanthanum	La	57	138.9	1839	C. G. Mosander (Swe.)	Gr. <i>lanthanein</i> , concealed
Lawrencium	Lr	103	(257)	1961	A. Ghiorso (USA) T. Sikkeland (USA) A. E. Larsh (USA) R. M. Latimer (USA)	E. O. Lawrence (USA), inventor of the cyclotron
Lead	Pb	82	207.2	Ancient		Symbol, <i>L. plumbum</i> , lead, meaning heavy
Lithium	Li	3	6.941	1817	A. Arfvedson (Swe.)	Gr. <i>lithos</i> , rock (because it occurs in rocks)
Lutetium	Lu	71	175.0	1907	G. Urbain (Fr.) C. A. von Welsbach (Au.)	<i>Luteria</i> , ancient name for Paris

(Continued)

Element	Symbol	Atomic No.	Atomic Mass <sup>†</sup>	Date of Discovery	Discoverer and Nationality <sup>‡</sup>	Derivation
Magnesium	Mg	12	24.31	1808	Sir Humphry Davy (GB)	<i>Magnesia</i> , a district in Thessaly; possibly derived from L. <i>magnesia</i>
Manganese	Mn	25	54.94	1774	J. G. Gahn (Swe.)	L. <i>magnes</i> , magnet
Mendelevium	Md	101	(256)	1955	A. Ghiorso (USA) G. R. Choppin (USA) G. T. Seaborg (USA) B. G. Harvey (USA) S. G. Thompson (USA)	Mendeleev, Russian chemist who prepared the periodic chart and predicted properties of undiscovered elements
Mercury	Hg	80	200.6	Ancient		Symbol, L. <i>hydrargyrum</i> , liquid silver
Molybdenum	Mo	42	95.94	1778	G. W. Scheele (Swe.)	Gr. <i>molybdos</i> , lead
Neodymium	Nd	60	144.2	1885	C. A. von Welsbach (Au.)	Gr. <i>neos</i> , new; <i>didymos</i> , twin
Neon	Ne	10	20.18	1898	Sir William Ramsay (GB) M. W. Travers (GB)	Gr. <i>neos</i> , new
Neptunium	Np	93	(237)	1940	E. M. McMillan (USA) P. H. Abelson (USA)	Planet Neptune
Nickel	Ni	28	58.69	1751	A. F. Cronstedt (Swe.)	Swe. <i>kopparnickel</i> , false copper; also Ge. <i>nickel</i> , referring to the devil that prevented copper from being extracted from nickel ores
Niobium	Nb	41	92.91	1801	Charles Hatchett (GB)	Gr. <i>Niobe</i> , daughter of Tantalus (niobium was considered identical to tantalum, named after <i>Tantalus</i> , until 1884)
Nitrogen	N	7	14.01	1772	Daniel Rutherford (GB)	Fr. <i>nitrogene</i> , derived from L. <i>nitrum</i> , native soda, or Gr. <i>nitron</i> , native soda, and Gr. <i>genes</i> , forming
Nobelium	No	102	(253)	1958	A. Ghiorso (USA) T. Sikkeland (USA) J. R. Walton (USA) G. T. Seaborg (USA)	Alfred Nobel
Osmium	Os	76	190.2	1803	S. Tennant (GB)	Gr. <i>osme</i> , odor
Oxygen	O	8	16.00	1774	Joseph Priestley (GB) C. W. Scheele (Swe.)	Fr. <i>oxygene</i> , generator of acid, derived from Gr. <i>oxys</i> , acid, and L. <i>genes</i> , forming (because it was once thought to be a part of all acids)

(Continued)

Element	Symbol	Atomic No.	Atomic Mass <sup>†</sup>	Date of Discovery	Discoverer and Nationality <sup>‡</sup>	Derivation
Palladium	Pd	46	106.4	1803	W. H. Wollaston (GB)	Asteroid Pallas
Phosphorus	P	15	30.97	1669	H. Brandt (Ge.)	Gr. <i>phosphoros</i> , light bearing
Platinum	Pt	78	195.1	1735 1741	A. de Ulloa (Sp.) Charles Wood (GB)	Sp. <i>platina</i> , silver
Plutonium	Pu	94	(242)	1940	G. T. Seaborg (USA) E. M. McMillan (USA) J. W. Kennedy (USA) A. C. Wahl (USA)	Planet Pluto
Polonium	Po	84	(210)	1898	Marie Curie (P.)	Poland
Potassium	K	19	39.10	1807	Sir Humphry Davy (GB)	Symbol, L. <i>kalium</i> , potash
Praseodymium	Pr	59	140.9	1885	C. A. von Welsbach (Au.)	Gr. <i>prasios</i> , green; <i>didymos</i> , twin
Promethium	Pm	61	(147)	1945	J. A. Marinsky (USA) L. E. Glendenin (USA) C. D. Coryell (USA)	Gr. mythology, <i>Prometheus</i> , the Greek Titan who stole fire from heaven
Protactinium	Pa	91	(231)	1917	O. Hahn (Ge.) L. Meitner (Au.)	Gr. <i>protos</i> , first; <i>actinium</i> (because it disintegrates into actinium)
Radium	Ra	88	(226)	1898	Pierre and Marie Curie (Fr., P.)	L. <i>radius</i> , ray
Radon	Rn	86	(222)	1900	F. E. Dorn (Ge.)	Derived from radium
Rhenium	Re	75	186.2	1925	W. Noddack (Ge.) I. Tacke (Ge.) Otto Berg (Ge.)	L. <i>Rhenus</i> , Rhine
Rhodium	Rh	45	102.9	1804	W. H. Wollaston (GB)	Gr. <i>rhodon</i> , rose (because some of its salts are rose-colored)
Rubidium	Rb	37	85.47	1861	R. W. Bunsen (Ge.) G. Kirchhoff (Ge.)	L. <i>rubidus</i> , dark red (discovered with the spectroscope, its spectrum shows red lines)
Ruthenium	Ru	44	101.1	1844	K. K. Klaus (R.)	L. <i>Ruthenia</i> , Russia
Samarium	Sm	62	150.4	1879	Lecoq de Boisbaudran (Fr.)	Samarskite, after Samarski, a Russian engineer
Scandium	Sc	21	44.96	1879	L. F. Nilson (Swe.)	Scandinavia
Selenium	Se	34	78.96	1817	J. J. Berzelius (Swe.)	Gr. <i>selene</i> , moon (because it resembles tellurium, named for the earth)
Silicon	Si	14	28.09	1824	J. J. Berzelius (Swe.)	L. <i>silex</i> , <i>silicis</i> , flint
Silver	Ag	47	107.9	Ancient		Symbol, L. <i>argentum</i> , silver

(Continued)

Element	Symbol	Atomic No.	Atomic Mass <sup>†</sup>	Date of Discovery	Discoverer and Nationality <sup>‡</sup>	Derivation
Sodium	Na	11	22.99	1807	Sir Humphry Davy (GB)	L. <i>sodanum</i> , headache remedy; symbol, L. <i>natrium</i> , soda
Strontium	Sr	38	87.62	1808	Sir Humphry Davy (GB)	Strontian, Scotland, derived from mineral strontionite
Sulfur	S	16	32.07	Ancient		L. <i>sulphurium</i> (Sanskrit, <i>sulvere</i> )
Tantalum	Ta	73	180.9	1802	A. G. Ekeberg (Swe.)	Gr. mythology, <i>Tantalus</i> , because of difficulty in isolating it
Technetium	Tc	43	(99)	1937	C. Perrier (I.)	Gr. <i>technetos</i> , artificial (because it was the first artificial element)
Tellurium	Te	52	127.6	1782	F. J. Müller (Au.)	L. <i>tellus</i> , earth
Terbium	Tb	65	158.9	1843	C. G. Mosander (Swe.)	Ytterby, Sweden
Thallium	Tl	81	204.4	1861	Sir William Crookes (GB)	Gr. <i>thallos</i> , a budding twig (because its spectrum shows a bright green line)
Thorium	Th	90	232.0	1828	J. J. Berzelius (Swe.)	Mineral thorite, derived from <i>Thor</i> , Norse god of war
Thulium	Tm	69	168.9	1879	P. T. Cleve (Swe.)	<i>Thule</i> , early name for Scandinavia
Tin	Sn	50	118.7	Ancient		Symbol, L. <i>stannum</i> , tin
Titanium	Ti	22	47.88	1791	W. Gregor (GB)	Gr. giants, the Titans, and L. <i>titans</i> , giant deities
Tungsten	W	74	183.9	1783	J. J. and F. de Elhuyar (Sp.)	Swe. <i>tung sten</i> , heavy stone; symbol, wolframite, a mineral
Uranium	U	92	238.0	1789 1841	M. H. Klaproth (Ge.) E. M. Peligot (Fr.)	Planet Uranus
Vanadium	V	23	50.94	1801 1830	A. M. del Rio (Sp.) N. G. Sefstrom (Swe.)	<i>Vanadis</i> , Norse goddess of love and beauty
Xenon	Xe	54	131.3	1898	Sir William Ramsay (GB) M. W. Travers (GB)	Gr. <i>xenos</i> , stranger
Ytterbium	Yb	70	173.0	1907	G. Urbain (Fr.)	Ytterby, Sweden
Yttrium	Y	39	88.91	1843	C. G. Mosander (Swe.)	Ytterby, Sweden
Zinc	Zn	30	65.39	1746	A. S. Marggraf (Ge.)	Ge. <i>zink</i> , of obscure origin
Zirconium	Zr	40	91.22	1789	M. H. Klaproth (Ge.)	Zircon, in which it was found, derived from Ar. <i>zargum</i> , gold color

# Appendix 4

## *Isotopes of the First Ten Elements*

Element	Isotope*	Mass (in u)	Natural Abundance (%)	Primary Decay Process	Half-Life
Hydrogen	<sup>1</sup> H	1.0078250	99.9885		
	<sup>2</sup> H	2.0141018	0.0115		
	<sup>3</sup> H	3.0160493		$\beta^-$ to <sup>3</sup> He	12.33 y
Helium	<sup>3</sup> He	3.0160293	0.000137		
	<sup>4</sup> He	4.0026032	99.999863		
	<sup>6</sup> He	6.018886		$\beta^-$ to <sup>6</sup> Li	807 ms
	<sup>8</sup> He	8.033922		$\beta^-$ to <sup>8</sup> Li	119 ms
Lithium	<sup>6</sup> Li	6.015122	7.6		
	<sup>7</sup> Li	7.016004	92.4		
	<sup>8</sup> Li	8.022486		$\beta^-$ to <sup>8</sup> Be	838 ms
	<sup>9</sup> Li	9.026789		$\beta^-$ to <sup>9</sup> Be	178.3 ms
	<sup>11</sup> Li	11.043796		$\beta^-$ to <sup>11</sup> Be	8.5 ms
Beryllium	<sup>7</sup> Be	7.016880		EC <sup>†</sup> to <sup>7</sup> Li	53.28 d
	<sup>9</sup> Be	9.012182	100		
	<sup>10</sup> Be	10.013534		$\beta^-$ to <sup>10</sup> B	1.52 × 10 <sup>6</sup> y
	<sup>11</sup> Be	11.021658		$\beta^-$ to <sup>11</sup> B	13.81 s
	<sup>12</sup> Be	12.026921		$\beta^-$ to <sup>12</sup> B	23.6 ms
Boron	<sup>8</sup> B	8.024607		$\beta^+$ (or EC) + $\alpha$ to <sup>4</sup> He	770 ms
	<sup>9</sup> B	9.013339		2 × $\alpha$ to <sup>1</sup> H	8 × 10 <sup>-19</sup> s
	<sup>10</sup> B	10.012937	19.9		
	<sup>11</sup> B	11.009305	80.1		
	<sup>12</sup> B	12.014352		$\beta^-$ to <sup>12</sup> C	20.20 ms
	<sup>13</sup> B	13.017780		$\beta^-$ to <sup>13</sup> C	17.36 ms
	<sup>14</sup> B	14.025404		$\beta^-$ to <sup>14</sup> C	13.8 ms
Carbon	<sup>15</sup> B	15.031097		$\beta^-$ to <sup>15</sup> C	10.5 ms
	<sup>10</sup> C	10.016853		$\beta^+$ (or EC) to <sup>10</sup> B	19.255 s
	<sup>11</sup> C	11.011434		$\beta^+$ (or EC) to <sup>11</sup> B	20.39 min
	<sup>12</sup> C	12.000000	98.89		
	<sup>13</sup> C	13.003355	1.11		
	<sup>14</sup> C	14.003242		$\beta^-$ to <sup>14</sup> N	5730 y
	<sup>15</sup> C	15.010599		$\beta^-$ to <sup>15</sup> N	2.449 s
	<sup>16</sup> C	16.014701		$\beta^-$ to <sup>16</sup> N	747 ms
	<sup>17</sup> C	17.033584		$\beta^-$ to <sup>17</sup> N	193 ms
	<sup>18</sup> C	18.026757		$\beta^-$ to <sup>18</sup> N	95 ms

\*Naturally occurring isotopes in black, radioisotopes in red.

<sup>†</sup>EC = electron capture

(Continued)

Element	Isotope*	Mass (in u)	Natural Abundance (%)	Primary Decay Process	Half-Life
Nitrogen	<sup>12</sup> N	12.018613		$\beta^+$ (or EC) to <sup>12</sup> C	11 ms
	<sup>13</sup> N	13.005739		$\beta^+$ (or EC) to <sup>13</sup> C	9.965 min
	<sup>14</sup> N	14.003074	99.634		
	<sup>15</sup> N	15.000109	0.366		
	<sup>16</sup> N	16.006101		$\beta^-$ to <sup>16</sup> O	7.13 s
	<sup>17</sup> N	17.008450		$\beta^-$ to <sup>17</sup> O	4.173 s
	<sup>18</sup> N	18.014082		$\beta^-$ to <sup>18</sup> O	624 ms
	<sup>19</sup> N	19.017927		$\beta^-$ to <sup>19</sup> O	290 ms
Oxygen	<sup>13</sup> O	13.024810		$\beta^+$ (or EC) to <sup>13</sup> N	8.58 ms
	<sup>14</sup> O	14.008595		$\beta^+$ (or EC) to <sup>14</sup> N	70.61 s
	<sup>15</sup> O	15.003065		$\beta^+$ (or EC) to <sup>15</sup> N	122.24 s
	<sup>16</sup> O	15.994915	99.762		
	<sup>17</sup> O	16.999132	0.038		
	<sup>18</sup> O	17.999160	0.200		
	<sup>19</sup> O	19.003579		$\beta^-$ to <sup>19</sup> F	26.91 s
	<sup>20</sup> O	20.004076		$\beta^-$ to <sup>20</sup> F	13.51 s
	<sup>21</sup> O	21.008655		$\beta^-$ to <sup>21</sup> F	3.42 s
	<sup>22</sup> O	22.009967		$\beta^-$ to <sup>22</sup> F	2.25 s
	<sup>23</sup> O	23.015691		$\beta^-$ to <sup>23</sup> F	82 ms
Fluorine	<sup>17</sup> F	17.002095		$\beta^+$ (or EC) to <sup>17</sup> O	64.49 s
	<sup>18</sup> F	18.000938		$\beta^+$ (or EC) to <sup>18</sup> O	109.77 min
	<sup>19</sup> F	18.998403	100		
	<sup>20</sup> F	19.999981		$\beta^-$ to <sup>20</sup> Ne	11.16 s
	<sup>21</sup> F	20.999949		$\beta^-$ to <sup>21</sup> Ne	4.158 s
	<sup>22</sup> F	22.002999		$\beta^-$ to <sup>22</sup> Ne	4.23 s
	<sup>23</sup> F	23.003574		$\beta^-$ to <sup>23</sup> Ne	2.23 s
	<sup>24</sup> F	24.008099		$\beta^-$ to <sup>24</sup> Ne	0.34 s
	<sup>25</sup> F	25.012095		$\beta^-$ to <sup>25</sup> Ne	87 ms
Neon	<sup>18</sup> Ne	18.005697		$\beta^+$ (or EC) to <sup>18</sup> F	1672 ms
	<sup>19</sup> Ne	19.001880		$\beta^+$ (or EC) to <sup>19</sup> F	17.22 s
	<sup>20</sup> Ne	19.992440	90.48		
	<sup>21</sup> Ne	20.993847	0.27		
	<sup>22</sup> Ne	21.991386	9.25		
	<sup>23</sup> Ne	22.994467		$\beta^-$ to <sup>23</sup> Na	37.24 s
	<sup>24</sup> Ne	23.993615		$\beta^-$ to <sup>24</sup> Na	3.38 min
	<sup>25</sup> Ne	24.997790		$\beta^-$ to <sup>25</sup> Na	602 ms
	<sup>26</sup> Ne	26.000462		$\beta^-$ to <sup>26</sup> Na	0.23 s
	<sup>27</sup> Ne	27.007615		$\beta^-$ to <sup>27</sup> Na	32 ms



# Glossary

The number in parentheses is the number of the section in which the term first appears.

## A

- absolute zero of temperature.** Theoretically the lowest attainable temperature. (5.1)
- acceptor impurities.** Impurities that can accept electrons from semiconductors. (6.4)
- accuracy.** The closeness of a measurement to the true value of the quantity that is measured. (A.1)
- acid.** A substance that yields hydrogen ions ( $H^-$ ) when dissolved in water. (0.3, 11.1)
- acid ionization constant ( $K_a$ ).** The equilibrium constant for the acid ionization. (11.3)
- actinide series.** Elements that have incompletely filled  $5f$  subshells or readily give rise to cations that have incompletely filled  $5f$  subshells. (2.2)
- activated complex.** The species temporarily formed by the reactant molecules as a result of the collision before they form the product. (14.4)
- activated-complex theory.** See transition-state theory. (14.4)
- activation energy ( $E_a$ ).** The minimum amount of energy required to initiate a chemical reaction. (14.4)
- activity.** (1) A measure of the effective concentration of a species in an equilibrium constant expression (9.2); (2) In nuclear chemistry, the activity is defined as the number of nuclei decaying per unit time. (10.1, 17.3)
- activity series.** A summary of the results of many possible displacement reactions. (4.4)
- actual yield.** The amount of product actually obtained in a reaction. (0.6)
- addition reaction.** Reactions involving the addition of atoms to compounds at the site of double or triple bonds. (16.2, 16.4)
- adhesion.** Attraction between unlike molecules. (6.1)
- adiabatic process.** A process for which the heat inflow and outflow is zero (that is,  $q = 0$ ). (7.1)
- alcohol.** An organic compound containing the hydroxyl group— $\text{OH}$ . (16.3)
- aldehydes.** Compounds with a carbonyl functional group and the general formula  $\text{RCHO}$ , where R is an H atom, an alkyl, or an aromatic group. (16.3)

- aliphatic hydrocarbons.** Hydrocarbons that do not contain the benzene group or the benzene ring. (16.1)
- alkali metals.** The Group 1A elements (Li, Na, K, Rb, Cs, and Fr). (0.2)
- alkaline earth metals.** The Group 2A elements (Be, Mg, Ca, Sr, Ba, and Ra). (0.2)
- alkanes.** Hydrocarbons having the general formula  $\text{C}_n\text{H}_{2n+2}$ , where  $n = 1, 2, \dots$  (16.1)
- alkenes.** Hydrocarbons that contain one or more carbon-carbon double bonds. They have the general formula  $\text{C}_n\text{H}_{2n}$ , where  $n = 2, 3, \dots$  (16.1)
- alkyl group.** An organic functional group consisting of an alkane less one hydrogen. (16.1)
- alkynes.** Hydrocarbons that contain one or more carbon-carbon triple bonds. They have the general formula  $\text{C}_n\text{H}_{2n-2}$ , where  $n = 2, 3, \dots$  (16.1)
- allotropes.** Two or more forms of the same element that differ significantly in chemical and physical properties. (0.3)
- alpha decay.** The emission of an alpha particle by an unstable nucleus. (17.1)
- alpha ( $\alpha$ ) particles.** Helium nuclei with a positive charge of 2. (17.1)
- amines.** Organic bases that have the functional group— $\text{NR}_2$ , where R may be H, an alkyl group, or an aromatic group. (16.3)
- amino acids.** A compound that contains at least one amino group and at least one carboxyl group. (16.5)
- amorphous solid.** A solid that lacks a regular three-dimensional arrangement of atoms or molecules. (6.3)
- amphoteric oxide.** An oxide that exhibits both acidic and basic properties. (11.1)
- amplitude.** The vertical distance between the midline of a wave and its peak or trough. (1.1)
- angular momentum.** The vector cross product of momentum and force:  $\mathbf{L} = \mathbf{p} \times \mathbf{F}$ . (1.2)
- angular momentum quantum number.** The quantum number  $l$  that determines the shape of atomic orbitals. (1.4)
- anion.** An ion with a net negative charge. (0.2)
- anode.** The electrode at which oxidation occurs. (13.2)
- antibonding molecular orbital.** A molecular orbital that is of higher energy and lower stability than the atomic orbitals from which it was formed. (3.5)
- aqueous solution.** A solution in which the solvent is water. (0.4)
- aqueous species.** Substances dissolved in water solution. (0.4)
- aromatic hydrocarbon.** A hydrocarbon that contains one or more benzene rings. (16.1)
- Arrhenius equation.** An equation describing the temperature dependence of reaction rates. (14.4)
- atmospheric pressure.** The pressure exerted by Earth's atmosphere. (5.1)
- atom.** The basic unit of an element that can enter into chemical combination. (0.2)
- atomic mass.** The mass of an atom in atomic mass units. (0.5)
- atomic mass unit (u).** A mass exactly equal to  $1/12^{\text{th}}$  the mass of one carbon-12 atom. (0.5)
- atomic number (Z).** The number of protons in the nucleus of an atom. (0.2)
- atomic orbital.** The wave function  $\phi$  of a single electron in an atom. (1.4)
- atomic radius.** One-half the distance between the two nuclei in two adjacent atoms of the same element in a metal. For elements that exist as diatomic units, the atomic radius is one-half the distance between the nuclei of the two atoms in a particular molecule. (2.5)
- Aufbau principle.** As protons are added one by one to the nucleus to build up the elements, electrons similarly are added to the atomic orbitals. (2.2)
- autoionization of water.** The reaction of two water molecules to form an  $\text{OH}^-$  ion and an  $\text{H}_3\text{O}^+$  ion. (11.2)
- average atomic mass.** The average of the atomic masses of the different isotopes of an element, weighted by their natural abundances. (0.5)
- Avogadro's law.** At constant pressure and temperature, the volume of a gas is directly proportional to the number of moles of the gas present. (5.3)
- Avogadro's number ( $N_A$ ).**  $6.022 \times 10^{23}$ ; the number of particles in a mole. (0.5)
- azeotrope.** A point of phase coexistence in a binary mixture in which each phase has identical composition. (9.3)

## B

- back bonding.** The lowering of  $3d_{xy}$ ,  $3d_{xz}$ , and  $3d_{yz}$  orbital energies of a metal ion center in a coordination compound due to mixing with unoccupied pi-antibonding orbitals on the ligand.

**band theory of conductivity.** Delocalized electrons move freely through “bands” formed by overlapping molecular orbitals. (6.4)

**bar.**  $10^5$  Pa. (5.1, A.1)

**barometer.** An instrument that measures atmospheric pressure. (5.1)

**base.** A substance that yields hydroxide ions ( $\text{OH}$ ) when dissolved in water. (0.3, 11.1)

**base ionization constant ( $K_b$ ).** The equilibrium constant for the base ionization. (11.3)

**battery.** A galvanic cell, or a series of combined galvanic cells, that can be used as a source of direct electric current at a constant voltage. (13.6)

**beta decay.** Emission of a beta particle (electron or positron) by an unstable nucleus. (17.1)

**beta ( $\beta$ ) particles.** Electrons ( $\beta^-$ ) or positrons ( $\beta^+$ ) emitted by an unstable nucleus. (17.1)

**bimolecular reaction.** An elementary step involving two reactant molecules. (14.5)

**binary compounds.** Compounds formed from just two elements. (0.3)

**blackbody radiation.** Radiation emitted by an object solely as a consequence of its temperature. (1.1)

**body-centered cubic (bcc).** Having a crystal unit cell with lattice points at the vertices and at the center of a cube. (6.2)

**Bohr model.** An early quantum model of the hydrogen atom. (1.2)

**Bohr radius.** A constant equal to about 0.59 Å. (1.2)

**boiling point.** The temperature at which the vapor pressure of a liquid is equal to the external atmospheric pressure. (5.2)

**boiling-point elevation.** The raising of the boiling point of a liquid through the addition of a solute. (9.4)

**bond dissociation energy.** The energy required to break a bond. (3.1)

**bond enthalpy.** The enthalpy change required to break a bond in a mole of gaseous molecules. (7.5)

**bond length.** The distance between the nuclei of two bonded atoms in a molecule. (3.1)

**bond order.** The difference between the numbers of electrons in bonding molecular orbitals and antibonding molecular orbitals, divided by two. (3.2, 3.6)

**bonding molecular orbital.** A molecular orbital that is of lower energy and greater stability than the atomic orbitals from which it was formed. (3.5)

**boundary surface diagram.** A surface containing 90 percent of the electron density in an orbital. (1.4)

**Boyle's law.** The volume of a fixed amount of gas maintained at constant temperature is inversely proportional to the gas pressure. (5.3)

**Boyle temperature ( $T_B$ ).** The temperature at which the second virial coefficient of a real gas is equal to zero. (5.5)

**Bravais lattices.** The 14 basic types of unit cells for a crystal lattice. (6.2)

**breeder reactor.** A nuclear reactor that produces more fissionable materials than it uses. (17.5)

**Brønsted acid.** A substance capable of donating a proton. (11.1)

**Brønsted base.** A substance capable of accepting a proton. (11.1)

**buffer solution.** A solution of (a) a weak acid or base and (b) its salt; both components must be present. The solution has the ability to resist changes in pH upon the addition of small amounts of either acid or base. (12.2)

## C

**calorimetry.** The measurement of heat changes. (7.3)

**carboxylic acids.** Acids that contain the carboxyl group —COOH. (16.3)

**catalyst.** A substance that increases the rate of a chemical reaction without itself being consumed. (14.6)

**cathode.** The electrode at which reduction occurs. (13.2)

**cation.** An ion with a net positive charge. (0.2)

**cell diagram.** A notation for representing electrochemical cells. (13.2)

**cell voltage.** Difference in electrical potential between the anode and the cathode of a galvanic cell. (13.2)

**Charles's and Gay-Lussac's law.** See Charles's law.

**Charles's law.** The volume of a fixed amount of gas maintained at constant pressure is directly proportional to the absolute temperature of the gas. (5.3)

**chelating agent.** A substance that forms complex ions with metal ions in solution. (15.1)

**chemical bond.** An attractive force between atoms in a molecule that is strong enough for the atoms to not be pulled apart in the course of normal interactions with the environment. (3.1)

**chemical energy.** Energy stored within the structural units of chemical substances. (0.1)

**chemical equation.** An equation that uses chemical symbols to show what happens during a chemical reaction. (0.4)

**chemical equilibrium.** A state in which the rates of the forward and reverse reactions are equal. (10.1)

**chemical formula.** An expression showing the chemical composition of a compound in terms of the symbols for the atoms of the elements involved. (0.3)

**chemical kinetics.** The area of chemistry concerned with the speeds, or rates, at which chemical reactions occur. (14.1)

**chemical property.** Any property of a substance that cannot be studied without converting the substance into some other substance. (0.1)

**chemical reaction.** A process in which a substance (or substances) is changed into one or more new substances. (0.4)

**chemistry.** The study of matter and the changes it undergoes. (0.1)

**chiral.** Compounds or ions that are not superimposable with their mirror images. (22.4)

**Clapeyron equation.** An equation relating the slope ( $dP/dT$ ) of a phase diagram boundary to the enthalpy and volume changes of the phase transition. (9.1)

**Clausius-Clapeyron equation.** An equation describing the temperature dependence of vapor pressure. (9.1)

**Clausius inequality.** The heat absorbed by a system in a process is always less than or equal to the change in entropy of the system during the process. (8.2)

**closed system.** A system that enables the exchange of energy (usually in the form of heat), but not of mass, with its surroundings. (6.2)

**closest packing.** The most efficient arrangements for packing atoms, molecules, or ions in a crystal. (6.2)

**cohesion.** The intermolecular attraction between like molecules. (6.1)

**colligative properties.** Properties of solutions that depend on the number of solute particles in solution and not on the nature of the solute particles. (9.4)

**colloid.** A dispersion of particles of one substance (the dispersed phase) throughout a dispersing medium made of another substance. (12.8)

**common ion effect.** The shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substances. (12.1)

**complex ion.** An ion containing a central metal cation bonded to one or more molecules or ions. (12.7)

**compound.** A substance composed of atoms of two or more elements chemically united in fixed proportions. (0.1)

**compression factor.** The quantity  $Z = PV/nRT$ . (5.3)

**concentration equilibrium constant**

( $K_c$ ). The equilibrium constant for a reaction expressed as a ratio of reactant and product concentrations. (10.1)

**concentration of a solution.** The amount of solute present in a given quantity of solvent or solution. (0.5)

**concentration cell.** An electrochemical cell that generates a potential difference from a gradient in concentration. (13.5)

**condensation.** The phenomenon of going from the gaseous state to the liquid state. (5.2)

**condensation reaction.** A reaction in which two smaller molecules combine to form a larger molecule. Water is invariably one of the products of such a reaction. (16.3)

**conducting polymer.** A polymer that conducts electricity. (16.4)

**conduction band.** A band of closely spaced unfilled molecular orbitals just above the valence band. (6.4)

**conductor.** Substance capable of conducting electric current. (6.4)

**conformations.** Different spatial arrangements of a molecule that are generated by rotation about single bonds. (16.1)

**conjugate acid-base pair.** An acid and its conjugate base or a base and its conjugate acid. (11.1)

**constant-pressure heat capacity ( $C_p$ ).** The heat capacity of a substance in a constant-pressure process. (7.3)

**constant-pressure process.** A process that takes place at constant pressure. (7.1)

**constant-volume heat capacity ( $C_v$ ).** The heat capacity of a substance in a constant-volume process. (7.3)

**constant-volume process.** A process that takes place at constant volume. (7.1)

**coordinate covalent bond.** A bond in which the pair of electrons is supplied by one of the two bonded atoms; also called a dative bond. (3.4)

**coordination compound.** A neutral species containing one or more complex ions. (15.2)

**coordination number.** In a crystal lattice it is defined as the number of atoms (or ions) surrounding an atom (or ion) (6.2). In coordination compounds it is defined as the number of donor atoms surrounding the central metal atom in a complex. (15.2)

**copolymer.** A polymer containing two or more different monomers. (16.4)

**core electrons.** The inner shell electrons of an atom. (2.4)

**Coulomb's law.** The potential energy between two ions is directly proportional to the product of their charges and inversely proportional to the distance between them. (0.1)

**coupled reactions.** A pair of reactions in which a nonspontaneous reaction is driven by a spontaneous one. (8.6)

**covalent bond.** A bond in which two electrons are shared by two atoms. (3.2)

**covalent compounds.** Compounds containing only covalent bonds. (3.2)

**covalent crystal.** A crystal in which atoms are held together with an extensive three-dimensional network of covalent bonds. (6.3)

**covalent radius.** A measure of the size of an atom based on the lengths of the covalent bonds that it forms with other atoms. (3.2)

**critical mass.** The minimum mass of fissionable material required to generate a self-sustaining nuclear chain reaction. (17.5)

**critical point.** A point on a phase diagram where a coexistence line ends. (5.2)

**critical pressure.** The minimum pressure necessary to bring about liquefaction at the critical temperature. (5.2)

**critical temperature.** The temperature above which a gas will not liquefy. (5.2)

**crystal field splitting ( $\Delta$ ).** The energy difference between two sets of  $d$  orbitals in a metal atom when ligands are present. (15.3)

**crystal field theory.** A theory explaining the bonding in complex ions purely in terms of electrostatic forces. (15.3)

**crystalline solid.** A solid that possesses rigid and long-range order; its atoms, molecules, or ions occupy specific positions. (6.2)

**crystallization.** The process in which dissolved solute comes out of solution and forms crystals. (9.2)

**cycloalkanes.** Alkanes whose carbon atoms are joined in rings. (16.1)

## D

**Dalton's law of partial pressures.** The total pressure of a mixture of gases is just the sum of the pressures that each gas would exert if it were present alone. (5.3)

**deBroglie wavelength.** The wavelength associated with a particle due to its momentum. (1.3)

**degenerate orbitals.** Atomic orbitals with equal energy. (1.4)

**delocalized molecular orbitals.** Molecular orbitals that are not confined between two adjacent bonding atoms but actually extend over three or more atoms. (4.5)

**denatured protein.** Protein that does not exhibit normal biological activities. (16.5)

**density.** The mass of a substance divided by its volume. (0.5)

**deoxyribonucleic acids (DNA).** A type of nucleic acid. (16.6)

**deposition.** The process in which the molecules go directly from the vapor into the solid phase. (5.2)

**detailed balance.** The principle that states that, at equilibrium, the rates of forward and reverse processes are equal. (14.3)

**diagonal relationship.** Similarities between pairs of elements in different groups and periods of the periodic table. (2.5)

**diamagnetic.** Repelled by a magnet; a diamagnetic substance contains only paired electrons. (2.1)

**diatomic molecule.** A molecule that consists of two atoms. (0.2)

**diffusion.** The gradual mixing of molecules of one gas with molecules of another by virtue of their kinetic motion. (5.5)

**dipole-dipole interactions.** Forces that act between polar molecules. (4.6)

**dipole-induced dipole interaction.** The interaction between a polar molecule with the dipole moment it induces in a nearby atom or molecule. (4.6)

**dipole moment ( $\mu$ ).** A vector measuring the degree of charge separation in a molecule. The magnitude ( $\mu$ ) is the product of charge

separated times the charge separation distance in a molecule. The dipole moment vector points from the negative to the positive end of the molecule. (4.2)

**diprotic acid.** Each unit of the acid yields two hydrogen ions upon ionization. (11.1)

**dispersion interactions.** The attractive forces that arise as a result of temporary dipoles induced in the atoms or molecules; also called London forces. (4.6)

**donor atom.** The atom in a ligand that is bonded directly to the metal atom. (15.2)

**donor impurities.** Impurities that provide conduction electrons to semiconductors. (6.4)

**double bond.** Two atoms are held together by two pairs of electrons. (3.2)

**duet.** The two electrons in the electronic configuration in helium. (3.2)

**dynamic equilibrium.** The condition in which the rate of a forward process is exactly balanced by the rate of a reverse process. (5.2)

## E

**effective nuclear charge.** The effective charge felt by an electron in an atom due to interactions with the nucleus and all other electrons. (2.5)

**effusion.** Escape of a gas through a small hole in a container. (5.5)

**electrochemistry.** The branch of chemistry that deals with the interconversion of electrical energy and chemical energy. (13.1)

**electrode.** The parts of an electrochemical cell where electron transfer (oxidation or reduction) takes place. (13.2)

**electrolysis.** A process in which electrical energy is used to cause a nonspontaneous chemical reaction to occur. (13.7)

**electrolyte.** A substance that dissociates into ions in water to form a conducting solution. (9.4)

**electrolytic cell.** An apparatus for carrying out electrolysis. (13.7)

**electromagnetic force.** Force between electrically charged objects or magnetic materials. (0.1)

**electromagnetic radiation.** The emission and transmission of energy in the form of electromagnetic waves. (1.1)

**electromagnetic wave.** A wave that has an electric field component and a mutually perpendicular magnetic field component. (1.1)

**electromotive force (emf).** The voltage difference between electrodes. (13.2)

**electron.** A subatomic particle that has a very low mass and carries a single negative electric charge. (0.2)

**electron affinity.** The negative of the energy change when an electron is accepted by an atom in the gaseous state to form an anion. (2.5)

**electron configuration.** The distribution of electrons among the various orbitals in an atom or molecule. (2.1)

**electron spin.** An intrinsic angular momentum associated with an electron. (1.4)

**electron spin quantum number.** The quantum number ( $m_s$ ) associated with electron spin. The value of  $m_s$  can be +1/2 (up) or -1/2 (down). (1.4)

**electronegativity.** The ability of an atom to attract electrons toward itself in a chemical bond. (3.3)

**element.** A substance that cannot be separated into simpler substances by chemical means. (0.1)

**elementary steps.** A series of simple reactions that represent the progress of the overall reaction at the molecular level. (14.5)

**emission spectra.** Continuous or line spectra emitted by substances. (1.2)

**empirical formula.** An expression showing the types of elements present and the simplest ratios of the different kinds of atoms. (0.3)

**enantiomers.** Optical isomers, that is, compounds and their nonsuperimposable mirror images. (4.4)

**endothermic processes.** Processes that absorb heat from the surroundings. (7.1)

**end point.** The pH at which the indicator changes color. (12.4)

**energy.** The capacity to do work or to produce change. (0.1)

**energy level.** One of the quantized energy states of a molecule or atom. (1.4)

**energy shell.** The set of degenerate orbitals making up a particular energy level in an atom. (1.4)

**enthalpy ( $H$ ).** A thermodynamic quantity used to describe heat changes taking place at constant pressure. (7.2)

**enthalpy of dilution ( $\Delta H_{\text{dil}}$ ).** The enthalpy associated with the dilution process. (7.6)

**enthalpy of hydration ( $\Delta H_{\text{hydr}}$ ).** The enthalpy associated with the hydration process. (7.6)

**enthalpy of reaction ( $\Delta H$ ).** The difference between the enthalpies of the products and the enthalpies of the reactants. (7.2)

**enthalpy of solution ( $\Delta H_{\text{soln}}$ ).** The heat generated or absorbed when a certain amount of solute is dissolved in a certain amount of solvent. (7.6)

**entropy ( $S$ ).** A direct measure of the number of molecular states consistent with the macroscopic state of a system. (8.1)

**entropy of mixing.** The entropy change associated with the mixing of two substances to form a mixture. (8.5)

**enzyme.** A biological catalyst. (14.6)

**equation of state.** The pressure of a material as a function of temperature, volume, and composition. (5.3)

**equilibrium constant ( $K$ ).** A number equal to the ratio of the equilibrium concentrations

of products to the equilibrium concentrations of reactants, each raised to the power of its stoichiometric coefficient. (10.1)

**equilibrium state.** A thermodynamic state in which all macroscopic properties of the system are unchanging in time and remain so even if the system is disconnected from its surroundings. (7.1)

**equilibrium vapor pressure.** The vapor pressure measured under dynamic equilibrium of condensation and evaporation at some temperature. (5.2)

**equipartition of energy theorem.** The energy in a molecule is, on average, distributed evenly among all types of molecular motion (degrees of freedom). (7.3)

**equivalence point.** The point at which the acid has completely reacted with or been neutralized by the base. (12.3)

**esters.** Compounds that have the general formula  $R'\text{COOR}$ , where  $R'$  can be H or an alkyl group or an aromatic group and R is an alkyl group or an aromatic group. (16.3)

**ether.** An organic compound containing the  $R-\text{O}-R'$  linkage, where R and R' are alkyl and/or aromatic groups. (16.3)

**evaporation.** The process in which a liquid is transformed into a gas; also called vaporization. (5.2)

**excess reagents.** One or more reactants present in quantities greater than necessary to react with the quantity of the limiting reagent. (0.6)

**excited state (or level).** A state that has higher energy than the ground state. (1.2)

**exothermic processes.** Processes that give off heat to the surroundings. (7.1)

**extensive property.** A property that depends on how much matter is being considered. (0.1)

## F

**face-centered cubic (fcc).** Having a crystal unit cell with lattice points both at the vertices of a cube and in the center of each face. (6.2)

**Faraday constant.** Charge contained in 1 mole of electrons, equivalent to 96,485.3 coulombs. (13.4)

**first law of thermodynamics.** Energy can be converted from one form to another, but cannot be created or destroyed. (7.1)

**first-order reaction.** A reaction whose rate depends on reactant concentration raised to the first power. (14.3)

**force.** The quantity that causes an object to change its course of motion (either in direction or speed). (0.1)

**force constant.** The proportionality constant between the force on a Hooke's-law spring and its displacement. (4.2)

**formal charge.** The difference between the valence electrons in an isolated atom and the number of electrons assigned to that atom in a Lewis structure. (3.4)

**formation constant ( $K_f$ ).** The equilibrium constant for the complex ion formation. (12.7)

**fractional crystallization.** The separation of a mixture of substances into pure components on the basis of their different solubilities. (9.2)

**fractional distillation.** A procedure for separating liquid components of a solution that is based on their different boiling points. (9.3)

**freezing.** The transformation of a liquid into a solid. (5.2)

**freezing point.** The temperature at which the solid and liquid phases of a substance coexist at equilibrium. (5.2)

**freezing-point depression ( $\Delta T_f$ ).** The freezing point of the pure solvent ( $T^{\circ}\text{f}$ ) minus the freezing point of the solution ( $T_f$ ). (9.4)

**frequency ( $\gamma$ ).** The number of waves that pass through a particular point per unit time. (1.1)

**frequency factor.** The preexponential factor in the Arrhenius equation. (14.4)

**fuel cell.** A galvanic cell that requires a continuous supply of reactants to keep functioning. (13.6)

**functional group.** That part of a molecule characterized by a special arrangement of atoms that is largely responsible for the chemical behavior of the parent molecule. (16.1)

## G

**galvanic cell.** The experimental apparatus for generating electricity through the use of a spontaneous redox reaction. (13.2)

**gamma ( $\gamma$ ) emission.** Emission of very high-energy electromagnetic radiation by an unstable nucleus. (17.1)

**gas.** A substance that resists neither changes in volume nor changes in shape. (0.1)

**Gay-Lussac's law.** At a constant amount of gas and volume, the pressure of an ideal gas is proportional to temperature. (5.3)

**geometric isomers.** Compounds with the same type and number of atoms and the same chemical bonds but different spatial arrangements; such isomers cannot be interconverted without breaking a chemical bond. (4.4)

**glass.** An amorphous solid formed by supercooling a liquid well below its melting temperature. (11.7)

**Gibbs free energy ( $G$ ).** A quantity equal to the enthalpy less the entropy times absolute temperature ( $H - TS$ ). The maximum amount of nonexpansion that can be extracted from a process is equal to the change in Gibbs free energy for that process. (8.4)

**Gibbs free energy of mixing.** The Gibbs free energy change associated with the mixing of two substances to form a mixture. (8.5)

**Gibbs phase rule.** For a system with  $c$  components and  $r$  phases in equilibrium, the dimensionality of the phase coexistence region is given by  $f = c - r + 2$ . (5.2)

**gravitational force.** The force between objects due to their mass. (0.1)

**ground state (or level).** The lowest energy state of a system. (1.2)

**group.** The elements in a vertical column of the periodic table. (0.2)

## H

**half-cell reactions.** Oxidation and reduction reactions at the electrodes. (13.2)

**half-life ( $t_{1/2}$ ).** The time required for the concentration of a reactant to decrease to half of its initial concentration. (14.3)

**half-reaction.** A reaction that explicitly shows electrons involved in either oxidation or reduction. (13.1)

**halogens.** The nonmetallic elements in Group 7A (F, Cl, Br, I, and At). (0.2)

**heat.** Transfer of energy between two bodies that are at different temperatures. (7.1)

**heat capacity (C).** The amount of heat required to raise the temperature of a given quantity of the substance by one degree Celsius. (7.3)

**heat of dilution.** See *enthalpy of dilution*. (7.6)

**heat of hydration.** See *enthalpy of hydration*. (7.6)

**heat of solution.** See *enthalpy of solution*. (7.6)

**heavy water reactor.** A nuclear reactor that uses D<sub>2</sub>O (heavy water) as a moderator. (17.5)

**Heisenberg uncertainty principle.** It is impossible to know simultaneously both the momentum and the position of a particle with certainty. (1.3)

**Henderson-Hasselbalch equation.** An equation relating the pH to the pK<sub>a</sub> in terms of the concentrations (or activities) of an acid and its conjugate base. (12.1)

**Henry's law.** The solubility of a gas in a liquid is proportional to the pressure of the gas over the solution. (9.2)

**Hess's law.** When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps. (7.4)

**heterogeneous catalyst.** A catalyst that is in a different physical phase than the reactants. (14.6)

**heterogeneous equilibrium.** An equilibrium state in which the reacting species are not all in the same phase. (10.1)

**heterogeneous mixture.** The individual components of a mixture remain physically

separated and can be seen as separate components. (0.1)

**high-boiling azeotrope.** An azeotrope occurring at a minimum of the temperature-composition diagram. (9.3)

**highest occupied molecular orbital (HOMO).** The highest energy molecular orbital in a molecule that contains electrons. (4.5)

**homogeneous equilibrium.** An equilibrium state in which all reacting species are in the same phase. (10.1)

**homogeneous catalysis.** A catalyst that is in the same physical phase as the reactants. (14.6)

**homogeneous mixture.** The composition of a mixture, after sufficient stirring, is the same throughout the solution. (0.1)

**homopolymer.** A polymer that is made from only one type of monomer. (16.4)

**Hund's rule.** The most stable arrangement of electrons in subshells is the one with the greatest number of parallel spins. (2.2)

**hybrid orbitals.** Atomic orbitals obtained when two or more nonequivalent orbitals of the same atom combine. (4.3)

**hybridization.** The process of mixing the atomic orbitals in an atom (usually the central atom) to generate a set of new atomic orbitals. (4.3)

**hydrates.** Compounds that have a specific number of water molecules attached to them. (0.3)

**hydration.** Solvation by water. (9.2)

**hydrocarbons.** Compounds made up only of carbon and hydrogen. (16.1)

**hydrogenation.** The addition of hydrogen to compounds containing multiple bonds. (16.2)

**hydrogen bond.** A special type of dipole-dipole interaction between the hydrogen atom bonded to an atom of a very electronegative element (F, N, O) and another atom of one of the three electronegative elements. (4.6)

**hydrogenlike ion.** A monatomic ion with one electron. (1.2)

**hydronium ion.** The hydrated proton, H<sub>3</sub>O<sup>+</sup>. (11.1)

**hydrophilic.** Water-loving. (9.2)

**hydrophobic.** Water-fearing. (9.2)

## I

**ideal gas.** A hypothetical gas whose pressure-volume-temperature behavior can be completely accounted for by the ideal gas equation. (5.3)

**ideal gas equation of state.** An equation expressing the relationships among pressure, volume, temperature, and amount of gas ( $PV = nRT$ , where  $R$  is the gas constant). (5.3)

**ideal solution.** A solution for which the enthalpy of mixing is zero and the Gibbs free energy of mixing is the same as that for an ideal gas. An ideal liquid solution will obey Raoult's law. (8.5)

**indicators.** Substances that have distinctly different colors in acidic and basic media. (12.4)

**induced dipole.** The separation of positive and negative charges in a neutral atom (or a nonpolar molecule) caused by the proximity of an ion or a polar molecule. (4.6)

**inert complex.** A complex ion that undergoes very slow ligand exchange reactions. (15.4)

**inert pair effect.** The tendency of heavier elements in group 3A to form both 1+ and 2+ ions; similarly for group 4A elements to form 2+ and 4+ ions. (2.3)

**infrared spectroscopy.** The study of the infrared frequencies that are absorbed by a particular material. (4.2)

**inorganic compounds.** Compounds other than organic compounds. (0.3)

**insulator.** A substance incapable of conducting electricity. (6.4)

**integrated rate law.** An equation relating the concentration of a species directly to time. (14.3)

**intensive property.** A property that does not depend on how much matter is being considered. (0.1)

**intermolecular interactions.** Attractive forces that exist between molecules. (4.6)

**internal conversion.** The process by which the excess energy of a nucleus is transferred to a core orbital electron, which is subsequently ejected from the atom. (17.1)

**internal energy.** Energy of a system that is left when the kinetic energy of overall motion is subtracted out. (7.1)

**International System of Units (SI).** A system of units based on metric units. (0.1)

**intramolecular interaction.** Forces that hold atoms together in a molecule. (4.6)

**ion.** An atom or a group of atoms that has a net positive or negative charge. (0.2)

**ion pair.** One or more cations and one or more anions held together by electrostatic forces. (9.4)

**ionic bond.** The electrostatic force that holds ions together in an ionic compound. (3.3)

**ionic compound.** Any neutral compound containing cations and anions. (0.3)

**ion-induced dipole interaction.** The interaction between an ion and the dipole that it induces in a nearby atom or nonpolar molecule. (4.6)

**ion-ion interactions.** The electrostatic interactions between ions. (4.6)

**ionic crystal.** A crystal composed of ionic species. (6.3)

**ionic radius.** The radius of a cation or an anion as measured in an ionic compound. (2.5)

**ionization.** Removal of an electron (or electrons) from an atom, molecule, or ion. (1.2)

**ionization energy.** The minimum energy required to remove an electron from an isolated atom (or an ion) in its ground state. (1.2)

**ion-dipole interactions.** Forces that operate between an ion and a dipole. (4.6)

**ion-product constant.** Product of hydrogen ion concentration and hydroxide ion concentration (both in molarity) at a particular temperature. (11.2)

**irreversible process.** A process that is not reversible. An irreversible process run in the forward direction will not be the exact opposite of the process run in the reverse direction. (7.1)

**isobaric process.** See *constant-pressure process*. (7.1)

**isochoric process.** See *constant-volume process*. (7.2)

**isoelectronic.** Ions, ions and atoms, or ions and molecules that possess the same number of electrons, and hence the same ground-state electron configuration, are said to be isoelectronic. (2.3)

**isolated system.** A system that does not allow the transfer of either mass or energy to or from its surroundings. (7.1)

**isomers.** Two or more different compounds that share the same molecular formula. (4.4)

**isothermal process.** A process that takes place at constant temperature (7.1)

**isotopes.** Atoms having the same atomic number but different mass numbers. (0.2)

## J

**joule (J).** Unit of energy given by  $\text{kg m}^2 \text{s}^{-2}$ . (0.1, A.1)

## K

**kelvin (K).** The SI base unit of temperature. (A.1)

**ketones.** Compounds with a carbonyl functional group and the general formula  $\text{R}'\text{RCO}$ , where R and R' are alkyl and/or aromatic groups. (16.3)

**kinetic energy (KE).** Energy available because of the motion of an object. (0.1)

**kinetic molecular theory of gases.** Treatment of gas behavior in terms of the random motion of molecules. (5.4)

**Kirchhoff's law.** An equation (Eq. 7.49) governing the temperature dependence of enthalpy changes. (7.7)

## L

**labile complex.** Complexes that undergo rapid ligand exchange reactions. (15.4)

**lanthanide (rare earth) series.** Elements that have incompletely filled  $4f$  subshells or readily give rise to cations that have incompletely filled  $4f$  subshells. (2.2)

**latent heat.** The enthalpy change for a phase transition. (7.6)

**lattice constant.** One of the edge lengths of a unit cell in a crystal lattice. (6.2)

**lattice energy.** The energy required to completely separate one mole of a solid ionic compound into gaseous ions. (7.6)

**law of conservation of energy.** The total quantity of energy in the universe is constant. (0.1)

**law of conservation of mass.** Matter can be neither created nor destroyed. (0.2)

**law of definite proportions.** Different samples of the same compound always contain its constituent elements in the same proportions by mass. (0.2)

**law of mass action.** For a reversible reaction at equilibrium and a constant temperature, a certain ratio of reactant and product concentrations has a constant value,  $K$  (the equilibrium constant). (10.1)

**law of multiple proportions.** If two elements can combine to form more than one type of compound, the masses of one element that combine with a fixed mass of the other element are in ratios of small whole numbers. (0.2)

**Le Châtelier's principle.** If an external stress is applied to a system at equilibrium, the system will adjust itself in such a way as to partially offset the stress as the system reaches a new equilibrium position. (10.4)

**Lennard-Jones potential.** A model for the interaction between nonpolar molecules that includes both a strong repulsion at short distances and a van der Waals interaction at long distances. (4.6)

**lever rule.** An equation for determining the fraction of different phases in a region of phase coexistence. (9.3)

**Lewis acid.** A substance that can accept a pair of electrons. (11.1)

**Lewis base.** A substance that can donate a pair of electrons. (11.1)

**Lewis dot symbol.** The symbol of an element with one or more dots that represent the number of valence electrons in an atom of the element. (3.2)

**Lewis structure.** A representation of covalent bonding using Lewis symbols. Shared electron pairs are shown either as lines or as pairs of dots between two atoms, and lone pairs are shown as pairs of dots on individual atoms. (3.2)

**ligand.** A molecule or an ion that is bonded to the metal ion in a complex ion. (15.2)

**ligand field theory.** A theory for bonding in coordination compounds based on molecular orbital theory. (15.3)

**light water reactor.** A nuclear reactor that uses  $\text{H}_2\text{O}$  as a moderator. (17.5)

**limiting law.** A scientific law that becomes exact only in some well-defined limit. (5.2)

**limiting reagent.** The reactant used up first in a reaction. (0.6)

**line spectra.** Spectra produced when radiation is absorbed or emitted by substances only at some wavelengths. (1.2)

**linear combination of atomic orbitals**

**(LCAO).** A molecular orbital constructed as a linear combination of atomic orbitals. (3.5)

**liquid.** A substance that resists changes in volume but not of shape. (0.1)

**liter.** The volume occupied by one cubic decimeter. (A.1)

**London interactions.** See dispersion interactions.

**lone pairs.** Valence electrons that are not involved in covalent bond formation. (3.2)

**low-boiling azeotrope.** An azeotrope occurring at a minimum of the temperature-composition diagram. (9.3)

**lowest unoccupied molecular orbital**

**(LUMO).** The lowest-energy molecular orbital in a molecule that does not contain electrons. (4.5)

## M

**macromolecules.** Molecules with very large molecular masses, for example, polymers, proteins, and DNA. (16.4)

**macroscopic.** Pertaining to objects that are large compared to the molecular scale. (5.1)

**macrostate.** See *thermodynamic state*. (7.1)

**magnetic quantum number.** The quantum number  $m_l$  that determines the orientation of an atomic orbital. (1.4)

**manometer.** A device used to measure the pressure of gases. (5.1)

**many-electron atoms.** Atoms that contain two or more electrons. (2.1)

**mass.** A measure of the quantity of matter contained in an object. (0.1)

**mass defect.** The difference between the mass of an atom and the sum of the masses of its protons, neutrons, and electrons. (17.2)

**mass number ( $A$ ).** The total number of neutrons and protons present in the nucleus of an atom. (0.2)

**mass spectrometer.** Determination of the masses of atoms, molecules, and ions using a mass spectrometer, a device that uses magnetic fields to separate atomic and molecular species by mass. (0.5)

**matter.** Anything that occupies space and possesses mass. (0.1)

**Maxwell-Boltzmann distribution of molecular speeds.** The distribution of molecular speeds in a gas, given by Equation 5.36. (5.4)

**melting.** The transformation of a solid into a liquid. (5.2)

**melting point.** The temperature at which solid and liquid phases coexist in equilibrium. (5.2)

**metallic crystal.** A crystal lattice held together by metallic bonds. (6.3)

**metalloid.** An element with properties intermediate between those of metals and nonmetals. (0.2)

**metals.** Elements that are good conductors of heat and electricity and have the tendency to form positive ions in ionic compounds. (0.2)

**microstate.** See *molecular state*. (7.1)

**microwave spectroscopy.** The study of the microwave frequencies that are absorbed by a material. (3.3)

**miscible.** Two liquids that are completely soluble in each other in all proportions are said to be miscible. (9.2)

**mixture.** A combination of two or more substances in which the substances retain their identity. (0.1)

**moderator.** A substance that can reduce the kinetic energy of neutrons. (17.5)

**molal boiling-point elevation constant ( $K_b$ ).** The constant of proportionality between the molality of a dilute solution and its boiling point. (9.4)

**molal freezing-point depression constant ( $K_f$ ).** The constant of proportionality between the molality of a dilute solution and its freezing point. (9.4)

**molality ( $m$ ).** The number of moles of solute dissolved in one kilogram of solvent. (0.5)

**molar concentration.** See *molarity*.

**molar enthalpy of fusion ( $\Delta H_{\text{fus}}$ ).** The enthalpy change associated with the melting (fusion) of 1 mole of a liquid. (7.6)

**molar enthalpy of sublimation ( $\Delta H_{\text{sub}}$ ).** The enthalpy change associated with the sublimation of 1 mole of a liquid. (7.6)

**molar enthalpy of vaporization ( $\Delta H_{\text{vap}}$ ).** The enthalpy change associated with the vaporization of 1 mole of a liquid. (7.6)

**molar heat capacity ( $C$ ).** The heat capacity of 1 mole of a substance. (7.3)

**molar mass ( $M$ ).** The mass (in grams or kilograms) of one mole of atoms, molecules, or other particles. (0.5)

**molar solubility.** The number of moles of solute in one liter of a saturated solution ( $\text{mol L}^{-1}$ ). (12.6)

**molarity ( $M$ ).** The number of moles of solute in one liter of solution. (0.5)

**mole (mol).** The amount of substance that contains as many elementary entities (atoms, molecules, or other particles) as there are atoms in exactly 12 grams (or 0.012 kilograms) of the carbon-12 isotope. (0.5)

**molecular crystal.** A crystal in which the molecules are held together by attractive intermolecular (van der Waals) interactions. (6.3)

**molecular formula.** An expression showing the exact numbers of atoms of each element in a molecule. (0.3)

**molecular geometry.** The three-dimensional arrangement of atoms in a molecule. (4.1)

**molecular mass.** The sum of the atomic masses (in amu) present in the molecule. (0.5)

**molecular model.** A three-dimensional representation of a molecule. (0.3)

**molecular orbital.** An orbital that is not associated with a particular atom but extends over the entire molecule or ion. (3.5)

**molecular orbital energy-level diagram (MO diagram).** A diagram illustrating the molecular orbitals of a molecule in terms of their relative energy. (3.5)

**molecular orbital theory.** The use of molecular orbitals to describe bonding in ions and molecules. (3.5)

**molecularity of a reaction.** The number of molecules reacting in an elementary step. (14.5)

**molecular speed.** The magnitude of a velocity of a molecule. (5.4)

**molecular state.** A description of a system in terms of the properties (for example, positions and velocities) of its constituent molecules. (7.1)

**molecule.** An aggregate of at least two atoms in a definite arrangement held together by special forces. (0.2)

**monatomic ion.** An ion that contains only one atom. (0.2)

**monomer.** The single repeating unit of a polymer. (16.4)

**monoprotic acid.** Each unit of the acid yields one hydrogen ion upon ionization. (11.1)

**multiple bonds.** Bonds formed when two atoms share two or more pairs of electrons. (3.2)

## N

**Nernst equation.** The relation between the emf of a galvanic cell and the standard emf and the concentrations of the oxidizing and reducing agents. (13.5)

**net ionic equation.** An equation that indicates only the ionic species that actually take part in the reaction. (4.2)

**neutralization reaction.** A reaction between an acid and a base. (11.1)

**neutron.** A subatomic particle that bears no net electric charge. Its mass is slightly greater than a proton's. (0.2)

**Newman projection.** A scheme for illustrating conformations in organic molecules. (16.1)

**newton (N).** The SI unit for force. (0.1, A.1)

**noble gas core.** The electron configuration of the noble gas element that most nearly precedes the element being considered. (2.2)

**noble gases.** Nonmetallic elements in Group 8A (He, Ne, Ar, Kr, Xe, and Rn). (2.4)

**node.** The point at which the amplitude of the wave is zero. (1.3)

**nonelectrolytes.** Molecules that do not dissociate in aqueous solution. (9.4)

**nonmetals.** Elements that are usually poor conductors of heat and electricity. (0.2)

**nonpolar molecule.** A molecule with a zero dipole moment. (4.2)

**nonvolatile.** Liquids not having a measurable vapor pressure. (9.4)

**normal boiling point.** The temperature at which the vapor pressure of a liquid is equal to 1 atm. (5.2)

**normal melting point.** The melting point of a substance at 1 atm pressure. (5.2)

**n-type semiconductors.** Semiconductors that contain donor impurities. (6.4)

**nuclear binding energy.** The energy required to break up a nucleus into its protons and neutrons. (17.2)

**nuclear chain reaction.** A self-sustaining sequence of nuclear fission reactions. (17.5)

**nuclear fission.** A heavy nucleus (mass number 200) divides to form smaller nuclei of intermediate mass and one or more neutrons. (17.5)

**nuclear fusion.** The combining of small nuclei into larger ones. (17.6)

**nuclear magnetic resonance (NMR) spectroscopy.** A type of spectroscopy that studies the excitation of nuclear spin with an electromagnetic field (radio waves). (16.3)

**nuclear transmutation.** The change undergone by a nucleus as a result of bombardment by neutrons or other particles. (17.1)

**nucleic acids.** High molar mass polymers that play an essential role in protein synthesis. (16.6)

**nucleon.** A general term for the protons and neutrons in a nucleus. (17.2)

**nucleotide.** The repeating unit in each strand of a DNA molecule which consists of a base-deoxyribose-phosphate linkage. (16.6)

**nucleus.** The central core of an atom. (0.2)

## O

**octet rule.** An atom other than hydrogen tends to form bonds until it is surrounded by eight valence electrons. (3.2)

**open system.** A system that can exchange mass and energy (usually in the form of heat) with its surroundings. (7.1)

**optical isomers.** Compounds that are non-superimposable mirror images. (4.4)

**orbital.** See atomic orbital and molecular orbital.

**orbital electron capture.** Radioactive decay process closely related to  $\beta^+$  decay in which an orbital electron is captured by the nucleus and combined with a proton to produce a neutron. (17.1)

**orbital energy.** The negative of the amount of energy required to remove an electron from a particular atomic or molecular orbital. (2.2)

**orbital diagram.** A pictorial representation of the electron configuration that shows the spin of the electron. (2.1)

**organic chemistry.** The branch of chemistry that deals with carbon compounds. (16.1)

**organic compounds.** Compounds that contain carbon, usually in combination with

elements such as hydrogen, oxygen, nitrogen, and sulfur. (0.3)

**orientation factor.** A factor used in the collision theory of reaction rates that reflects the probability of two molecules colliding in an orientation that is favorable to reaction. (14.4)

**osmosis.** The net movement of solvent molecules through a semipermeable membrane from a pure solvent or from a dilute solution to a more  $\pi$  concentrated solution. (9.4)

**osmotic pressure (II).** The pressure required to stop osmosis. (9.4)

**overvoltage.** The difference between the electrode potential and the actual voltage required to cause electrolysis. (13.7)

**oxidation.** The loss of electrons by a species in a reaction. (13.1)

**oxidation number.** The number of charges an atom would have in a molecule if electrons were transferred completely in the direction indicated by the difference in electronegativity. (13.1)

**oxidation reaction.** The half-reaction that involves the loss of electrons. (13.1)

**oxidation-reduction reaction.** A reaction that involves the transfer of electron(s) or the change in the oxidation state of reactants. (13.1)

**oxidation state.** See oxidation number.

**oxidizing agent.** A substance that can accept electrons from another substance or increase the oxidation numbers in another substance. (13.1)

**oxoacid.** An acid containing hydrogen, oxygen, and another element (the central element). (0.3)

**oxoanion.** An anion derived from an oxoacid. (0.3)

## P

**paramagnetic.** Attracted by a magnet. A paramagnetic substance contains one or more unpaired electrons. (2.1)

**partial pressure.** Pressure of one component in a mixture of gases. (5.3)

**particle-in-a-box model.** A simple model of a quantum particle that is confined completely within a region of space. (1.3)

**pascal (Pa).** A pressure of one newton per square meter ( $1 \text{ N m}^{-2}$ ). (5.1, A.1)

**Pauli exclusion principle.** No two electrons in an atom can have the same four quantum numbers. (2.1)

**percent by mass.** The ratio of the mass of a solute to the mass of the solution, multiplied by 100 percent. (0.5)

**percent composition by mass.** The percent by mass of each element in a compound. (0.5)

**percent ionization.** Ratio of ionized acid concentration at equilibrium to the initial concentration of acid. (11.4)

**percent yield.** The ratio of actual yield to theoretical yield, multiplied by 100 percent. (0.6)

**period.** A horizontal row of the periodic table. (0.2)

**periodic table.** A tabular arrangement of the elements. (0.2)

**pH.** The negative logarithm of the hydrogen ion concentration. (11.2)

**phase.** A homogeneous part of a system in contact with other parts of the system but separated from them by a well-defined boundary. (5.2)

**phase transition.** Transformation from one phase to another. (5.2)

**phase boundary.** The boundaries separating different phases in a phase diagram. (5.2)

**phase diagram.** A diagram showing the conditions at which a substance exists as a solid, liquid, or vapor. (5.2)

**photoelectric effect.** A phenomenon in which electrons are ejected from the surface of certain metals exposed to light of at least a certain minimum frequency. (1.1)

**photoelectron spectroscopy.** An experimental technique to determine the orbital energies of an atom or molecule. (2.2)

**photons.** Quanta of electromagnetic radiation. (1.1)

**physical equilibrium.** An equilibrium in which only physical properties change. (5.2)

**physical property.** Any property of a substance that can be observed without transforming the substance into some other substance. (0.1)

**pi bond ( $\pi$ ).** A covalent bond between two atoms in which the electron wavefunction between the bonded atoms changes sign when rotated by  $180^\circ$  about the bond axis. (3.2)

**pi molecular orbital.** A molecular orbital in which the electron density is concentrated above and below the line joining the two nuclei of the bonding atoms. (3.5)

**plasma.** A gaseous mixture of positive ions and electrons. (17.6)

**polar covalent bond.** In such a bond, the electrons spend more time in the vicinity of one atom than the other. (3.3)

**polar molecule.** A molecule with a nonzero dipole moment. (4.2)

**polarimeter.** The instrument for measuring the rotation of polarized light by optical isomers. (4.4)

**polarizability.** A measure of the degree to which the electron cloud around an atom, molecule, or ion can be deformed in the presence of an external electric field. (4.6)

**polyatomic ion.** An ion that contains more than one atom. (0.2)

**polyatomic molecule.** A molecule that consists of more than two atoms. (0.2)

**polymer.** A compound distinguished by a high molar mass, ranging into thousands and millions of grams, and made up of many repeating units. (16.4)

**polymorphism.** The existence of a solid in more than one crystal form. (5.2)

**positron.** A particle that has the same mass as the electron, but bears a charge of +e. (17.1)

**potential energy.** Energy available by virtue of an object's position. (0.1)

**precipitate.** An insoluble solid that separates from the solution. (12.5)

**precipitation reaction.** A reaction that results in the formation of a precipitate. (12.5)

**precision.** The closeness of agreement of two or more measurements of the same quantity. (A.1)

**pressure.** Force applied per unit area. (5.1)

**pressure-composition diagram.** A fixed temperature phase diagram for a binary mixture. (9.3)

**principal quantum number.** The quantum number  $n$  that determines the size (and to some extent) the energy of an atomic orbital. (1.4)

**product.** The substance formed as a result of a chemical reaction. (0.4)

**protein.** Polymers of amino acids. (16.5)

**proton.** A subatomic particle having a single positive electric charge. The mass of a proton is about 1840 times that of an electron. (0.2)

**pseudo-first-order reaction.** A second-order reaction in which one reactant is present in such a large concentration that the rate law appears to be first order. (14.3)

**p-type semiconductors.** Semiconductors that contain acceptor impurities. (6.4)

## Q

**qualitative analysis.** The determination of the types of ions present in a solution. (12.8)

**quantitative analysis.** The determination of the amount of substances present in a sample. (12.8)

**quantum.** The smallest quantity of energy that can be emitted (or absorbed) in the form of electromagnetic radiation. (1.1)

**quantum-mechanical tunneling.** The ability of a quantum particle to exist in regions of space that are energetically forbidden in classical mechanics. (1.3)

**quantum mechanics.** The study of the wave-like properties of matter at the molecular scale. (1.3)

**quantum numbers.** Numbers that describe the distribution of electrons in hydrogen and other atoms. (1.2)

## R

**racemic mixture.** An equimolar mixture of the two enantiomers. (4.4)

**radial distribution function.** (1) A plot of the distribution of electron probability about the nucleus; (2) In liquids, it is a

- measure of the local density about a chosen central atom. (6.1)
- radial probability function.** A function  $P(r)$  that shows the probability of finding an electron at a distance  $r$  away from the nucleus. (1.4)
- radiant energy.** Energy transmitted in the form of waves. (0.1)
- radical.** Any neutral fragment of a molecule containing an unpaired electron. (17.8)
- radioactive decay series.** A sequence of nuclear reactions that ultimately result in the formation of a stable isotope. (17.2)
- radioactivity.** The spontaneous breakdown of an atom by emission of particles and/or radiation. (17.1)
- Raoult's law.** The partial pressure of the solvent over a solution is given by the product of the vapor pressure of the pure solvent and the mole fraction of the solvent in the solution. (9.3)
- rapid preequilibrium.** A reaction in which the mechanism contains a rapid and reversible step prior to the rate determining step. (14.5)
- rare earth series.** See *lanthanide series*.
- rate constant ( $k$ ).** Constant of proportionality between the reaction rate and the concentrations of reactants. (14.1)
- rate law.** An expression relating the rate of a reaction to the rate constant and the concentrations of the reactants. (14.2)
- rate-determining step.** The slowest step in the sequence of steps leading to the formation of products. (14.3)
- reactants.** The starting substances in a chemical reaction. (0.4)
- reaction intermediate.** A species that appears in the mechanism of the reaction (that is, the elementary steps) but not in the overall balanced equation. (14.5)
- reaction mechanism.** The sequence of elementary steps that leads to product formation. (14.5)
- reaction order.** The sum of the powers to which all reactant concentrations appearing in the rate law are raised. (14.2)
- reaction quotient ( $Q$ ).** A number equal to the ratio of product concentrations to reactant concentrations, each raised to the power of its stoichiometric coefficient at some point other than at equilibrium. (10.2)
- reaction rate.** The change in the concentration of reactant or product with time. (14.1)
- redox reaction.** A reaction in which there is either a transfer of electrons or a change in the oxidation numbers of the substances taking part in the reaction. (13.1)
- reducing agent.** A substance that can donate electrons to another substance or decrease the oxidation numbers in another substance. (13.1)
- reduction.** The gain of electrons by a species in a reaction. (13.1)
- reduction reaction.** The half-reaction that involves the gain of electrons. (13.1)
- representative elements.** Elements in Groups 1A through 7A, all of which have incompletely filled  $s$  or  $p$  subshells of highest principal quantum number. (2.4)
- residual entropy.** The value of the entropy at 0 K for systems for which the third law of thermodynamics is not applicable. (8.3)
- resonance.** The use of two or more Lewis structures to represent a particular molecule. (3.4)
- resonance structure.** One of two or more alternative Lewis structures for a molecule that cannot be described fully with a single Lewis structure. (3.4)
- reversible process.** A process that proceeds so slowly that the system always remains infinitesimally close to equilibrium with itself and its surroundings. A reversible process run in the forward direction will be the exact opposite of the process run in the reverse direction. (7.1)
- ribonucleic acid (RNA).** A form of nucleic acid. (16.6)
- root-mean-square (rms) speed ( $u_{\text{rms}}$ ).** A measure of the average molecular speed at a given temperature. (5.7)
- S**
- salt.** An ionic compound made up of a cation other than  $\text{H}^+$  and an anion other than  $\text{OH}^-$  or  $\text{O}_2^-$ . (11.1)
- salt hydrolysis.** The reaction of the anion or cation, or both, of a salt with water. (11.16)
- saponification.** Soapmaking. (16.3)
- saturated hydrocarbons.** Hydrocarbons that contain the maximum number of hydrogen atoms that can bond with the number of carbon atoms present. (16.1)
- saturated solution.** At a given temperature, the solution that results when the maximum amount of a substance has dissolved in a solvent. (9.2)
- scanning tunneling microscope (STM).** A molecular-level imaging device that uses quantum-mechanical tunneling to produce an image of the atoms at the surface of a sample. (1.4)
- second law of thermodynamics.** The entropy of any isolated system increases in a spontaneous process and remains unchanged in an equilibrium (reversible) process. (8.1)
- second-order reaction.** A reaction whose rate depends on reactant concentration raised to the second power or on the concentrations of two different reactants, each raised to the first power. (14.3)
- self-consistent field (SCF) method.** An iterative method for optimizing the atomic (or molecular) orbitals in a multielectron atom (or molecule). (2.1)
- semiconductors.** Elements that normally cannot conduct electricity, but can have their conductivity greatly enhanced either by raising the temperature or by adding certain impurities. (6.4)
- semipermeable membrane.** A membrane that enables solvent molecules to pass through, but blocks the movement of solute molecules. (9.4)
- shell model.** A model of the nucleus in which the nucleons in a nucleus populate independent quantum orbitals in much the same way as electrons occupy atomic orbitals in an atom. (17.2)
- sigma bond ( $\sigma$ ).** A covalent bond between two atoms for which the electron wavefunction in the bonding region is cylindrically symmetric about the bond axis. (3.2)
- sigma molecular orbital.** A molecular orbital in which the electron density is concentrated around a line between the two nuclei of the bonding atoms. (3.5)
- significant figures.** The number of meaningful digits in a measured or calculated quantity. (A.1)
- simple cubic (SC).** Having a crystal unit cell with lattice points at the vertices of a cube. (6.2)
- single bond.** Two atoms are held together by one electron pair. (3.2)
- solid.** A substance that resists changes in both volume and shape. (0.1)
- solubility.** The maximum amount of solute that can be dissolved in a given quantity of solvent at a specific temperature. (9.2, 12.6)
- solubility product ( $K_{\text{sp}}$ ).** The product of the molar concentrations of the constituent ions, each raised to the power of its stoichiometric coefficient in the equilibrium equation. (12.6)
- solute.** The substance present in smaller amount in a solution. (0.1)
- solution.** A homogeneous mixture of two or more substances. (0.1)
- solvation.** The process in which an ion or a molecule is surrounded by solvent molecules arranged in a specific manner. (9.2)
- solvent.** The substance present in larger amount in a solution. (0.1)
- solvent leveling.** The phenomenon that strong acids will yield identical  $\text{H}_3\text{O}^+$  concentrations in water, independent of their individual  $K_a$  values. (11.3)
- specific heat capacity ( $C_s$ ).** The heat capacity of 1 gram of a substance. (7.3)
- spectator ions.** Ions that are not involved in the overall reaction. (11.1)
- spectrochemical series.** A list of ligands arranged in increasing order of their abilities to split the  $d$ -orbital energy levels. (15.3)
- spontaneous fission.** The spontaneous decay of a heavy unstable nucleus into two or more smaller nuclei and some neutrons. (17.1)

**standard atmospheric pressure (atm).** A unit of pressure equal to 1.01325 bar, exactly. (5.1)

**spontaneous process.** A process that occurs without external intervention under a given set of conditions. (8.1)

**standard ambient temperature and pressure (SATP).** 25°C and 1 bar. (5.3)

**standard boiling point.** The temperature at which the vapor pressure of a liquid is equal to 1 bar. (5.2)

**standard emf.** The difference of the standard reduction potential of the substance that undergoes reduction and the standard reduction potential of the substance that undergoes oxidation. (13.3)

**standard enthalpy of reaction.** The enthalpy change when the reaction is carried out under standard-state conditions. (7.4)

**standard entropy change of reaction.** The entropy change when the reaction is carried out under standard-state conditions. (8.3)

**standard freezing point.** The temperature at which a solid and its melt coexist at 1 bar pressure. (5.2)

**standard Gibbs free-energy of reaction.** The Gibbs free-energy change when the reaction is carried out under standard-state conditions. (8.4)

**standard Gibbs free-energy of formation.** The Gibbs free-energy change when 1 mole of a compound is synthesized from its elements in their standard states. (8.4)

**standard melting point.** The melting point of a substance at 1 bar pressure. (5.2)

**standard molar enthalpy of formation ( $\Delta H_f^\circ$ ).** The enthalpy change that results when 1 mole of a compound in its standard state is formed from its elements in their standard states.

**standard molar entropy.** Absolute entropies measured at the standard pressure of 1 bar. (8.3)

**standard reduction potential.** The voltage measured as a reduction reaction occurs at the electrode when all solutes are 1 M and all gases are at 1 atm. (13.3)

**standard solution.** A solution of accurately known concentration. (12.3)

**standard state.** The condition of 1 atm of pressure. (7.4)

**standard temperature and pressure (STP).** 0°C and 1 atm. (5.3)

**standing wave.** A wave that does not propagate through space. (1.3)

**state function.** A property that is determined by the state of the system. (7.1)

**statistical mechanics.** The study of the molecular origin of thermodynamics. (7.3)

**steady state.** A thermodynamic state in which all macroscopic properties of the system are unchanging in time, but requires a continual inflow and outflow of energy and/or matter to remain unchanging. (7.1)

**steady-state approximation.** The approximation that the concentration of reaction intermediates is constant (in steady state) during a reaction. (14.5)

**steady-state rate law.** The rate law resulting from the steady-state approximation. (14.5)

**stereoisomers.** Compounds that are made up of the same types and numbers of atoms bonded together in the same sequence but with different spatial arrangements. (4.4)

**steric factor.** See *orientation factor*. (14.4)

**steric number.** The total number of electron pair sets surrounding a central atom in a molecule. (4.1)

**Stock system.** A systematic method for naming inorganic compounds (0.3)

**stoichiometric amounts.** The exact molar amounts of reactants and products that appear in the balanced chemical equation. (0.6)

**stoichiometry.** The quantitative study of reactants and products in a chemical reaction. (0.6)

**stoichiometric coefficient.** The constant multiplying a given element or compound in a chemical equation. (0.4)

**strong acids.** Strong electrolytes that are assumed to ionize completely in water. (11.1)

**strong bases.** Strong electrolytes that are assumed to ionize completely in water. (11.1)

**strong electrolyte.** A species that, for all practical purposes, dissociates completely in aqueous solution. (11.1)

**strong force.** The force that binds protons and neutrons together in the nucleus. (0.1)

**structural formula.** A chemical formula that shows how atoms are bonded to one another in a molecule. (0.3)

**structural isomers.** Molecules that have the same molecular formula but different structures. (4.4)

**sublimation.** The process in which molecules go directly from the solid into the vapor phase. (5.2)

**subshell.** The set of distinct orbitals within an energy shell that possess the same value of the quantum number  $l$ . (1.4)

**substance.** A form of matter that has a definite or constant composition (the number and type of basic units present) and distinct properties. (0.1)

**substitution reaction.** A reaction in which an atom or group of atoms replaces an atom or groups of atoms in another molecule. (16.3)

**supercooling.** Cooling of a liquid below its freezing point without forming the solid. (6.3)

**supercritical fluid (SCF).** A substance above its critical pressure and temperature. (5.2)

**supersaturated solution.** A solution that contains more of the solute than is present in a saturated solution. (9.2)

**surface tension.** The amount of energy required to stretch or increase the surface of a liquid by a unit area. (6.1)

**surroundings.** The rest of the universe outside a system. (7.1)

**system.** Any specific part of the universe that is of interest to us. (7.1)

## T

**temperature.** The quantity that controls the direction of energy flow between two systems. (5.1)

**temperature-composition phase diagram.** A fixed pressure phase diagram for a binary mixture. (9.3)

**termolecular reaction.** Elementary reactions involving three reactant molecules. (14.5)

**ternary compounds.** Compounds consisting of three elements. (0.3)

**theoretical yield.** The amount of product predicted by the balanced equation when all of the limiting reagent has reacted. (0.6)

**thermal energy.** Energy associated with the random motion of atoms and molecules. (0.1)

**thermal equilibrium.** Equilibrium with respect to heat flow. (5.1)

**thermochemical equation.** An equation that shows both the mass and enthalpy relations. (7.2)

**thermochimistry.** The study of heat changes in chemical reactions. (7.1)

**thermodynamics.** The scientific study of the interconversion of heat and other forms of energy. (7.1)

**thermodynamic state.** A description of a system in terms of macroscopic variables (temperature, volume, pressure, etc.). (7.1)

**thermometer.** A device for measuring temperature. (5.1)

**thermonuclear reactions.** Nuclear fusion reactions that occur at very high temperatures. (17.6)

**third law of thermodynamics.** The entropy of a pure substance in its thermodynamically most stable form is zero at the absolute zero of temperature. (8.3)

**titration.** The gradual addition of a solution of accurately known concentration to another solution of unknown concentration until the chemical reaction between the two solutions is complete. (12.3)

**tracers.** Isotopes, especially radioactive isotopes, that are used to trace the path of the atoms of an element in a chemical or biological process. (17.7)

**transition elements.** Elements that have incompletely filled *d* subshells or readily give rise to cations that have incompletely filled *d* subshells. (2.2)

**transition metals.** See *transition elements*. (2.2)

**transition state.** See activated complex. (14.4)

**transition-state theory.** A theory for reaction rates that assumes that the reactants are in equilibrium with the transition state during the reaction. (14.4)

**transuranium elements.** Elements with atomic numbers greater than 92. (17.4)

**triple bond.** Two atoms are held together by three pairs of electrons. (3.2)

**triple point.** The point at which the vapor, liquid, and solid states of a substance are in equilibrium. (5.2)

**triprotic acid.** Each unit of the acid yields three protons upon ionization. (11.1)

## U

**unimolecular reaction.** An elementary step in which only one reacting molecule participates. (14.5)

**unit cell.** The basic repeating unit of the arrangement of atoms, molecules, or ions in a crystalline solid. (6.2)

**universal gas constant.** The constant  $R$  that appears in the ideal gas equation. It is usually expressed as  $0.08314 \text{ L mol}^{-1} \text{ K}^{-1}$  or  $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ .  $R$  is equal to Boltzmann's constant times Avagadro's number. (5.2)

**unsaturated hydrocarbons.** Hydrocarbons that contain carbon-carbon double bonds or carbon-carbon triple bonds. (16.2)

**unsaturated solution.** A solution that contains less solute than it has the capacity to dissolve. (9.2)

## V

**valence band.** A band of closely spaced filled orbitals in a crystalline material. (6.4)

**valence bond theory.** A theory of bonding in which bonds are formed by the overlap of unfilled atomic orbitals on the bonded atoms. (3.2)

**valence electrons.** The outer electrons of an atom, which are those involved in chemical bonding. (2.4)

**valence shell.** The outermost electron-occupied shell of an atom, which holds the electrons that are usually involved in bonding. (4.1)

**valence-shell electron-pair repulsion (VSEPR) model.** A model that accounts for the geometrical arrangements of shared and unshared electron pairs around a central atom in terms of the repulsions between electron pairs. (4.1)

**van der Waals equation.** An equation that describes the  $P$ ,  $V$ , and  $T$  of a nonideal gas. (5.5)

**van der Waals interactions.** Intermolecular interactions that fall off as  $1/r^6$ . Includes dispersion forces as well as dipole-dipole and dipole-induced dipole interactions in liquids and gases. (4.6)

**van't Hoff equation.** An equation (Eq. 10.16) relating the temperature dependence of an equilibrium constant with its enthalpy of reaction. (10.4)

**van't Hoff factor.** The ratio of actual number of particles in solution after dissociation to the number of formula units initially dissolved in solution. (9.4)

**vapor-pressure lowering.** The lowering of the vapor pressure of a liquid through the addition of a solute. (9.4)

**vaporization.** The escape of molecules from the surface of a liquid; also called evaporation. (5.2)

**virial equation of state.** An equation of state for real gases given by Equation 5.44. (5.5)

**viscosity.** A measure of a fluid's resistance to flow. (6.1)

**volatile.** Has a measurable vapor pressure. (9.4)

**volume.** It is the length cubed. (0.1)

## W

**wave.** A vibrating disturbance by which energy is transmitted. (1.1)

**wavefunction.** A function that describes the quantum state of a particle. (1.3)

**wavelength ( $\lambda$ ).** The distance between identical points on successive waves. (1.1)

**weak acids.** Weak electrolytes that ionize only to a limited extent in water. (11.1)

**weak bases.** Weak electrolytes that ionize only to a limited extent in water. (11.3)

**weak force.** The force responsible for the beta decay of radioactive nuclei. (0.1, 17.2).

**work.** Directed energy change resulting from a process. (7.1)

## X

**X-ray diffraction.** The scattering of X rays by the units of a regular crystalline solid. (6.2)

## Z

**zero-point energy.** The energy of the lowest energy level of a quantum system. (1.3)

**zeroth law of thermodynamics.** If two systems are in thermal equilibrium with a third system, then they are also in thermal equilibrium with each other. (5.1)



# Answers

## to Even-Numbered Problems

### Chapter 0

- 0.2** (a) Physical. (b) Chemical. (c) Physical. (d) Chemical.  
**0.4** (a) homogeneous mixture. (b) element.  
(c) compound. (d) homogeneous mixture.  
(e) heterogeneous mixture. (f) homogeneous mixture.  
(g) heterogeneous mixture. **0.6** 8.1 kJ. **0.8** 24.5 m s<sup>-1</sup>.  
**0.10** (a) Isotope  $^4\text{He}$ ,  $^{20}\text{Ne}$ ,  $^{18}\text{Ar}$ ,  $^{40}\text{Kr}$ ,  $^{132}\text{Xe}$ ,  $^{222}\text{Rn}$ ; No. protons 2, 10, 18, 36, 54, 86; No. neutrons 2, 10, 22, 48, 78, 136. (b) n/p ratio 1.00, 1.00, 1.22, 1.33, 1.44, 1.58. The n/p ratio increases with increasing atomic number.  
(c) This trend does hold for other elements. **0.12** 0.20 km.  
**0.14** 145. **0.16** Isotope  $^{15}\text{N}$ ,  $^{33}\text{S}$ ,  $^{63}\text{Cu}$ ,  $^{84}\text{Sr}$ ,  $^{130}\text{Ba}$ ,  $^{186}\text{W}$ ,  $^{202}\text{Hg}$ ; No. protons 7, 16, 29, 38, 56, 74, 80; No. neutrons 8, 17, 34, 46, 74, 112, 122; No. electrons 7, 16, 29, 38, 56, 74, 80. **0.18** (a)  $^{186}\text{W}$ . (b)  $^{201}\text{Hg}$ . **0.20** (a) H<sub>2</sub> and N<sub>2</sub>. (b) CO and HF. (c) S<sub>8</sub> and C<sub>60</sub>. (d) HClO and HIO. **0.22** Ion K<sup>+</sup>, Mg<sup>2+</sup>, Fe<sup>3+</sup>, Br<sup>-</sup>, Mn<sup>2+</sup>, C<sup>4-</sup>, Cu<sup>2+</sup>, No. protons 19, 12, 26, 35, 25, 6, 29; No. electrons 18, 10, 23, 36, 23, 10, 27. **0.24** The molecular formula of ethanol is C<sub>2</sub>H<sub>6</sub>O. **0.26** (a) potassium dihydrogen phosphate. (b) potassium hydrogen phosphate. (c) hydrogen bromide (molecular compound). (d) lithium carbonate. (e) sodium dichromate. (f) ammonium sulfate. (g) iodic acid. (h) phosphorus pentafluoride. (i) tetraphosphorus hexoxide. (j) cadmium iodide. (k) strontium sulfate. (l) aluminum hydroxide. **0.28** (a) cobalt(II) nitrate hexahydrate. (b) nickel(II) bromide trihydrate. (c) zinc(II) sulfate heptahydrate. (d) sodium sulfate monohydrate.  
**0.30** (a) Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O. (b) CaSO<sub>4</sub>·2H<sub>2</sub>O. (c) MgCl<sub>2</sub>·6H<sub>2</sub>O.  
(d) Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O. **0.32** (a) 2C + O<sub>2</sub> → 2CO. (b) 2CO + O<sub>2</sub> → 2CO<sub>2</sub>. (c) H<sub>2</sub> + Br<sub>2</sub> → 2HBr. (d) 2H<sub>2</sub>O<sub>2</sub> → 2H<sub>2</sub>O + O<sub>2</sub>. (e) 2C<sub>4</sub>H<sub>10</sub> + 13O<sub>2</sub> → 8CO<sub>2</sub> + 10H<sub>2</sub>O. (f) 3KOH + H<sub>3</sub>PO<sub>4</sub> → K<sub>3</sub>PO<sub>4</sub> + 3H<sub>2</sub>O. (g) N<sub>2</sub> + 3H<sub>2</sub> → 2NH<sub>3</sub>. (h) NH<sub>4</sub>NO<sub>3</sub> → N<sub>2</sub>O + 2H<sub>2</sub>O. (i) 2C<sub>6</sub>H<sub>6</sub> + 15O<sub>2</sub> → 12CO<sub>2</sub> + 6H<sub>2</sub>O. (j) 3Na<sub>2</sub>O + 2Al → Al<sub>2</sub>O<sub>3</sub> + 6Na.  
**0.34** 35.45 u. **0.36** (a) 16.04 u. (b) 46.01 u. (c) 80.07 u. (d) 78.11 u. (e) 149.9 u. (f) 174.27 u. (g) 310.18 u. **0.38** 9.96 × 10<sup>-15</sup> mol.  
**0.40** 3.44 × 10<sup>-10</sup> g Pb. **0.42** (a) 73.89 g. (b) 76.15 g. (c) 119.37 g. (d) 176.12 g. (e) 101.11 g. (f) 352.0 g. (g) 84.01 g. **0.44** 3.01 × 10<sup>22</sup> C atoms; 3.01 × 10<sup>22</sup> O atoms; 6.02 × 10<sup>22</sup> H atoms. **0.46** 8.56 × 10<sup>22</sup> molecules. **0.48** (a) CH<sub>2</sub>O. (b) KCN. **0.50** The molecular formula and the empirical formula are C<sub>6</sub>H<sub>10</sub>S<sub>2</sub>O.  
**0.52** There will be seven peaks of the following mass numbers: 34, 35, 36, 37, 38, 39, and 40. **0.54** 288 g I<sub>2</sub>. **0.56** (a) NH<sub>4</sub>NO<sub>3(s)</sub> → N<sub>2</sub>O(g) + 2H<sub>2</sub>O(g). (b) 20 g. **0.58** 0.709 g NO<sub>2</sub>. **0.60** 93.0%. **0.62** 53.85%. **0.64** (a) 4.41 × 10<sup>-40</sup>. (b) 4.6 × 10<sup>-18</sup> J.  
**0.66** 2C<sub>2</sub>H<sub>6</sub> + 7O<sub>2</sub> → 4CO<sub>2</sub> + 6H<sub>2</sub>O. **0.68** 9.58 × 10<sup>5</sup> g.  
**0.70** (a) The formula should be (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>. (b) The formula should be Ca(OH)<sub>2</sub>. (c) The correct formula is CdS. (d) The correct formula is ZnCr<sub>2</sub>O<sub>7</sub>. **0.72** 103.3 g mol<sup>-1</sup>. **0.74** C:30.20%, H:5.069%, Cl:44.57%, S:20.16%. **0.76** 700. g. **0.78** (a) Zn(s) + H<sub>2</sub>SO<sub>4(aq)</sub> → ZnSO<sub>4(aq)</sub> + H<sub>2(g)</sub>. (b) 64.2%. (c) We assumed that the impurities are inert and do not react with the sulfuric acid to produce hydrogen. **0.80** 89.5%. **0.82** (a) 6.532 × 10<sup>4</sup> g mol<sup>-1</sup>. (b) 7.6 × 10<sup>2</sup> g.

**0.84** NaCl: 32.17%; Na<sub>2</sub>SO<sub>4</sub>: 20.09%; NaNO<sub>3</sub>: 47.75%.

**0.86** (a) 16 u, CH<sub>4</sub> 17 u, NH<sub>3</sub> 18 u, H<sub>2</sub>O 64 u, SO<sub>2</sub>. (b) A CH<sub>3</sub> fragment could break off from this C<sub>5</sub>H<sub>8</sub> giving a peak at 15 u. (c) ±0.030 u. **0.88** 2.01 × 10<sup>21</sup>. **0.90** 16.00 u.

**0.92** (e) 0.50 mol Cl<sub>2</sub>. **0.94** X<sub>2</sub>O<sub>3(s)</sub> + 3CO(g) → 2X(s) + 3CO<sub>2</sub>(g). **0.96** 54.57% of the molecules. **0.98** (a) Compound X: MnO<sub>2</sub>, compound Y: Mn<sub>3</sub>O<sub>4</sub>. (b) 3MnO<sub>2</sub> → Mn<sub>3</sub>O<sub>4</sub> + O<sub>2</sub>.

**0.100** 6.1 × 10<sup>5</sup>. **0.102** PbC<sub>8</sub>H<sub>20</sub>. **0.104** 1.85 × 10<sup>5</sup> kg.

**0.106** (a) 2.0 × 10<sup>24</sup> cm<sup>3</sup>. (b) 3.9 × 10<sup>3</sup> m. **0.108** (a) 4.3 × 10<sup>23</sup>.

(b) 160 pm. **0.110** (a) C<sub>3</sub>H<sub>8(g)</sub> + 3H<sub>2</sub>O(g) → 3CO(g) + 7H<sub>2(g)</sub>.

(b) 909 kg. **0.112** Gently heat the liquid to see if any solid remains after the liquid evaporates. Also, collect the vapor and then compare the densities of the condensed liquid with the original liquid. The composition of a mixed liquid would change with evaporation along with its density. **0.114** The predicted change (loss) in mass is only 1.91 × 10<sup>-8</sup> g, which is too small a quantity to measure. Therefore, for all practical purposes, the law of conservation of mass is assumed to hold for ordinary chemical processes. **0.116** The acids, from left to right, are chloric acid, nitrous acid, hydrocyanic acid, and sulfuric acid. **0.118** (a) 0.307 g. (b) 0.410 g. (c) 90.1%. **0.120** 6.022 g of Mg<sub>3</sub>N<sub>2</sub>, 25.66 g MgO.

**0.122** 9.6 g Fe<sub>2</sub>O<sub>3</sub>, 7.4 g KClO<sub>3</sub>.

### Chapter 1

**1.2** (a) 6.58 × 10<sup>14</sup> Hz. (b) 1.22 × 10<sup>8</sup> nm. **1.4** 4.95 × 10<sup>14</sup> Hz.

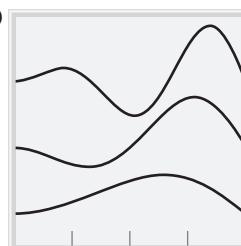
**1.6** (a) 4.0 × 10<sup>2</sup> nm. (b) 5.0 × 10<sup>-19</sup> J. **1.8** 1.2 × 10<sup>2</sup> nm, which is in the ultraviolet region. **1.10** (a) 370 nm, 3.70 × 10<sup>-7</sup> m.

(b) ultraviolet region. (c) 5.38 × 10<sup>-19</sup> J. **1.12** 3.3 × 10<sup>28</sup>.

**1.14** The radiation emitted by the star is measured as a function of wavelength ( $\lambda$ ). The wavelength corresponding to the maximum intensity is then plugged in to Wien's law ( $T\lambda_{\max} = 1.44 \times 10^{-2}$  K m) to determine the surface temperature. **1.16** Each laser will eject the same number of electrons. The electrons ejected by the blue laser will have higher kinetic energy because the photons from the blue laser have higher energy. **1.18** (a) 3.28 × 10<sup>-19</sup> J. (b) 5.9 × 10<sup>-20</sup> J. **1.20** The emitted light could be analyzed by passing it through a prism. **1.22** Excited atoms of the chemical elements emit the same characteristic frequencies or lines in a terrestrial laboratory, in the sun, or in a star many light-years distant from Earth. **1.24** 3.027 × 10<sup>-19</sup> J. **1.26** 6.17 × 10<sup>14</sup> Hz and 486 nm. **1.28** 21.17 nm and 47.64 nm. **1.30** 3.289832496 × 10<sup>15</sup> Hz. **1.32** 0.565 nm. **1.34** 1.99 × 10<sup>-31</sup> cm. **1.36** 1 × 10<sup>6</sup> m s<sup>-1</sup>.

**1.38** 1.20 × 10<sup>-18</sup> J.

**1.40**



The average value for  $x$  will be greater than  $L/2$ .

**1.42** (a)  $n = 2$ ,  $l = 1$ ,  $m_l = 1, 0$ , or  $-1$ . (b)  $n = 6$ ,  $l = 0$ ,  $m_l = 0$  (only allowed value). (c)  $n = 5$ ,  $l = 2$ ,  $m_l = 2, 1, 0, -1$ , or  $-2$ .

**1.44** The allowed values of  $l$  are 0, 1, 2, 3, 4, and 5 [ $l = 0$  to  $(n - 1)$ , integer values]. These  $l$  values correspond to the  $6s$ ,  $6p$ ,  $6d$ ,  $6f$ ,  $6g$ , and  $6h$  subshells. These subshells each have 1, 3, 5, 7, 9, and 11 orbitals, respectively (number of orbitals =  $2l + 1$ ).

**1.46** A  $2s$  orbital is larger than a  $1s$  orbital. Both have the same spherical shape. The  $1s$  orbital is lower in energy than the  $2s$ . The  $1s$  orbital does not have a node while the  $2s$  orbital does.

**1.48**  $\text{He}^+$  has an ionization energy of  $5.248 \times 10^3 \text{ kJ mol}^{-1}$ .  $\text{Li}^{2+}$  has an ionization energy of  $1.181 \times 10^4 \text{ kJ mol}^{-1}$ .

**1.50** (a) False. (b) False. (c) True. (d) False. (e) True.

**1.52** The color of the flame would be blue. **1.54**  $4.10 \times 10^{23}$ .

**1.56** The longest wavelength for the Lyman series is 121 nm. The shortest wavelength for the Balmer series is 365 nm. **1.58** 483 nm.

**1.60** For hydrogen, the percent change of the Rydberg constant is 0.0547%. For the He-4, the percent change of the Rydberg constant is 0.014%. **1.62**  $2.8 \times 10^6 \text{ K}$ . **1.64**  $2.0 \times 10^{-5} \text{ m s}^{-1}$ .

**1.66**  $1.8 \times 10^5 \text{ J}$ . **1.68**  $2.76 \times 10^{-11} \text{ m}$ . **1.70** 17.4 pm.

**1.72** (a)  $6.171 \times 10^{-21} \text{ J}$ . (b)  $1.635 \times 10^{-18} \text{ J}$ . (c)  $7.90 \times 10^4 \text{ K}$ .

**1.74** An electron confined to the nucleus would have an uncertainty in its velocity of  $5.8 \times 10^{10} \text{ m s}^{-1}$ , which is impossible because it far exceeds the speed of light. The uncertainty of the velocity of a proton confined to the nucleus is  $3.2 \times 10^7 \text{ m s}^{-1}$ , which is less than the speed of light.

**1.76** For the  $1s$  orbital, the average value for  $r$  is  $\frac{2}{3}a_0$  and the most likely value of  $r$  is  $a_0$ . For the  $2s$  orbital, the average value for  $r$  is  $6a_0$  and the most likely value of  $r$  is  $(3 + \sqrt{5})a_0$ .

**1.78** The five lowest energy levels correspond to the following sets of quantum numbers:  $(n_x, n_y)$ : (1,1); (1,2) and (2,1); (2,2); (1,3) and (3,1); (2,3) and (3,2). There are more than five states here because the second, fourth, and fifth energy levels are degenerate.

## Chapter 2

**2.2** There are three coordinates for each electron. Sodium has 11 electrons, hence its wavefunction would be a function of 33 ( $11 \times 3 = 33$ ) variables. The sodium ion has one less electron, hence its wavefunction would be a function of 30 ( $10 \times 3 = 30$ ) variables.

**2.4** 0.66. **2.6** In the many-electron atom, the  $3p$  orbital electrons are more effectively shielded by the inner electrons of the atom (that is, the  $1s$ ,  $2s$ , and  $2p$  electrons) than the  $3s$  electrons. The  $3s$  orbital is said to be more “penetrating” than the  $3p$  and  $3d$  orbitals. In the hydrogen atom, there is only one electron and hence there cannot be any shielding, so the  $3s$ ,  $3p$ , and  $3d$  orbitals have the same energy. **2.8** For aluminum, there are not enough electrons in the  $2p$  subshell. (The  $2p$  subshell holds six electrons.) The number of electrons (13) is correct. The electron configuration should be  $1s^2 2s^2 2p^6 3s^2 3p^1$ . The configuration shown might be an excited state of an aluminum atom. For boron, there are too many electrons. (Boron only has five electrons.) The electron configuration should be  $1s^2 2s^2 2p^1$ . For fluorine, there are also too many electrons. (Fluorine only has nine electrons.) The configuration shown is that of the  $\text{F}^-$  ion. The correct electron configuration is  $1s^2 2s^2 2p^5$ . **2.10** Tc:  $[\text{Kr}]5s^2 4d^5$ . **2.12** Ge is:  $[\text{Ar}]4s^2 3d^{10} 4p^2$ ; Fe:  $[\text{Ar}]4s^2 3d^6$ ; Zn:  $[\text{Ar}]4s^2 3d^{10}$ ; Ni:  $[\text{Ar}]4s^2 3d^8$ ; W:  $[\text{Xe}]6s^2 4f^{14} 5d^4$ ; Ti:  $[\text{Xe}]6s^2 4f^{14} 5d^{10} 6p^1$ . **2.14** S $^+$  has the most unpaired electrons. It has 3 unpaired electrons in the  $3p$  orbitals.

**2.16** (a)  $[\text{Ne}]3s^2 3p^5$ . (b) paramagnetic. **2.18** Cr. **2.20** Na $^+$ :  $[\text{Ne}]$ ; Mg $^{2+}$ :  $[\text{Ne}]$ ; Cl $^-$ :  $[\text{Ar}]$ ; K $^+$ :  $[\text{Ar}]$ ; Ca $^{2+}$ :  $[\text{Ar}]$ ; Cu $^{2+}$ :  $[\text{Ar}]3d^9$ ; Zn $^{2+}$ :

$[\text{Ar}]3d^{10}$ . **2.22** C and B $^-$ ; Mn $^{2+}$  and Fe $^{3+}$ ; Ar and Cl $^-$ ; Zn and Ge $^{2+}$ . **2.24** B: 1; Ne: 0; P: 3; Sc: 1; Mn: 5; Se: 2; Kr: 0; Fe: 4; Cd: 0; I: 1; Pb: 2. **2.26** Fe $^{2+}$ : 4; Fe $^{3+}$ : 5; Cr $^{3+}$ : 3; Cr $^{4+}$ : 2; Cu $^+$ : 0; Cu $^{2+}$ : 1. **2.28** When palladium forms a cation, it loses two or four  $d$ -electrons, obtaining an incompletely filled  $d$  subshell.

**2.30** P( $s$ ) extensive three-dimensional structure; I<sub>2</sub>( $s$ ) molecular; Mg( $s$ ) extensive three-dimensional structure; Ne( $g$ ) atomic; C( $s$ ) extensive three-dimensional structure; S( $s$ ) molecular; Cs( $s$ ) extensive three-dimensional structure; O<sub>2</sub>( $g$ ) molecular.

**2.32** Zn does not have incompletely filled  $d$  subshells and does not readily give rise to cations that have incompletely filled subshells. Zn forms a cation by losing its outer  $s$  electrons.

**2.34** The electron configuration of nitrogen is  $[\text{He}]2s^2 2p^3$ . The half-filled  $2p$  subshell is extra stable, which is why the electron affinity for nitrogen is nearly zero. **2.36** (a) Cs. (b) Ba. (c) Sb. (d) Br. (e) Xe. **2.38** Mg $^{2+}$  < Na $^+$  < F $^-$  < O $^{2-}$  < N $^{3-}$ . **2.40** Te $^-$

**2.42** Cs < Na < Al < S < Cl. **2.44** Apart from the small irregularities, the ionization energies of elements in a period increase with increasing atomic number. We can explain this trend by referring to the increase in effective nuclear charge from left to right. A larger effective nuclear charge means a more tightly held outer electron, and hence a higher first ionization energy. Thus, in the third period, sodium has the lowest and neon has the highest first ionization energy. **2.46** To form the +2 ion of calcium, it is only necessary to remove two valence electrons. For potassium, however, the second electron must come from the atom's noble gas core, which accounts for the much higher second ionization energy. **2.48** (a)  $5.25 \times 10^3 \text{ kJ mol}^{-1}$ . (b)  $1.18 \times 10^4 \text{ kJ mol}^{-1}$ .

**2.50** (a) K < Na < Li. (b) I < Br < F < Cl. **2.52** Based on electron affinity values, we would not expect the alkali metals to form anions. However, in the early seventies a chemist named J.L. Dye at Michigan State University discovered that under very special circumstances alkali metals could be coaxed into accepting an electron to form negative ions! These ions are called alkalide ions. **2.54** All of the noble gases have completely filled shells, which leads to greater stability. Consequently, these elements are very stable chemically. **2.56** (a) He:  $1s^2$ . (b) N:  $1s^2 2s^2 2p^3$ . (c) Na:  $1s^2 2s^2 2p^6 3s^1$ . (d) As:  $[\text{Ar}]4s^2 3d^{10} 4p^3$ . (e) Cl:  $[\text{Ne}]3s^2 3p^5$ .

**2.58** 242 nm. **2.60** (a) Mg $^{2+}$  < Na $^+$  < F $^-$  < O $^{2-}$ . (b) O $^{2-}$  < F $^-$  < Na $^+$  < Mg $^{2+}$ . **2.62** Bromine, iodine, chlorine, fluorine.

**2.64** Fluorine. **2.66** Noble gases have filled shells or subshells. Therefore, they have little tendency to accept electrons (endothermic). **2.68** 574%.

**2.70** O $^+$  and N, Ar and S $^{2-}$ , Ne and N $^{3-}$ , Zn and As $^{3+}$ , Cs $^+$  and Xe. **2.72** LiH (lithium hydride), LiH + H<sub>2</sub>O → LiOH + H<sub>2</sub>; CH<sub>4</sub> (methane), CH<sub>4</sub> + H<sub>2</sub>O → no reaction at room temperature; NH<sub>3</sub> (ammonia), NH<sub>3</sub> + H<sub>2</sub>O → NH<sub>4</sub> $^+$  + OH $^-$ ; H<sub>2</sub>O (water), H<sub>2</sub>O + H<sub>2</sub>O → H<sub>3</sub>O $^+$  + OH $^-$ ; HF (hydrogen fluoride), HF + H<sub>2</sub>O → H<sub>3</sub>O $^+$  + F $^-$ . **2.74** The heat generated from the radioactive decay can break bonds; therefore, few radon compounds exist.

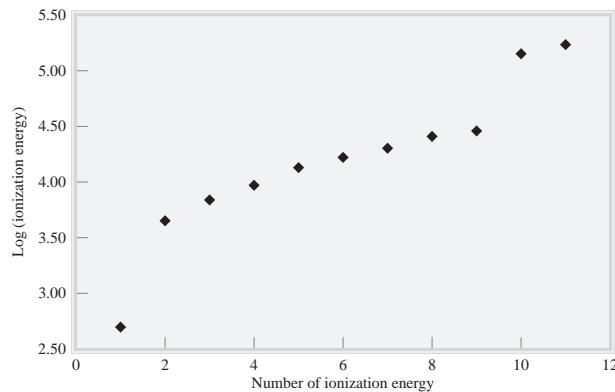
**2.76** (a) It was determined that the periodic table was based on atomic number, not atomic mass. (b) Argon: 39.95 u, Potassium: 39.10 u. **2.78** Both ionization energy and electron affinity are affected by atomic size—the smaller the atom, the greater the attraction between the electrons and the nucleus. If

it is difficult to remove an electron from an atom (that is, high ionization energy), then it follows that it would also be favorable to add an electron to the atom (large electron affinity). Noble gases are an exception to this generalization because they do not tend to gain electrons or lose electrons. **2.80** Helium should be named helon to match the other noble gases: neon, argon, xenon, krypton,

and radon. The ending, -ium, suggests that helium has properties similar to some metals (i.e., sodium, magnesium, barium, etc.).

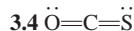
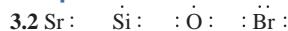
**2.82** In general, as the effective nuclear charge increases, the outer-shell electrons are held more strongly, and hence the atomic radius decreases. **2.84**  $7.28 \times 10^3 \text{ kJ mol}^{-1}$ .

**2.86** The plot is: (a)  $I_1$  corresponds to the electron in  $3s^1$ ;  $I_2$  corresponds to the first electron in  $2p^6$ ;  $I_3$  corresponds to the first electron in  $2p^5$ ;  $I_4$  corresponds to the first electron in  $2p^4$ ;  $I_5$  corresponds to the first electron in  $2p^3$ ;  $I_6$  corresponds to the first electron in  $2p^2$ ;  $I_7$  corresponds to the electron in  $2p^1$ ;  $I_8$  corresponds to the first electron in  $2s^2$ ;  $I_9$  corresponds to the electron in  $2s^1$ ;  $I_{10}$  corresponds to the first electron in  $1s^2$ ;  $I_{11}$  corresponds to the electron in  $1s^1$ . (b) It requires more energy to remove an electron from a closed shell. The breaks indicate electrons in different shells and subshells.



**2.88** 419 nm. **2.90** In He,  $r$  is greater than that in H. Also, the shielding in He makes  $Z_{\text{eff}}$  less than 2. Therefore,  $I_1(\text{He}) < 2I(\text{H})$ . In  $\text{He}^+$ , there is only one electron, so there is no shielding. The greater attraction between the nucleus and the lone electron reduces  $r$  to less than the  $r$  of hydrogen. Therefore,  $I_2(\text{He}) > 2I(\text{H})$ .

### Chapter 3



**3.6** The triple bond is composed of a sigma ( $\sigma$ ) and two pi ( $\pi$ ) bonds. The  $\sigma$  bond is a result of the head-on overlap of  $2p_x$  orbitals. The two pi bonds formed by the overlap of the  $2p_y$  and  $2p_z$  orbitals on the carbon atom with their counterparts on the nitrogen atom. The two lone pairs of electrons remain in the  $2s$  orbitals of each atom. **3.8** Because of the electron spin, electrons tend to be paired. Hence, a single bond is composed of a pair of electrons. If electrons did not have a magnetic moment, it is possible that a bond would consist of a single electron and atoms could form twice as many bonds and still obtain the noble gas configuration.

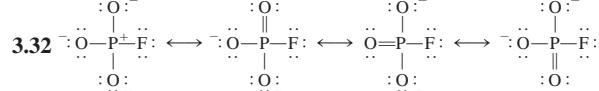
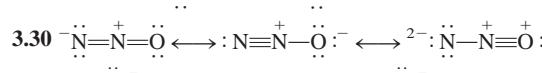
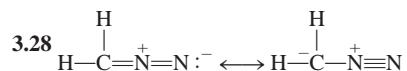
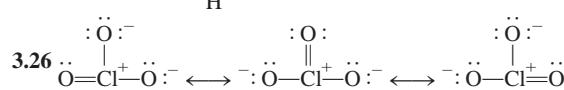
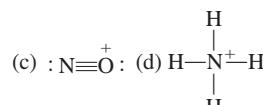
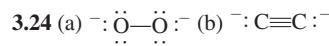
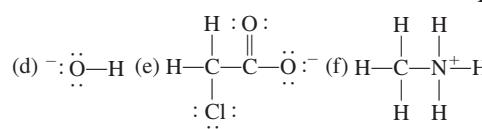
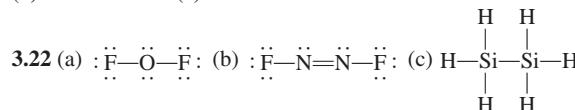
**3.10** C—H < F—H < B—H, Li—Cl < Na—Cl < K—F.

**3.12** Cl—Cl < Br—Cl < Si—C < Cs—F. **3.14** (a) covalent.

(b) polar covalent. (c) ionic. (d) polar covalent. **3.16** 358.0  $\text{kJ mol}^{-1}$ , which is close to the value of 363.6  $\text{kJ mol}^{-1}$  given in Table 3.3.

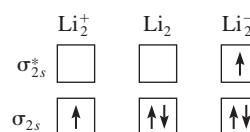
**3.18** (a) energy decrease. (b) energy is tripled. (c) energy is

quadrupled. (d) energy is doubled. **3.20** (a) 225  $\text{kJ mol}^{-1}$ . (b) 163  $\text{kJ mol}^{-1}$ . (c) 71  $\text{kJ mol}^{-1}$ .



**3.34** The  $\text{H}_2$  molecule has two electrons in the  $\sigma_{1s}$  orbital, giving it a bond order of one. The  $\text{H}_2^+$  ion has a single electron in the  $\sigma_{1s}$  orbital, giving it a bond order of one-half. The  $\text{H}_2^{2+}$  ion has no electrons. Hence, in terms of bond distances:  $\text{H}_2 < \text{H}_2^+ < \text{H}_2^{2+}$ .

**3.36**  $\text{Li}_2^- = \text{Li}_2^+ < \text{Li}_2$



**3.38** The bond order of the carbide ion

$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_x})^2(\pi_{2p_x}^*)^2$  is 3 and that of  $\text{C}_2$   $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_x})^2(\pi_{2p_x}^*)^2$  is only 2.

**3.40** In forming the  $\text{N}_2^+$  from  $\text{N}_2$ , an electron is removed from the sigma bonding molecular orbital. Consequently, the bond order decreases to 2.5 from 3.0. In forming the  $\text{O}_2^+$  ion from  $\text{O}_2$ , an electron is removed from the pi antibonding molecular orbital. Consequently, the bond order increases to 2.5 from 2.0.

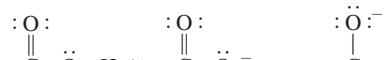
**3.42** The bond order of  $\text{F}_2^+$ :  $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_x})^2(\pi_{2p_y})^2(\pi_{2p_z})^2(\sigma_{2p_x}^*)^2$  is 1.5 compared to 1 for

$\text{F}_2$ :  $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_x})^2(\pi_{2p_y})^2(\pi_{2p_z})^2(\sigma_{2p_x}^*)^2$ . Therefore,  $\text{F}_2^+$  should have a shorter bond length.

**3.44** In general, the more *s*-character of the bonding electrons, the shorter the bond. The carbon atoms in  $\text{C}_2\text{H}_2$  are *sp* hybridized and hence the bonding electrons in  $\text{C}_2\text{H}_2$  has the most *s*-character and the C—H bonds in  $\text{C}_2\text{H}_2$  are the shortest. The carbon atoms in  $\text{C}_2\text{H}_6$  are *sp}^3 hybridized and hence the bonding electrons in  $\text{C}_2\text{H}_6$  have the least amount of *s*-character and the C—H bonds in  $\text{C}_2\text{H}_6$  are the longest.*



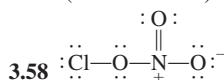
**3.48** (a)  $\text{AlCl}_4^-$ . (b)  $\text{AlF}_6^3-$ . (c)  $\text{AlCl}_3$ . **3.50** If the central atom were more electronegative, there would be a concentration of negative charges at the central atom. This would lead to instability.



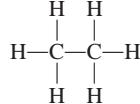
**3.52** (a)  $\ddot{\text{C}}-\text{H}$  paramagnetic (b)  $\ddot{\text{O}}-\text{H}$  paramagnetic

(c)  $\text{:C}=\text{C}:$  diamagnetic (d)  $\text{H}-\overset{+}{\text{N}}\equiv\ddot{\text{C}}:$  diamagnetic  
(e)  $\text{H}-\dot{\text{C}}=\ddot{\text{O}}$  paramagnetic

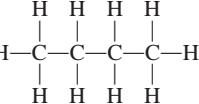
**3.56** It is much easier to dissociate  $\text{F}_2$  into two neutral F atoms ( $154.4 \text{ kJ mol}^{-1}$ ) than it is to dissociate it into a fluorine cation and anion ( $1506 \text{ kJ mol}^{-1}$ ).



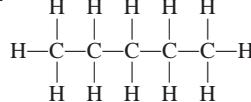
**3.60**  $\text{C}_2\text{H}_6$



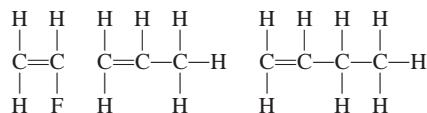
$\text{C}_4\text{H}_{10}$



$\text{C}_5\text{H}_{12}$



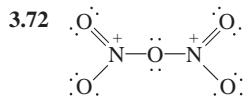
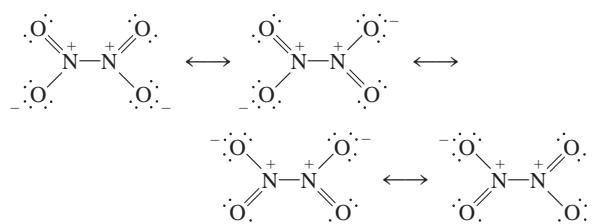
**3.62** The structures are (the nonbonding electron pairs on fluorine have been omitted for simplicity):



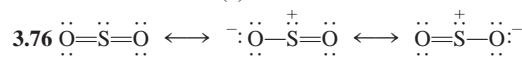
**3.64** (a)  $\ddot{\text{C}}\equiv\text{O}^{\cdot+}$  (b)  $\ddot{\text{N}}\equiv\text{O}^{\cdot+}$  (c)  $\ddot{\text{C}}\equiv\text{N}:$  (d)  $\ddot{\text{N}}\equiv\text{N}:$

**3.66** True. Each noble gas atom already has completely filled  $ns$  and  $np$  subshells. If a noble gas shares electrons with other atoms, it will have more than an octet. **3.68** The description involving a griffin and a unicorn is more appropriate. Mules and donkeys are real animals, whereas resonance structures do not exist.

**3.70** The unpaired electron on each N atom will be shared to form a covalent bond:



**3.74** (a)  $\ddot{\text{O}}-\text{H}$  (b) The O–H bond is quite strong ( $460 \text{ kJ mol}^{-1}$ ). To complete its octet, the OH radical has a strong tendency to form a bond with a H atom. (c) 260 nm.



The resonance structure with formal charges of zero (the one on the left) is the most plausible.

**3.78**  $2 \times 10^2 \text{ kJ mol}^{-1}$ . **3.80** (1) You could determine the magnetic properties of the solid. An  $\text{Mg}^+\text{O}^-$  solid would be paramagnetic while  $\text{Mg}^{2+}\text{O}^{2-}$  solid is diamagnetic. (2) You could determine the lattice energy of the solid.  $\text{Mg}^+\text{O}^-$  would have a lattice energy similar to  $\text{Na}^+\text{Cl}^-$ . This lattice energy is much lower than the lattice energy of  $\text{Mg}^{2+}\text{O}^{2-}$ .

**3.82** (a)  $[\text{Ne}_2](\sigma_{3s})^2(\sigma_{3s}^*)^2(\pi_{3p_x})^2(\pi_{3p_y})^2(\pi_{3p_z})^2(\sigma_{3p_z})^2$ . (b) 3.

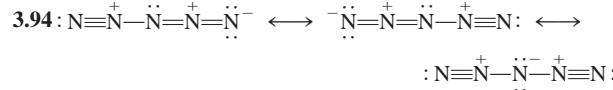
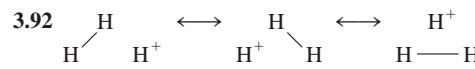
(c) diamagnetic. **3.84**  $\text{CN}^+$ . **3.86** The wavefunction determined from molecular orbital (MO) theory contains the same terms as the wavefunction determined from valence bond (VB) theory. The wavefunction determined from MO theory also contains terms corresponding to both electrons being on the same atom. If the likelihood of the two electrons being on the same atom is negligible (such as for a homonuclear diatomic molecule), then the wavefunctions from the two theories are identical.

**3.88**

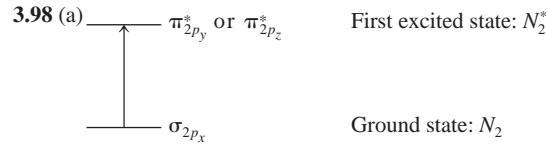
	$\text{BN}^-$	$\text{CO}^-$	$\text{OF}^+$
$\sigma_{2p_x}^*$	$\boxed{\phantom{x}}$	$\boxed{\phantom{x}}$	$\boxed{\phantom{x}}$
$\pi_{2p_y}^*, \pi_{2p_z}^*$	$\boxed{\phantom{x}} \boxed{\phantom{x}}$	$\boxed{\uparrow} \boxed{\phantom{x}}$	$\boxed{\uparrow} \boxed{\uparrow}$
$\sigma_{2p_x}$	$\boxed{\uparrow}$	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow\uparrow\downarrow}$
$\pi_{2p_y}, \pi_{2p_z}$	$\boxed{\downarrow\uparrow} \boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}$
$\sigma_{2s}^*$	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}$
$\sigma_{2s}$	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}$

Bond order: 2.5 2.5 2

**3.90** 163.8 pm.



**3.96** (a)  $\text{H}_2$ , (b)  $\text{N}_2$ , (c) O, (d) F.



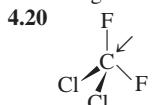
(b) The bond order for  $\text{N}_2$  is 3. The bond order for  $\text{N}_2^*$  is 2.  $\text{N}_2^*$  should have a longer bond length than  $\text{N}_2$ . (c) diamagnetic. (d)  $4.23 \times 10^{-19} \text{ J}$ .

## Chapter 4

**4.2** (a) trigonal planar. (b) linear. (c) tetrahedral. **4.4** (a) tetrahedral. (b) T-shaped. (c) bent. (d) trigonal planar. (e) trigonal pyramidal.

**4.6** (a) tetrahedral. (b) bent. (c) trigonal planar. (d) linear.

(e) square planar. (f) tetrahedral. (g) trigonal bipyramidal.  
 (h) trigonal pyramidal. (i) tetrahedral. **4.8** The carbon in the  $\text{CH}_3$  group has a tetrahedral geometry. The carbon bound to the two oxygen has a trigonal planar geometry. The oxygen bound to the hydrogen has a bent geometry. **4.10** (a)  $180^\circ$ . (b)  $120^\circ$ . (c)  $109.5^\circ$ . (d)  $180^\circ$ . (e)  $120^\circ$ . (f)  $109.5^\circ$ . (g)  $109.5^\circ$ . **4.12** (c). **4.14**  $\text{H}_2\text{Te} < \text{H}_2\text{Se} < \text{H}_2\text{S} < \text{H}_2\text{O}$ . **4.16** OCS,  $\text{OCl}_2$ ,  $\text{PCl}_3$ ,  $\text{SF}_4$ . **4.18** While  $\text{CS}_2$  is nonpolar, OCS is polar because oxygen is more electronegative than carbon.



**4.22**  $6.98 \times 10^{-20} \text{ C}$ . **4.24** (b) = (d) < (c) < (a). **4.26**  $sp^3$  for both.

**4.28** Before the reaction, boron is  $sp^2$  hybridized and nitrogen is  $sp^3$  hybridized. After the reaction, boron and nitrogen are both  $sp^3$ .

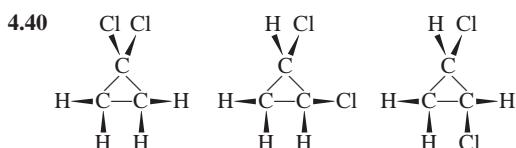
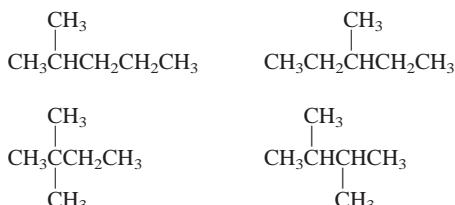
**4.30** (a)  $sp^3$ . (b)  $sp^3$ . (c)  $sp^2$ . **4.32** (a)  $sp$ . (b)  $sp$ . (c)  $sp$ .

**4.34** The two end carbons are  $sp^2$  hybridized. The central carbon is  $sp$  hybridized.



**4.36** (a) 4  $\sigma$  bonds and 0  $\pi$  bonds. (b) 5  $\sigma$  bonds and 1  $\pi$  bonds. (c) 10  $\sigma$  bonds and 3  $\pi$  bonds.

**4.38**  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$



The first and second, and first and third are structural isomers. The second and third are geometric isomers.

**4.42** The nitrate ion has a trigonal planar geometry. The  $2p_z$  orbitals on the oxygen and nitrogen atoms overlap producing a molecular orbital that is above and below all three N—O bonds.

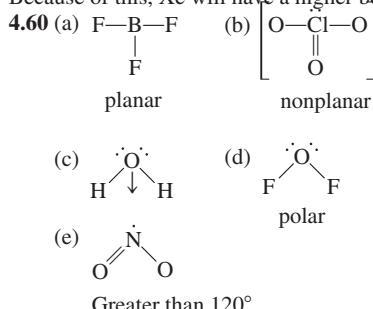
The molecular orbital can be written as a linear combination of the  $2p_z$  orbitals. From the symmetry of the molecule, we know that the coefficient for the oxygen atomic orbitals are the same.

**4.44**  $\text{NO}_2^-$  has a bent geometry and has two electrons in the lowest energy  $\pi$  orbital. This  $\pi$  orbital is formed from the  $2p_z$  orbitals of the nitrogen and oxygen atoms and is above and below both nitrogen-oxygen bonds.  $\text{NO}_2^+$  has a linear geometry and has four electrons in  $\pi$  orbitals. The lowest energy  $\pi$  orbital of  $\text{NO}_2^+$  is similar to that of  $\text{NO}_2^-$ , in that it could be composed of the  $2p_z$  orbitals of the nitrogen and oxygen atoms and is above and below both nitrogen-oxygen bonds. The lowest energy  $\pi$  orbital of  $\text{NO}_2^+$  could also be composed of the  $2p_y$  orbitals of the nitrogen and oxygen atoms. Hence,  $\text{NO}_2^+$  has two degenerate  $\pi$  orbitals. Notice that because of the symmetry of both  $\text{NO}_2^-$

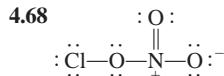
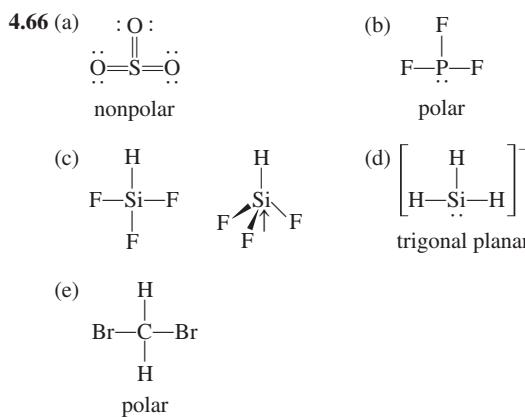
and  $\text{NO}_2^+$ , the coefficients for the oxygen atomic orbitals are the same.

$$\begin{aligned}\pi_z &= c_1\phi_{O,1p_z} + c_2\phi_{N,2p_z} + c_1\phi_{O,2p_z} \\ \pi_y &= c_1\phi_{O,1p_y} + c_2\phi_{N,2p_y} + c_1\phi_{O,2p_y}\end{aligned}$$

**4.46** The ion contains 24 valence electrons. Of these, six are involved in three sigma bonds between the nitrogen and oxygen atoms. The hybridization of the nitrogen atom is  $sp^2$ . There are 16 nonbonding electrons on the oxygen atoms. The remaining two electrons are in a delocalized  $\pi$  molecular orbital which results from the overlap of the  $p_z$  orbital of nitrogen and the  $p_z$  orbitals of the three oxygen atoms. **4.48**  $\text{ICl}$  has a dipole moment and  $\text{Br}_2$  does not. The dipole moment increases the intermolecular attractions between  $\text{ICl}$  molecules and causes that substance to have a higher melting point than bromine. **4.50**  $\text{CO}_2 < \text{CH}_3\text{Br} < \text{CH}_3\text{OH} < \text{RbF}$ .  $\text{CO}_2$  is a nonpolar molecular compound.  $\text{CH}_3\text{Br}$  is a polar molecule.  $\text{CH}_3\text{OH}$  is polar and can form hydrogen bonds.  $\text{RbF}$  is an ionic compound. **4.52** (a) Ne. (b)  $\text{CO}_2$ . (c)  $\text{CH}_4$ . (d)  $\text{F}_2$ . (e)  $\text{PH}_3$ . **4.54**  $\text{LiF}$ , ionic bonding and dispersion forces;  $\text{BeF}_2$ , ionic bonding and dispersion forces;  $\text{BF}_3$ , dispersion forces;  $\text{CF}_4$ , dispersion forces;  $\text{NF}_3$ , dipole-dipole interaction and dispersion forces;  $\text{OF}_2$ , dipole-dipole interaction and dispersion forces;  $\text{F}_2$ , dispersion forces. **4.56**  $-3.3 \times 10^{-21} \text{ J}$ . **4.58** The minimum of the potential energy curve for Xe is lower (more negative) than for Ar, indicating that the Xe–Xe interatomic interactions are stronger than the Ar–Ar interactions. Because of this, Xe will have a higher boiling point than Ar.



**4.62**  $sp^3$ d. **4.64** yes.

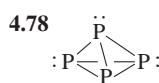
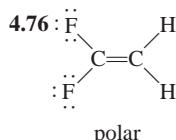


The nitrogen is  $sp^2$  and has a trigonal planar geometry resulting in O—N—O bond angles of  $120^\circ$ . The oxygen is  $sp^3$  and has a bent geometry resulting in a Cl—O—N bond angle of less than  $109.5^\circ$ .

**4.70**  $\text{XeF}_3^+$ : T-shaped;  $\text{XeF}_5^+$ : square pyramidal;  $\text{SbF}_6^-$ : octahedral.

**4.72** Only  $\text{ICl}_2^-$  and  $\text{CdBr}_2$  will be linear. The rest are bent.

**4.74** The azide ion ( $\text{N}_3^-$ ), has a linear geometry and has four electrons in  $\sigma$  orbitals and four electrons in  $\pi$  orbitals. The two  $\sigma$  orbitals connect adjacent nitrogen. The two  $\pi$  orbitals are degenerate and both lie above and below both nitrogen-nitrogen bonds. One of the  $\pi$  orbitals is composed of the  $2p_z$  orbitals of the three nitrogen atoms. The other  $\pi$  orbital is composed of the  $2p_y$  orbitals of the three nitrogen atoms.



The four P atoms occupy the corners of a tetrahedron. Each phosphorus atom is  $sp^3$  hybridized. The  $\text{P}_2$  molecule has a triple bond, which is composed of one sigma bond and two pi bonds. The pi bonds are formed by sideways overlap of  $3p$  orbitals. Because the atomic radius of P is larger than that of N, the overlap is not as extensive as that in the  $\text{N}_2$  molecule. Consequently, the  $\text{P}_2$  molecule is much less stable than  $\text{N}_2$  and also less stable than  $\text{P}_4$ , which contains only sigma bonds. **4.80** (a)  $-3.35 \times 10^{-2} \text{ J}$ ; (b)  $-4.60 \times 10^{-3} \text{ J}$ . **4.82** The carbons are in  $sp^2$  hybridization states. The nitrogens are in the  $sp^3$  hybridization state, except for the ring nitrogen double-bonded to a carbon that is  $sp^2$  hybridized. The oxygen atom is  $sp^2$  hybridized. **4.84** Butane should have the higher boiling point because the butane molecule has a larger surface area resulting in more intermolecular interactions. **4.86**  $\text{SiO}_2$  has an extensive three-dimensional structure.  $\text{CO}_2$  exists as discrete molecules. It will take much more energy to break the strong network covalent bonds of  $\text{SiO}_2$ ; therefore,  $\text{SiO}_2$  has a much higher boiling point than  $\text{CO}_2$ . **4.88** (a) Each nitrogen is  $sp^2$  hybridized. (b) The structure on the right has a dipole moment. **4.90** Each of the oxygen atoms in  $\text{O}_2$  is  $sp^2$  hybridized. Two of the hybrid orbitals on each oxygen contain lone pairs of electrons. The remaining hybrid orbital on each oxygen overlaps with each other forming a  $\sigma$  bond. The two unhybridized  $2p$  orbitals on each oxygen overlap forming a  $\pi$  bond. If we think about the bonding of  $\text{O}_2$  in terms of unhybridized orbitals, we can imagine that the  $\sigma$  and  $\pi$  bonds are formed by the overlap of  $2p$  orbitals and that one lone pair on each atom remains in a  $2s$  orbital and the other in a  $2p$  orbital. **4.92** 180 $\text{\AA}$ .

**4.94**

The four carbons marked with an asterisk are  $sp^2$  hybridized. The remaining carbons are  $sp^3$  hybridized.

## Chapter 5

**5.2** 1.2 bar. **5.4** Two phase changes occur in this process. First, the liquid is turned to solid (freezing), then the solid ice is turned to gas (sublimation). **5.6** Initially, the ice melts because of the increase in pressure. As the wire sinks into the ice, the water above the wire refreezes. Eventually the wire actually moves completely through the ice block without cutting it in half. **5.8** Region labels: The region containing point A is the solid region. The region containing point B is the liquid region. The region containing point C is the gas region. (a) Raising the temperature at constant pressure beginning at A implies starting with solid ice and warming until melting occurs. If the warming continued, the liquid water would eventually boil and change to steam. Further warming would increase the temperature of the steam. (b) At point C water is in the gas phase. Cooling without changing the pressure would eventually result in the formation of solid ice. Liquid water would never form. (c) At B the water is in the liquid phase. Lowering the pressure without changing the temperature would eventually result in boiling and conversion to water in the gas phase. **5.10** 2, a plane.

**5.12** 45.1 torr. **5.14** 44.1 L. **5.16** 6.3 bar. **5.18** 472°C. **5.20** 1.30  $\times 10^3$  mL. **5.22**  $8.4 \times 10^2$  L. **5.24** 9.0 L. **5.26** 71 mL. **5.28** 6.2  $\times 10^{-3}$  bar. **5.30** 35.1 g mol $^{-1}$ . **5.32**  $\text{N}_2$ :  $1.9 \times 10^{22}$ ;  $\text{O}_2$ :  $5.1 \times 10^{21}$ ; Ar:  $2.4 \times 10^{20}$ . **5.34** 2.98 g L $^{-1}$ . **5.36**  $\text{SF}_4$ . **5.38** 370 L. **5.40** 87.7%.

**5.42**  $\text{M}_2\text{O}_3$  and  $\text{M}_2(\text{SO}_4)_3$ . **5.44** 94.7%, assuming that none of the impurities reacted with HCl to produce  $\text{CO}_2$  gas.

**5.46**  $\text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \longrightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l)$ ;  $1.71 \times 10^3$  L. **5.48** Temperature is a microscopic concept, in that it is a measure of motion at the atomic level. **5.50**  $\text{N}_2$ : 472 m s $^{-1}$ ;  $\text{O}_2$ : 441 m s $^{-1}$ ;  $\text{O}_3$ : 360 m s $^{-1}$ . **5.52**  $5.3 \times 10^{-2}$  J;  $5.3 \times 10^{-5}$  bar. **5.54** –235.9°C. **5.56**  $6.07 \times 10^{-19}$  J;  $3.65 \times 10^5$  J. **5.58** 1.0043.

**5.60** van der Waals: 18.2 bar; ideal: 18.7 bar. **5.62**  $\text{SO}_2$  should behave less ideally because it has stronger intermolecular forces (it is polar) and it is larger. **5.64** virial: 1.04 L; ideal: 1.11 L.

**5.66** Neon has the smallest van der Waals constants of the three gases and hence should behave the most ideally. **5.68**  $\text{C}_6\text{H}_6$ .

**5.70** (a) 0.89 bar. (b) 1.5 L. **5.72** 349 torr. **5.74** 4.8%. **5.76** 451 mL.

**5.78** The partial pressure of carbon dioxide is higher in the winter because carbon dioxide is utilized less by photosynthesis in plants.

**5.80**  $1.28 \times 10^{22}$ ;  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ , and  $\text{H}_2\text{O}$ .

$$\text{5.82 } X_{\text{CH}_4} = \frac{232}{294} = 0.789 \quad X_{\text{C}_2\text{H}_6} = \frac{62}{294} = 0.211.$$

**5.84** 50.1%. **5.86**  $5.25 \times 10^{18}$  kg. **5.88** 0.0701 M. **5.90** He: 0.16 bar; Ne: 2.0 bar. **5.92** When the water enters the flask from the dropper, some hydrogen chloride dissolves, creating a partial vacuum. Pressure from the atmosphere forces more water up the vertical tube. **5.94** 7. **5.96** (a) 61.2 m s $^{-1}$ . (b)  $4.58 \times 10^{-4}$  s.

(c) The Bi atoms traveled at 328 m s $^{-1}$ , compared to the average root-mean-square speed of 366 m s $^{-1}$ . These are comparable. It is not surprising that they are a little different. **5.98** The fruit ripens more rapidly because the quantity (partial pressure) of ethylene gas inside the bag increases. **5.100** As the pen is used, the amount of ink decreases, increasing the volume inside the pen. As the volume increases, the pressure inside the pen decreases. The hole is needed to equalize the pressure as the volume inside the pen increases. **5.102**  $4.2 \times 10^5 \text{ m}^2 \text{ s}^{-2}$ . **5.104** 86.0 g mol $^{-1}$ .

**5.106** (a)  $\text{CaO}(s) + \text{CO}_2(g) \longrightarrow \text{CaCO}_3(s)$ ;

$\text{BaO}(s) + \text{CO}_2(g) \longrightarrow \text{BaCO}_3(s)$ . (b) CaO: 10.5%, BaO: 89.5%.

**5.108** (a) 0.112 mol CO min $^{-1}$ ; 20 min. **5.110** (a) –44°C;

(b) 72.4%. **5.112**  $1.7 \times 10^{12}$ . **5.114** The nitrogen oxide is most likely  $\text{NO}_2$ , although  $\text{N}_2\text{O}$  cannot be completely ruled out.

**5.116**  $7.04 \times 10^{-3} \text{ m s}^{-1}$ ,  $3.52 \times 10^{-30} \text{ J}$ .

$$\text{5.118 (a)} \frac{PV}{nRT} = \frac{1}{1 - \frac{b}{v}} - \frac{a}{VRT}; B = b - \frac{a}{RT}; C = b^2, D = b^3.$$

$$\text{(b)} T = \frac{a}{bR}. \text{(c)} 1090^\circ\text{C}.$$

**5.120** The ice condenses the water vapor inside. Since the water is still hot, it will begin to boil at reduced pressure. **5.122** 1.4 g.

**5.124**  $P_{\text{CO}_2} = 8.7 \times 10^6 \text{ Pa}$ ;  $P_{\text{N}_2} = 3.2 \times 10^5 \text{ Pa}$ ;  $P_{\text{SO}_2} = 1.4 \times 10^3 \text{ Pa}$ . **5.126 (a)** (i) Since the two He samples are at the same temperature, their rms speeds and the average kinetic energies are the same; (ii) The He atoms in  $V_1$  (smaller volume) collide with the walls more frequently. Since the average kinetic energies are the same, the force exerted in the collisions is the same in both flasks. (b) (i) The rms speed is greater at the higher temperature,  $T_2$ ; (ii) The He atoms at the higher temperature,  $T_2$ , collide with the walls with greater frequency and with greater force. (c) (i) False; (ii) True; (iii) True. **5.128 (a)** The plots dip due to intermolecular attractions between gas particles. Consider the approach of a particular molecule toward the wall of a container. The intermolecular attractions exerted by its neighbors tend to soften the impact made by this molecule against the wall. The overall effect is a lower gas pressure than we would expect for an ideal gas. Thus,  $PV/RT$  decreases. The plots rise because at higher pressures (smaller volumes), the molecules are close together and repulsive forces among them become dominant. Repulsive forces increase the force of impact of the gas molecules with the walls of the container. The overall effect is a greater gas pressure than we would expect for an ideal gas. Hence,  $PV/RT > 1$  and the curves rise above the horizontal line. (b) For 1 mole of an ideal gas,  $PV/RT = 1$ , no matter what the pressure of the gas. At very low pressures, all gases behave ideally; therefore,  $PV/RT$  converges to 1 as the pressure approaches zero. As the pressure of a gas approaches zero, a gas behaves more and more like an ideal gas. (c) The intercept on the ideal gas line means that  $PV/RT = 1$ .

However, this does **not** mean that the gas behaves ideally. It just means that at this particular pressure, molecular attraction is equal to molecular repulsion so the net interaction is zero. **5.130** 10.1 bar. **5.132 (a)** Two triple points: Diamond/graphite/liquid and graphite/liquid/vapor. (b) Diamond. (c) Apply high pressure at high temperature. **5.134** CO. **5.136** 1200 K.

## Chapter 6

**6.2** Past the critical point (higher temperature and higher pressure) the liquid can no longer exist, so gases can no longer be liquified. **6.4** Due to the water's relatively strong intermolecular forces (hydrogen bonding) water molecules at the surface are attracted to other water molecules resulting in an unusually strong surface tension. **6.6** As temperature increases, viscosity decreases. The higher the temperature, the faster the motion at the atomic-level and hence molecules can more easily move relative to one another leading to a lower viscosity. **6.8** Because a Kr atom is larger than an Ar atom, the maximum in the radial distribution function for Kr will at a larger value of  $r$  than for that of Ar. Because krypton has stronger intermolecular forces, liquid krypton should have a more defined structure than liquid argon, resulting in fluctuations in krypton's radial distribution at larger  $r$ . **6.10 (a)** Six. **(b)** Eight. **(c)** Twelve. **6.12** 2 atoms/unit cell. **6.14** Two. **6.16** 8 atoms/unit cell. **6.18** XY<sub>3</sub>. **6.20**  $6.020 \times 10^{23}$ . **6.22** Molecular solid. **6.24** Molecular solids: Se<sub>8</sub>, HBr, CO<sub>2</sub>, P<sub>4</sub>O<sub>6</sub>, and SiH<sub>4</sub>. Covalent

solids: Si, C. **6.26** Na, Mg, and Al are metals. Si is a covalent solid. P, S, Cl, and Ar are molecular solids. The metals should have the highest boiling and melting points. The molecular solids should have the lowest boiling and melting points. **6.28** Each C atom in diamond is covalently bonded to four other C atoms.

Graphite has delocalized electrons in two dimensions. **6.30** The ability of a metal to conduct electricity *decreases* with increasing temperature, because the enhanced vibration of atoms at higher temperatures tends to disrupt the flow of electrons. **6.32** Doping silicon with Ga and Al would form p-type semiconductors, while doping with Sb and As would form n-type. **6.34** Metals are shiny because they reflect light. Conduction electrons are able to absorb and then re-emit light. **6.36** Covalent crystal. **6.38** Oil is made up of nonpolar molecules and therefore does not mix with water. To minimize contact, the oil drop assumes a spherical shape, which has a small surface area. **6.40 (a)** Si and SiO<sub>2</sub> for covalent solids. **(b)**  $5.00 \times 10^9$ , yes. **6.42** That metals can conduct electricity indicates that some of their electrons are delocalized. **6.44** 172 pm. **6.46** 458 pm. **6.48**  $1.69 \text{ g cm}^{-3}$ . **6.50** gas:  $34 \text{ \AA}$ , liquid:  $0.15 \text{ \AA}$ .

Molecules in a liquid are much closer than molecules in a gas. **6.52** The gas phase LiCl molecules share electrons enabling them to be closer. **6.54** Na (186 pm and  $0.965 \text{ g cm}^{-3}$ ). **6.56**  $6.020 \times 10^{23}$ . **6.58** The critical point occurs because at high enough temperature and pressure, gases and liquids cannot be distinguished. A solid and a liquid never become so similar that they cannot be differentiated.

## Chapter 7

**7.2 (a)** 0 J. **(b)** 9.4 J. **(c)** 18 J. **7.4**  $-1.04 \times 10^3 \text{ J}$ .

$$\text{7.6 van der Waals: } P = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2$$

$$w = \int_{V_1}^{V_2} Pdv = -nRT \int_{V_1}^{V_2} \frac{dV}{V - nb} + an^2 \int_{V_1}^{V_2} \frac{dV}{V^2}$$

$$w = nRT \ln\left(\frac{V_1 - nb}{V_2 - nb}\right) + an^2 \left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

**7.8** As energy consumers, we are interested in the availability of *usable* energy. **7.10**  $-1.57 \times 10^4 \text{ kJ}$ . **7.12** No work was done. The pressure is the same before and after the reaction.  $\Delta U = -553.8 \text{ kJ}$ . **7.14**  $-3.31 \times 10^3 \text{ J} = -3.31 \text{ kJ}$ . **7.16**  $31^\circ\text{C}$ .

**7.18**  $26.3^\circ\text{C}$ . **7.20** Because the humidity is very low in deserts, there is little water vapor in the air to trap and hold the heat radiated back from the ground during the day. Once the sun goes down, the temperature drops dramatically.  $40^\circ\text{F}$  temperature drops between day and night are common in desert climates. Coastal regions have much higher humidity levels compared to deserts. The water vapor in the air retains heat, which keeps the temperature at a more constant level during the night. In addition, sand and rocks in the desert have small specific heats compared with water in the ocean. The water absorbs much more heat during the day compared to sand and rocks, which keep the temperature warmer at night.

**7.22 (a)**  $\Delta H_{\text{f}}^\circ[\text{Br}_2(l)] = 0$ ;  $\Delta H_{\text{f}}^\circ[\text{Br}_2(g)] > 0$ . **(b)**  $\Delta H_{\text{f}}^\circ[\text{I}_2(s)] = 0$ ;  $\Delta H_{\text{f}}^\circ[\text{I}_2(g)] > 0$ . **7.24** Measure  $\Delta H^\circ$  for the formation of Ag<sub>2</sub>O from Ag and O<sub>2</sub> and of CaCl<sub>2</sub> from Ca and Cl<sub>2</sub>.

**7.26 (a)**  $-167.2 \text{ kJ mol}^{-1}$ . **(b)**  $-56.2 \text{ kJ mol}^{-1}$ .

**7.28 (a)**  $-1411 \text{ kJ mol}^{-1}$ . **(b)**  $-1124 \text{ kJ mol}^{-1}$ .

**(c)**  $-2044.0 \text{ kJ mol}^{-1}$ . **7.30**  $218.2 \text{ kJ mol}^{-1}$ . **7.32**  $0.30 \text{ kJ mol}^{-1}$ .

**7.34**  $-238.7 \text{ kJ mol}^{-1}$ . **7.36** The bond enthalpy is a measure of the strength of the chemical bond. It has to be defined in the gas phase where intermolecular forces are negligible. Otherwise, the

difference in intermolecular forces of the molecule versus the fragments would affect the size of the bond enthalpy.

**7.38** (a)  $-234 \text{ kJ mol}^{-1}$ . **7.40**  $\Delta H^\circ_{\text{c}}(\text{C}_n\text{H}_{2n+2}) = [(n-1) 347 \text{ kJ mol}^{-1} + (2n+2) 414 \text{ kJ mol}^{-1} + \frac{1}{2}(n+1) 498.7 \text{ kJ mol}^{-1}] - [2n(799 \text{ kJ mol}^{-1}) + (2n+2) 460 \text{ kJ mol}^{-1}]$ . **7.42**  $2.68 \times 10^3 \text{ kJ}$ . **7.44**  $50.02 \text{ kJ mol}^{-1}$ . **7.46**  $-1.12 \text{ kJ mol}^{-1}$ . **7.48**  $5.62 \text{ kJ mol}^{-1}$ .

**7.50**  $7.60\%$ . **7.52**  $\Delta H^\circ_{\text{f}}(\text{AgNO}_3) = -44.35 \text{ kJ mol}^{-1}$ .

**7.54**  $-173.7 \text{ kJ mol}^{-1}$ . **7.56** (a) Although we cannot measure  $\Delta H^\circ_{\text{rxn}}$  for this reaction, the reverse process is the combustion of glucose. We could easily measure  $\Delta H^\circ_{\text{rxn}}$  for this combustion in a bomb calorimeter. (b)  $1.1 \times 10^{19} \text{ kJ}$ . **7.58**  $-17 \text{ J}$ . **7.60**  $0.492 \text{ J g}^{-1}\text{C}^{-1}$ .

**7.62** The first reaction, which is exothermic, can be used to promote the second reaction, which is endothermic.

**7.64**  $2.92 \times 10^3 \text{ L}$ . **7.66**  $5.60 \text{ kJ mol}^{-1}$ . **7.68** (a) The heat capacity of the food is greater than the heat capacity of air; hence, the cold in the freezer will be retained longer. (b) Tea or coffee has a greater amount of water, which has a higher specific heat than noodles.

**7.70**  $1.64 \times 10^3 \text{ g H}_2\text{O}$ . **7.72**  $1.07 \text{ kJ}$ . **7.74** (a)  $758^\circ\text{C}$ . (b)  $-986.6 \text{ kJ mol}^{-1}$ . **7.76**  $25 \text{ kg}$ . **7.78**  $-360 \text{ kJ mol}^{-1}$  Zn.

**7.80** Carbon dioxide is linear and hence has only two modes of rotation and a lower heat capacity than ammonia. So, the container with the carbon dioxide will have the higher temperature.

**7.82** (a)  $-65.2 \text{ kJ mol}^{-1}$ . (b)  $-9.0 \text{ kJ mol}^{-1}$ . **7.84**  $5.8 \times 10^2 \text{ m}$ .

**7.86**  $6.9 \text{ g}$  assuming that all of the kinetic energy of the probe was converted into heat, that the liquid methane was at its boiling point ( $-164^\circ\text{C}$ ), and that the enthalpy of vaporization is not affected by the different pressure on the surface of Titan.

**7.88**  $-277.0 \text{ kJ mol}^{-1}$ . **7.90**  $104 \text{ g}$ . **7.92** (a)  $0^\circ\text{C}$ . (b)  $100 \text{ g}$  of Al,  $41.7 \text{ g}$  of ice,  $58.3 \text{ g}$  of water. **7.94** Energy must be supplied to break a chemical bond. By the same token, energy is released when a bond is formed. **7.96**  $\Delta E = -5153 \text{ kJ mol}^{-1}$ ;

$\Delta H = -5158 \text{ kJ mol}^{-1}$ . **7.98** The heat capacity of the reactants should be larger than that of the products because the reactants are composed of more gas particles. Hence, the enthalpy change for the reaction should decrease with increasing temperature.

**7.100**

	$q$	$w$	$\Delta U$	$\Delta H$
(a)	—	—	—	—
(b)	—	+	0	0
(c)	—	—	—	—
(d)	+	—	+	+
(e)	+	0	+	+
(f)	+	+	+	+

**7.102** (a)  $48^\circ\text{C}$ . (b)  $4.1 \times 10^3 \text{ g H}_2\text{O}$ . **7.104**  $-1 \text{ L}\cdot\text{bar}$ ;  $-100 \text{ J}$ .

**7.106**  $43 \text{ kJ mol}^{-1}$ .

## Chapter 8

**8.4** Least probable is all balls in one box. **8.6** (a) no. (b) yes.

**8.8**  $112 \text{ J mol K}^{-1}$ . **8.10**  $5.8 \text{ J K}^{-1}$ . **8.12**  $9.1 \text{ J K}^{-1}$ .

**8.14** (a)  $\Delta S_{\text{sys}} = 5.8 \text{ J K}^{-1}$ ;  $\Delta S_{\text{surr}} = -5.8 \text{ J K}^{-1}$ ;  $\Delta S_{\text{univ}} = 0 \text{ J K}^{-1}$ . (b)  $\Delta S_{\text{sys}} = 5.8 \text{ J K}^{-1}$ ;  $\Delta S_{\text{surr}} = -4.1 \text{ J K}^{-1}$ ;  $\Delta S_{\text{univ}} = 1.7 \text{ J K}^{-1}$ .

**8.16**  $92.8 \text{ J mol}^{-1}\text{K}^{-1}$ . **8.18** (a)  $9.13 \text{ J mol}^{-1}\text{K}^{-1}$ . (b)  $11.5 \text{ J mol}^{-1}\text{K}^{-1}$ . (c)  $13.4 \text{ J mol}^{-1}\text{K}^{-1}$ . **8.22** (a)  $48.7 \text{ J mol}^{-1}\text{K}^{-1}$ . (b)  $-12.0 \text{ J mol}^{-1}\text{K}^{-1}$ . (c)  $-242.8 \text{ J mol}^{-1}\text{K}^{-1}$ . **8.24** (a) negative.

(b) negative. (c) positive. (d) ~zero (small). **8.26**  $\Delta S_{\text{sys}} = 25 \text{ J K}^{-1}\text{mol}^{-1}$ ;  $\Delta S_{\text{surr}} = -613 \text{ J K}^{-1}\text{mol}^{-1}$ ;  $\Delta S_{\text{univ}} = -588 \text{ J K}^{-1}\text{mol}^{-1}$ .

If this reaction had a positive  $\Delta S_{\text{univ}}$ , it could consume almost all of the oxygen gas in the atmosphere. **8.28**  $352^\circ\text{C}$ .

**8.30** (a)  $175.2 \text{ kJ mol}^{-1}$ . (b)  $8.5 \text{ kJ mol}^{-1}$ . (c)  $-2471.6 \text{ kJ mol}^{-1}$ .

**8.32** (b) is spontaneous,  $350 \text{ K}$ . **8.34**  $979 \text{ K}$ . **8.36** In all cases,

$\Delta H > 0$  and  $\Delta S > 0$ .  $\Delta G < 0$  for (a),  $= 0$  for (b), and  $> 0$  for (c).

**8.38** (a)  $57.5 \text{ kJ mol}^{-1}$ . (b)  $57.5 \text{ kJ mol}^{-1}$ . **8.40** (a)  $-11.5 \text{ J K}^{-1} - 3.44 \text{ kJ}$ . (b)  $58.4 \text{ J K}^{-1}$ ;  $-17.4 \text{ kJ}$ . **8.42** (a)  $0.4 \text{ kJ}$ . (b)  $3.4 \text{ kJ}$ .

**8.44**  $79.1 \text{ kJ}$ . **8.46** This only tells us whether it is possible for the reaction to occur under these conditions. It tells us nothing about how fast the reaction will occur. **8.48**  $0.055 \text{ J K}$ . **8.52**  $47^\circ\text{C}$ .

**8.54** (d). **8.56**  $21.1 \text{ J K}^{-1}$ . **8.58** See p. 456. **8.62**  $7420 \text{ m}$ .

$$\text{8.64 (a)} \Delta S^\circ = \int_{T_1}^{T_2} \frac{C}{T} dT = \int_{T_1}^{T_2} \frac{\alpha T^3}{T} dT = \alpha \int_{T_1}^{T_2} T^2 dT = \alpha \frac{T^3}{3} \Big|_{T_1}^{T_2}$$

(b)  $5.88 \times 10^{-5} \text{ J mol}^{-1}\text{K}^{-4}$ . (c)  $2.0 \times 10^{-5} \text{ J K}^{-1}$ ;  $2.4 \times 10^{-3} \text{ J K}^{-1}$ ;  $3.39 \times 10^{-2} \text{ J K}^{-1}$ .

## Chapter 9

**9.2** (a)  $59.8 \text{ kJ mol}^{-1}$ . (b)  $356^\circ\text{C}$ , which agrees with the experimental value of  $357^\circ\text{C}$ . **9.4** X  $<$  Y. **9.6** no. **9.8** Cyclohexane cannot form hydrogen bonds. **9.10** The longer chains become more nonpolar. **9.12**  $45.9 \text{ g}$ . **9.14** Some helium gas will dissolve into the solution. This will not change the concentration of air initially dissolved in the solution. **9.16**  $1.0 \times 10^{-5}$ . **9.18** Ethanol:  $30.0 \text{ mmHg}$ ; 1-propanol:  $26.3 \text{ mmHg}$ . **9.20** A =  $1.9 \times 10^2 \text{ mmHg}$ . B =  $4.0 \times 10^2 \text{ mmHg}$ . **9.22** Ethanol water mixture is a nonideal solution that exhibits positive deviations from Raoult's law. Therefore, this system has a minimum boiling point and will form a low boiling azeotrope that cannot be separated by fractional distillation. **9.24**  $1.3 \times 10^3 \text{ g}$ . **9.26**  $128 \text{ g}$ . **9.28**  $0.59 \text{ m}$ .

**9.30**  $120 \text{ g mol}^{-1}$ . C<sub>4</sub>H<sub>8</sub>O<sub>4</sub>. **9.32**  $-8.6^\circ\text{C}$ . **9.34**  $4.3 \times 10^2 \text{ g mol}^{-1}$ . C<sub>24</sub>H<sub>20</sub>P<sub>4</sub>. **9.36**  $1.75 \times 10^4 \text{ g mol}^{-1}$ . **9.38**  $342 \text{ g mol}^{-1}$ . **9.40** They also have the same boiling point, vapor pressure, and osmotic pressure. **9.42**  $0.50 \text{ m glucose} > 0.50 \text{ m acetic acid} > 0.50 \text{ m HCl}$ . **9.44**  $0.9420 \text{ m}$ . **9.46**  $7.2 \text{ bar}$ . **9.48** Steam; B: Water vapor. **9.52**  $2.05 \times 10^{-5} \text{ mmHg}$ ;  $8.90 \times 10^{-5} \text{ °C}$ ;  $2.5 \times 10^{-5} \text{ °C}$ ;  $1.17 \times 10^{-3} \text{ atm} = 0.889 \text{ mmHg}$ . **9.54** Water migrates through the semipermeable cell walls of the cucumber into the concentrated salt solution. **9.56** 3.5. **9.58** X is pure water; Y is NaCl solution; and Z is urea solution. **9.60** The increase in pressure pushes the elastic membrane to the right, causing the drug to exit through the small holes at a constant rate. **9.62** 33 bar.

**9.64**  $\mathcal{M}_z(B) = 248 \text{ g mol}^{-1}$ ;  $\mathcal{M}_z(A) = 124 \text{ g mol}^{-1} = \mathcal{M}_z(B)/2$ ; A dimerization process. **9.66** (a) Boiling under reduced pressure.

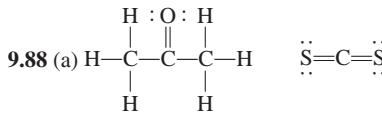
(b) CO<sub>2</sub> boils off, expands and cools, condensing water vapor to form fog. **9.68**  $33.3 \text{ mL}$ ;  $66.7 \text{ mL}$ . **9.70** To protect the red blood cells and other cells from shrinking (in a hypertonic solution) or expanding (in a hypotonic solution). **9.72** 14.3%.

**9.74** (a) Decreases with lattice energy. (b) Increases with polarity of solvent. (c) Increase with enthalpy of hydration. **9.76** 0.815.

**9.78** NH<sub>3</sub> can form hydrogen bonds with water. **9.80** 3%.

**9.82**  $1.2 \times 10^2 \text{ g mol}^{-1}$ . It forms a dimer in benzene.

**9.86**  $-0.737^\circ\text{C}$ .



The vapor pressure of the solution is greater than the sum of the vapor pressures as predicted by Raoult's law for the same concentration. (b) 410 mmHg. (c) Positive. **9.90** 168 m.

**9.92** 0.853, 64.5 torr. Ideal solution and ideal gas were assumed.

**9.94** 3.1 mol. **9.96** 600 K. **9.98** The values increase with increasing atomic mass, which is consistent with the Henry's law constants

increasing with increasing intermolecular attraction between the gas particles and the water molecules. **9.100** (a) 43.3 kJ mol<sup>-1</sup>.

## Chapter 10

- 10.2** (a) A + C  $\rightleftharpoons$  AC. (b) A + D  $\rightleftharpoons$  AD. **10.4**  $K_c = 1.08 \times 10^7$ ,  $K_p = 1.33 \times 10^5$ . **10.6**  $3.5 \times 10^{-7}$ . **10.8** (a) 0.082. (b) 0.29. **10.10**  $K_p = 0.106$ ;  $K_c = 2.05 \times 10^{-3}$ . **10.12**  $7.32 \times 10^{-3}$ . **10.14** 3.3. **10.16**  $3.53 \times 10^{-2}$ . **10.18**  $4.0 \times 10^{-6}$ . **10.20**  $5.6 \times 10^{23}$ . **10.22**  $[NH_3]$  will increase and  $[N_2]$  and  $[H_2]$  will decrease. **10.24**  $P_{NO} = 0.50$  bar;  $P_{NO_2} = 0.020$  bar. **10.26**  $[I] = 8.58 \times 10^{-4}$  M;  $[I_2] = 0.0194$  M. **10.28** (a) 0.52. (b)  $[CO_2] = 0.48$  M;  $[H_2] = 0.020$  M;  $[CO] = 0.075$  M;  $[H_2O] = 0.065$  M. **10.30**  $[H_2] = [CO_2] = 0.05$  M;  $[H_2O] = [CO] = 0.11$  M. **10.32**  $8.0 \times 10^1$  J mol<sup>-1</sup>. **10.34**  $\Delta G_{rxn}^\circ = 457.2$  kJ.  $K = 7.27 \times 10^{-81}$ . **10.36**  $-24.6$  kJ mol<sup>-1</sup> (b)  $-950$  J mol<sup>-1</sup>. **10.38**  $-341$  kJ mol<sup>-1</sup>. **10.40**  $3.1 \times 10^{-2}$  bar. **10.42** (a) Shift position of equilibrium to the right. (b) No effect. (c) No effect. **10.44** (a) No effect. (b) No effect. (c) Shift the position of equilibrium to the left. (d) No effect. (e) To the left. **10.46** (a) To the right. (b) To the left. (c) To the right. (d) To the left. (e) No effect. **10.48** (a) To the left. (b) No change. **10.50** (a) 1.67. (b)  $P_A = 0.69$  bar;  $P_B = 0.81$  bar. **10.52** (a)  $K_p = 7.76 \times 10^{24}$ . (b)  $K_p = 7.58 \times 10^{19}$ , assuming  $\Delta H$  and  $\Delta S$  are temperature independent in this temperature range. **10.54**  $-36.2$  kJ, assuming  $\Delta H$  and  $\Delta S$  are temperature independent in this temperature range. **10.56**  $P_{NO} = 0.24$  bar;  $P_{Cl_2} = 0.12$  bar. (b)  $K_p = 0.016$ . **10.58** (a) No effect. (b) More  $CO_2$  and  $H_2O$  will form. **10.60** (a)  $8 \times 10^{-44}$ . (b) The reaction has very large activation energy. **10.62** (a) 0.134. (b) 49.2%. (c) decrease. **10.64**  $K_p = 4.95 \times 10^{-3}$ . **10.66**  $K_p = \frac{4\alpha^2}{1 - \alpha^2} P_{total}$ . **10.68**  $2.34 \times 10^{-3}$  M. **10.70**  $P_{total} = 330$  bar. **10.72** Decrease in concentration of  $CO_2$  shifts equilibrium to left. Either cool the environment or feed carbonated water. **10.74** 0.56 and 0.44. (b)  $K_p = 8.0$ . **10.76** (a) 1.16. (b) 53.7%. **10.78** (a) 0.50. (b) 0.23. (c) 0.037. (d) Greater than 0.037 mol. **10.80**  $[H_2] = 0.070$  M,  $[I_2] = 0.182$  M,  $[HI] = 0.825$  M. **10.82**  $2.3 \times 10^{-9}$ . **10.84** (a) 4.2  $\times 10^{-4}$ . (b) 0.83. (c) 1.1. (d) In (b):  $2.3 \times 10^3$ ; in (c): 0.021. **10.86**  $K_p = 2.34 \times 10^{-2}$ ;  $K_c = 9.61 \times 10^{-4}$ . **10.88**  $P_{N_2O_4} = 0.14$  bar;  $P_{NO_2} = 1.2$  bar;  $K_p = 9.4$ . **10.90** (a) The equilibrium will shift to the right. (b) To the right. (c) No change. (d) No change. (e) No change. (f) To the left. **10.92**  $P_{N_2O_4} = 0.088$  bar;  $P_{NO_2} = 0.10$  bar. **10.94** (a) 1.04 bar. (b) 0.40 bar. (c) 1.69 bar. (d) 0.62. **10.96** (a)  $K_c = 1.1 \times 10^{-7}$ ;  $K_p = 2.7 \times 10^{-6}$ . (b) 22 mg m<sup>-3</sup>. Yes. **10.98** Temporary dynamic equilibrium between the melting ice cubes and the freezing of the water between the ice cubes. **10.100**  $[NH_3] = 0.042$  M;  $[N_2] = 0.086$  M;  $[H_2] = 0.26$  M. **10.102** The equilibrium constant for vaporization is equal to the pressure of the gas. **10.104**  $\Delta G^\circ = 62.5$  kJ mol<sup>-1</sup>;  $\Delta H^\circ = 157.8$  kJ mol<sup>-1</sup>;  $\Delta S^\circ = 109$  kJ mol<sup>-1</sup> K<sup>-1</sup>.

## Chapter 11

- 11.2** (a)  $NO_2^-$ . (b)  $HSO_4^-$ . (c)  $HS^-$ . (d)  $CN^-$ . (e)  $HCOO^-$ . **11.4** (a)  $H_2S$ . (b)  $H_2CO_3$ . (c)  $HCO_3^-$ . (d)  $H_3PO_4$ . (e)  $H_2PO_4^-$ . (f)  $HPO_4^{2-}$ . (g)  $H_2SO_4$ . (h)  $HSO_4^-$ . (i)  $HSO_3^-$ . **11.6** (a)  $CH_2ClCOO^-$ . (b)  $IO_4^-$ . (c)  $H_2PO_4^-$ . (d)  $HPO_4^{2-}$ . (e)  $PO_3^{3-}$ . (f)  $HSO_4^-$ . (g)  $SO_4^{2-}$ .

(h)  $IO_3^-$ . (i)  $SO_3^{2-}$ . (j)  $NH_3$ . (k)  $HS^-$ . (l)  $S^{2-}$ . (m)  $ClO_3^-$ . **11.8**  $AlCl_3$  is the Lewis acid;  $Cl^-$  is the Lewis base. **11.10**  $CO_2$  and  $BF_3$ .

- 11.12** Yes. 1.0 M  $HCl(aq)$ : pH = ~0; 2.0 M  $HCl(aq)$ : pH = ~-0.3. **11.14**  $1.6 \times 10^{-14}$  M. **11.16** (a) 10.75. (b) 3.28. **11.18** (a)  $6.3 \times 10^{-6}$  M. (b)  $1.0 \times 10^{-16}$  M. (c)  $2.7 \times 10^{-6}$  M. **11.20**  $1.98 \times 10^{-3}$  mol, 0.444. **11.22** 0.118. **11.24** (c). **11.26** 9.0. **11.28** (1) (c). (2) (b) and (d). **11.30** (a) Strong. (b) Weak. (c) Weak. (d) Weak. (e) Strong. **11.32** (b) and (c). **11.34** It will not proceed to any measurable extent. **11.36** They are assumed to completely ionize. **11.38** (c). **11.40**  $[H^+] = [CH_3COO^-] = 5.8 \times 10^{-4}$  M;  $[CH_3COOH] = 0.0187$  M. **11.42**  $1.7 \times 10^{-3}$  M. **11.44** (a) 3.5%. (b) 33%. (c) 79%. **11.46** (a) 3.9%. (b) 0.030%. **11.48**  $7.0 \times 10^{-7}$ . **11.50** 1.5%. **11.52** (a)  $HCl$ : 1.40;  $H_2SO_4$ : 1.31. (b)  $[H^+] = [SO_4^{2-}] = 0.045$  M;  $[HSO_4^-] = 0.16$  M. **11.54** 6.6. **11.56**  $K_{a_1} >> K_{a_2}$ . **11.58**  $H_2Se > H_2S > H_2O$ . **11.60**  $CHCl_2COOH$ . **11.62** (a) Neutral. (b) Acidic. (c) Neutral. (d) Acidic. **11.66** pH = 9.15. **11.68** pH > 7. **11.70** pH = 1.9. **11.72** (a)  $2HCl(aq) + Zn(OH)_2(s) \rightarrow ZnCl_2(aq) + 2H_2O(l)$ . (b)  $2OH^- (aq) + Zn(OH)_2(s) \rightarrow Zn(OH)_4^{2-} (aq)$ . **11.74** stronger. **11.76** (c). **11.78** (a) Forward reaction,  $NH_3$  (Brønsted acid),  $NH_3$  (Brønsted base); Reverse reaction,  $NH_4^+$  (Brønsted acid) and  $NH_2^-$  (Bronsted base). (b)  $NH_4^+$  corresponds to  $H^+$  and  $NH_2^-$  corresponds to  $OH^-$ .

$$11.80 [OH^-] = \frac{K_w}{K_a}$$

**11.82**  $\Delta H^\circ = 55.9$  kJ mol<sup>-1</sup>;  $\Delta S^\circ = -80.4$  J K<sup>-1</sup> mol<sup>-1</sup>;  $\Delta G^\circ = 80$  kJ mol<sup>-1</sup>; at 25°C  $K_w = 1.01 \times 10^{-14}$ ; at 60°C  $K_w = 1.08 \times 10^{-13}$ . **11.84**  $1.77 \times 10^{10}$ . **11.86**  $2.0 \times 10^{-5}$ .

- 11.88** 0.028. **11.90**  $NH_3$ . **11.92** Because D is heavier than H, the quantum-zero point energy of the O—D vibration will be lower than that for H, and more energy would be required to break the O—D bond than the O—H bond. **11.94** 1.79.

- 11.96**  $F^-$  reacts with HF to form  $HF_2^-$ , thereby shifting the ionization of HF to the right. **11.98** (a)  $HbO_2$ . (b)  $HbH^+$ . (c) To the right. **11.100**  $\alpha = 0.180$ ;  $K_p = 4.62 \times 10^{-3}$ .

- 11.104** The  $H^+$  ions convert  $CN^-$  to  $HCN$ , which escapes as a gas.

- 11.106** 0.25 g. **11.108** –0.20. **11.110** (a) Equilibrium will shift to the right. (b) To the left. (c) No effect. (d) To the right. **11.112** The amines are converted to their salts  $RNH_3^+$ . **11.114**  $1.4 \times 10^{-4}$ .

- 11.116** 4.40. **11.118** In a basic medium, the ammonium salt is converted to the pungent-smelling ammonia. **11.120** (c).

- 11.122** 21 mL. **11.126** The fluoride ion replaces the hydroxide ion during remineralization, making the enamel more resistant to acids.

## Chapter 12

- 12.2** (a) 11.28. (b) 9.08. **12.4** (a), (b), and (c). **12.6** 4.74 for both; (a) because it has a higher concentration. **12.8** 7.03. **12.10** 10; More effective against the acid. **12.12** (a) 4.82. (b) 4.64.

- 12.14** HC. **12.16** 90.1 g mol<sup>-1</sup>. **12.18** 0.467 M.

- 12.20**  $[H^+] = 3.0 \times 10^{-13}$  M;  $[OH^-] = 0.0335$  M;

- $[Na^+] = 0.0835$  M;  $[CH_3COO^-] = 0.0500$  M;

- $[CH_3COOH] = 8.4 \times 10^{-10}$  M. **12.22** 8.23. **12.24** (a) 11.36.

- (b) 9.55. (c) 8.95. (d) 5.19. (e) 1.70. **12.26**  $CO_2$  dissolves in water to form  $H_2CO_3$ , which neutralizes  $NaOH$ . **12.28** 5.70.

- 12.30** (a) Insoluble. (b) Soluble. (c) Soluble. (d) Insoluble.

- 12.34** (a)  $9.1 \times 10^{-9}$  M. (b)  $7.4 \times 10^{-8}$  M.

- 12.36**  $1.80 \times 10^{-11}$ . **12.38**  $2.2 \times 10^{-4}$  mol L<sup>-1</sup>. **12.40**  $2.3 \times 10^{-9}$ .

- 12.42**  $[Na^+] = 0.045$  M;  $[NO_3^-] = 0.076$  M;  $[Sr^{2+}] = 0.016$  M;

- $[F^-] = 1.1 \times 10^{-4}$  M. **12.44**  $2.68 < pH < 8.11$ . **12.46** (c) and (e).

- 12.48** (a) 0.013 M. (b)  $2.2 \times 10^{-4}$  M. (c)  $3.3 \times 10^{-3}$  M.

- 12.50** (a)  $1.0 \times 10^{-5} M$ . (b)  $1.0 \times 10^{-10} M$ . **12.52** (b), (c), (d), and (e). **12.54** (a)  $0.016 M$ . (b)  $1.6 \times 10^{-6} M$ . **12.56** Yes.
- 12.58**  $\text{Al(OH)}_3$ . **12.60**  $\text{Ag}^+(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(aq)$ ;  $\text{Zn}^{2+}(aq) + 4\text{NH}_3(aq) \rightleftharpoons \text{Zn}(\text{NH}_3)_4^+(aq)$ . Zinc hydroxide forms a complex ion with excess  $\text{OH}^-$ , and silver hydroxide does not.
- 12.62** Silver chloride will dissolve in aqueous ammonia because of the formation of a complex ion. Lead chloride will not dissolve; it doesn't form an ammonia complex. **12.64** Sodium hydroxide.
- 12.66**  $0.1 < 10$ . **12.68**  $\text{pH} = \text{p}K_a$ . **12.70**  $K_b = 5 \times 10^{-10}$ .
- 12.72**  $\text{Cd(OH)}_2(s) + 2\text{OH}^- \rightleftharpoons \text{Cd}(\text{OH})_4^{2-}(aq)$ ; Lewis acid-base reaction. **12.74** (d). **12.76**  $[\text{Ag}^+] = 2.0 \times 10^{-9} M$ ;  $[\text{Cl}^-] = 0.080 M$ ;  $[\text{Zn}^{2+}] = 0.070 M$ ;  $[\text{NO}_3^-] = 0.060 M$ . **12.78**  $> 8.11$  but  $< 9.54$ .
- 12.80**  $K_{sp} = 2.4 \times 10^{-13}$ . **12.82**  $1.0 \times 10^{-5} M$ . **12.84** (a)  $\text{AgBr}$ . (b)  $[\text{Ag}^+] = 1.8 \times 10^{-7} M$ . (c)  $\% \text{Ag}^+(aq) = 1.8 \times 10^{-3} \%$ .
- 12.86**  $3.0 \times 10^{-8}$ . **12.88** (a)  $1.0 \times 10^{14}$ . (b)  $1.8 \times 10^9$ . (c)  $3.2 \times 10^4$ . **12.92** The sulfur-containing air-pollutants react with  $\text{Pb}^{2+}$  to form  $\text{PbS}$ , which gives paintings a darkened look.
- 12.94**  $[\text{Ba}^{2+}] = 1.8 \times 10^{-7} M$ ;  $[\text{Sr}^{2+}] = [\text{SO}_4^{2-}] = 6.2 \times 10^{-4} M$ .
- 12.96** No. **12.98**  $V_{\text{NaOH}} = 13 \text{ mL}$ . **12.100** (a) The acidic hydrogen is from the carboxyl group. (b)  $5.2 \times 10^3$ , Less soluble. (c)  $\text{pH} = 7.93$ . **12.104**  $\text{pH} = \text{p}K_a \pm 1$ .
- 12.106** (b)  $\text{p}K_a + \text{p}K_b = 14.00$ .

## Chapter 13

- 13.2** (a)  $\text{Fe} \longrightarrow \text{Fe}^{3+} + 3e^-$ ;  $\text{O}_2 + 4e^- \longrightarrow 2\text{O}^{2-}$ . Oxidizing agent:  $\text{O}_2$ ; reducing agent,  $\text{Fe}$ . (b)  $2\text{Br}^- \longrightarrow \text{Br}_2 + 2e^-$ ;  $\text{Cl}_2 + 2e^- \longrightarrow 2\text{Cl}^-$ . Oxidizing agent:  $\text{Cl}_2$ ; reducing agent,  $\text{Br}^-$ . (c)  $\text{Si} \longrightarrow \text{Si}^{4+} + 4e^-$ ;  $\text{F}_2 + 2e^- \longrightarrow 2\text{F}^-$ . Oxidizing agent,  $\text{F}_2$ ; reducing agent,  $\text{Si}$ . (d)  $\text{H}_2 \longrightarrow 2\text{H}^+ + 2e^-$ ;  $\text{Cl}_2 + 2e^- \longrightarrow 2\text{Cl}^-$ . Oxidizing agent,  $\text{Cl}_2$ ; reducing agent,  $\text{H}_2$ . **13.4** (a) +5. (b) +1. (c) +3. (d) +5. (e) +5. **13.6** (a)  $\text{Cs}: +1$ ,  $\text{O}: -2$ . (b)  $\text{Ca}: +2$ ,  $\text{I}: -1$ . (c)  $\text{Al}: +3$ ,  $\text{O}: -2$ . (d)  $\text{H}: +1$ ,  $\text{As}: +3$ ,  $\text{O}: -2$ . (e)  $\text{Ti}: +4$ ,  $\text{O}: -2$ . (f)  $\text{Mo}: +6$ ,  $\text{O}: -2$ . (g)  $\text{Pt}: +2$ ,  $\text{Cl}: -1$ . (h)  $\text{Pt}: +4$ ,  $\text{Cl}: -1$ . (i)  $\text{Sn}: +2$ ,  $\text{F}: -1$ . (j)  $\text{Cl}: +3$ ,  $\text{F}: -1$ . (k)  $\text{Sb}: +5$ ,  $\text{F}: -1$ . **13.8**  $\text{N}_2\text{O}_5$ .
- 13.10** (a)  $2\text{Fe}^{2+} + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Fe}^{3+} + 2\text{H}_2\text{O}$ . (b)  $3\text{Cu} + 6\text{H}^+ + 2\text{HNO}_3 \rightarrow 3\text{Cu}^{2+} + 2\text{NO} + 4\text{H}_2\text{O}$ . (c)  $3\text{CN}^- + 2\text{MnO}_4^- + \text{H}_2\text{O} \rightarrow 3\text{CNO}^- + 2\text{MnO}_2 + 2\text{OH}^-$ . (d)  $3\text{Br}_2 + 6\text{OH}^- \rightarrow \text{BrO}_3^- + 5\text{Br}^- + 3\text{H}_2\text{O}$ . (e)  $2\text{S}_2\text{O}_5^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^-$ . **13.12** (a)  $E = -0.013 \text{ V}$ ,  $\text{Fe}$  (cathode),  $\text{Cr}$  (anode). (b)  $E = -0.943$ ,  $\text{Zn}$  (cathode),  $\text{Al}$  (anode). (c)  $E = +2.2467$ ,  $\text{Mg}$  (anode) and  $\text{Pb}$  (cathode). **13.14** Yes.
- 13.16** No. **13.18** (a)  $\text{Li}$ . (b)  $\text{H}_2$ . (c)  $\text{Fe}^{2+}$ . (d)  $\text{Br}^-$ . **13.20**  $0.368 \text{ V}$ .
- 13.22** (a)  $-432 \text{ kJ mol}^{-1}$ ,  $5 \times 10^{75}$ . (b)  $-104 \text{ kJ mol}^{-1}$ ,  $2 \times 10^{18}$ . (c)  $-178 \text{ kJ mol}^{-1}$ ,  $1 \times 10^{31}$ . (d)  $-1.27 \times 10^3 \text{ kJ mol}^{-1}$ ,  $8 \times 10^{21}$ . **13.24**  $0.37 \text{ V}$ ,  $-36 \text{ kJ mol}^{-1}$ ,  $2 \times 10^6$ .
- 13.26**  $478 \text{ J mol}^{-1} \text{ K}^{-1}$ . **13.28** (a)  $2.23 \text{ V}$ ,  $2.23 \text{ V}$ ,  $-430 \text{ kJ mol}^{-1}$ . (b)  $0.02 \text{ V}$ ,  $0.04 \text{ V}$ ,  $-23 \text{ kJ mol}^{-1}$ . **13.30**  $0.0789 \text{ V}$ , ideal solution, can replace activities with concentrations. **13.32**  $6.7 \times 10^{-38}$ .
- 13.34** 0.97 bar. **13.36** (a)  $0.076 \text{ L}$ . (b)  $0.16 \text{ L}$ . **13.38**  $0.64 \text{ g of Ba}$ . **13.40** sodium. **13.42** 0.012 moles  $e^-$ . **13.44** 0.084 moles of each. **13.46**  $7.70 \times 10^3 \text{ C}$ . **13.48**  $1.84 \text{ kg h}^{-1}$ . **13.50**  $63.1 \text{ g mol}^{-1}$ . **13.52**  $27.1 \text{ g mol}^{-1}$ . **13.56**  $9.44 \times 10^{-3} \text{ g SO}_2$ .
- 13.58** (a)  $2\text{MnO}_4^- + 5\text{H}_2\text{O}_2 + 6\text{H}^+ \rightarrow 5\text{O}_2 + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}$ . (b)  $0.0602 M$ . **13.60** 0.231 mg  $\text{Ca}^{2+}/\text{mL blood}$ . **13.62** (a)  $0.80 \text{ V}$ . (b)  $2\text{Ag}^+(aq) + \text{H}_2(g) \longrightarrow 2\text{Ag}(s) + 2\text{H}^+(aq)$ . (c) (i)  $0.92 \text{ V}$ ; (ii)  $1.10 \text{ V}$ . (d) The cell operates as a pH meter.
- 13.64** Fluorine gas reacts with water. **13.66**  $2.5 \times 10^2 \text{ h}$ .
- 13.68** The solution surrounding the anode will become brown because of the formation of the triiodide ion. The solution around

the cathode will become basic, which will cause the phenolphthalein indicator to turn red. **13.74** (a)  $0.222 \text{ L H}_2$ . (b)  $6.09 \times 10^{23} / \text{mol e}^-$ . **13.76** (a)  $-1357 \text{ kJ mol}^{-1}$ . (b)  $1.17 \text{ V}$ .

**13.78**  $1.10 \text{ V}$ . (b)  $5.3 \times 10^3$ . **13.80** Heating the garage will melt the snow on the car, which is contaminated with salt. The aqueous salt will hasten corrosion. **13.82** (a) Anode  $2\text{F}^- \rightarrow \text{F}_2(g) + 2e^-$ ; Cathode  $2\text{H}^+ + 2e^- \rightarrow \text{H}_2(g)$ ; Overall:  $2\text{H}^+ + 2\text{F}^- \rightarrow \text{H}_2(g) + \text{F}_2(g)$ . (b) The  $\text{K}^+$  is not reduced.

(c)  $2.8 \times 10^3 \text{ L}$ . **13.84** (c)  $4.44 \text{ hr}$ . **13.86**  $1.97 \text{ V}$ .

**13.88** (a)  $\text{Au}(s) + 3\text{HNO}_3(aq) + 4\text{HCl}(aq) \rightarrow \text{HAuCl}_4(aq) + 3\text{H}_2\text{O}(l) + 3\text{NO}_2(g)$ . (b) To increase the acidity and to form the stable complex ion,  $\text{AuCl}_4^-$ . **13.90**  $9.8 \times 10^{-12}$ . **13.92**  $E = 1.09 \text{ V}$ ; therefore, products are favored. **13.94** (a)  $\text{Sn}^{4+}(aq) + 2e^- \rightarrow \text{Sn}^{2+}(aq)$ ;  $2\text{Ti}(s) \rightarrow \text{Ti}^+(aq) + e^-$ ;  $\text{Sn}^{4+}(aq) + 2\text{Ti}(s) \rightarrow \text{Sn}^{2+}(aq) + 2\text{Ti}^+(aq)$ . (b)  $K = 8 \times 10^{15}$ . (c)  $0.41 \text{ V}$ . **13.96** Yes. **13.100** (b)  $104 \text{ A h}$ .

The concentration of  $\text{H}_2\text{SO}_4$  keeps decreasing.

(c)  $2.01 \text{ B}^-$ ;  $-3.88 \times 10^2 \text{ kJ mol}^{-1}$ . **13.102** (b)  $11.9 \text{ hr}$ .

**13.108**  $E^\circ = -0.85 \text{ V}$ . **13.110** The second one because it will have a larger change in entropy. **13.112**  $2 \times 10^{37}$ . **13.114** \$217. **13.118** (a)  $\text{Al} + 3\text{Ag}^+ \rightarrow \text{Al}^{3+} + 3\text{Ag}$ . (b) A  $\text{NaHCO}_3$  solution is basic.

## Chapter 14

- 14.2** (a) rate =  $-\frac{d[\text{H}_2]}{dt} = -\frac{d[\text{I}_2]}{dt} = \frac{1}{2} \frac{d[\text{HI}]}{dt}$ .  
(b) rate =  $-\frac{1}{5} \frac{d[\text{Br}^-]}{dt} = -\frac{d[\text{BrO}_3^-]}{dt} = -\frac{1}{6} \frac{d[\text{H}^+]}{dt} = \frac{1}{3} \frac{d[\text{Br}_2]}{dt}$ .
- 14.4**  $0.049 \text{ M s}^{-1}$ . (b)  $-0.025 \text{ M s}^{-1}$ . **14.6**  $2.4 \times 10^{-4} \text{ M s}^{-1}$ .  
**14.8** (a) Third order. (b)  $0.38 \text{ M s}^{-1}$ . **14.10**  $M^{-2} \text{ s}^{-1}$ .  
**14.12**  $k = 1.19 \times 10^{-4} \text{ s}^{-1}$ . **14.14** 30 min. **14.16** (a)  $0.01998 \text{ s}^{-1}$ . (b) 151 s. **14.18** 3.6 s. **14.20** (a)  $0.487 \text{ M}$ . (b)  $0.500 \text{ M}$ .  
**14.22**  $0.64 \text{ M}^{-2} \text{ s}^{-1}$ . **14.24** 135 kJ mol $^{-1}$ . **14.26** 644 K.  
**14.28** 51.0 kJ mol $^{-1}$ . **14.30** 86 kJ mol $^{-1}$ . **14.32** rate =  $k[\text{X}_2][\text{Y}]$ . (b) Reaction is zero order in Z. (c)  $\text{X}_2 + \text{Y} \longrightarrow \text{XY} + \text{X}$  (slow)  
 $\text{X} + \text{Z} \longrightarrow \text{XZ}$  (fast). **14.34** Mechanism I. **14.38** Temperature, energy of activation, concentration of reactants, catalyst.  
**14.40**  $22.6 \text{ cm}^2$ ,  $44.9 \text{ cm}^2$ . The large surface area of grain dust can result in a violent explosion. **14.42** (a) Third order.  
(b)  $0.38 \text{ M}^{-2} \text{ s}^{-1}$ . (c)  $\text{H}_2 + 2\text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O} + \text{O}$  (slow)  
 $\text{O} + \text{H}_2 \rightarrow \text{H}_2\text{O}$  (fast). **14.44** Water is present in excess so its concentration does not change appreciably. **14.46**  $10.7 \text{ M}^{-1} \text{ s}^{-1}$ .  
**14.48** 2.63 bar. **14.50**  $100 \text{ kJ mol}^{-1}$ ;  $3.4 \times 10^{16}$ . **14.52**  $P_{\text{azomethane}} = P_{\text{TX}_{\text{azomethane}}}$ . **14.54** 377 K. **14.58** (a) Increase. (b) Decrease.  
(c) Decrease. (d) Increase. **14.60**  $k = 1.0 \times 10^{-5} \text{ s}^{-1}$ .  
**14.62**  $\text{Br}_2 \rightarrow 2\text{Br}; \text{Br} + \text{CH}_4 \rightarrow \text{HBr} + \cdot\text{CH}_3; \text{CH}_3 + \text{Br}_2 \rightarrow \text{CH}_3\text{Br} + \text{Br}; \text{Br} + \text{CH}_4 \rightarrow \text{HBr} + \cdot\text{CH}_3$  and so on.  
**14.64** (a) rate =  $k[\text{X}][\text{Y}]$ . (b)  $1.9 \times 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$ . **14.66** Second order.  $2.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ . **14.68** Because the engine is relatively cold so the exhaust gases will not fully react with the catalytic converter. **14.70**  $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$  (slow),  $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$  (fast). **14.72** (a)  $\text{Mn}^{2+}; \text{Mn}^{3+}$ , first step. (b) Without the catalyst, reaction would be termolecular. (c) Homogeneous.  
**14.74** 0.45 bar. **14.76** (a)  $k_1[\text{A}] - k_2[\text{B}]$ . (b)  $[\text{B}] = (k_1/k_2)[\text{A}]$ .  
**14.78** (1)  $<$  (c)  $<$  (a); (2) (a) and (c) are exothermic, and (b) is endothermic. **14.80** Titanium acts as a catalyst to decompose steam. **14.82** (a)  $2.5 \times 10^{-5} \text{ M s}^{-1}$ . (b) Same as (a).  
(c)  $8.3 \times 10^{-6} \text{ M}$ . **14.84** d. **14.86** (a)  $1.13 \times 10^{-3} \text{ M min}^{-1}$ . (b)  $8.8 \times 10^{-3} \text{ M}$ . **14.88** Second order,  $0.42 \text{ M}^{-1} \text{ min}^{-1}$ .  
**14.90**  $6.4 \times 10^8 \text{ s}^{-1}$ .

## Chapter 15

**15.4**  $V^{5+}:[Ar]$ ;  $Cr^{3+}:[Ar]3d^1$ ;  $Mn^{2+}:[Ar]3d^3$ ;  $Fe^{2+}:[Ar]3d^5$ ;  $Cu^{2+}:[Ar]3d^9$ ;  $Sc^{3+}:[Ar]$ ;  $Ti^{4+}:[Ar]$ . **15.8** (a) +3. (b) 6. (c) oxalte.

**15.10** (a) Na: +1, Mo: +6. (b) Mg: +2, W: +6. (c) Fe: 0.

**15.12** (a) *cis*-dichlorobis(ethylenediamine)cobalt(III).

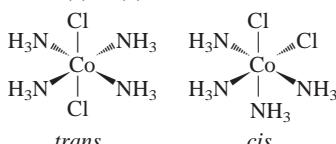
(b) pentaamminechloroplatinum(IV) chloride.

(c) pentaamminechlorocobalt(III) chloride.

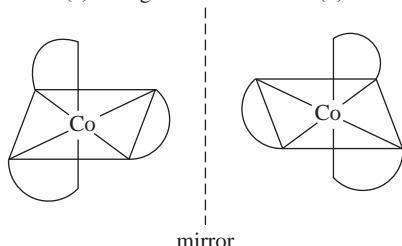
**15.14** (a)  $[Cr(en)_2Cl_2]^+$ . (b)  $Fe(CO)_5$ .

(c)  $K_2[Cu(CN)_4]$ . (d)  $[Co(NH_3)_4(H_2O)Cl]Cl_2$ .

**15.16** (a) 2. (b) 2.



**15.18** (a) Two geometric isomers. (b) Two optical isomers.



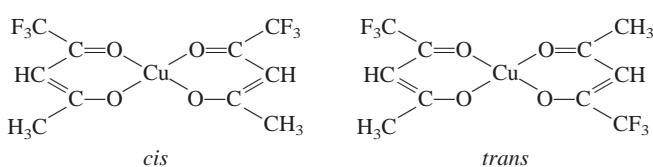
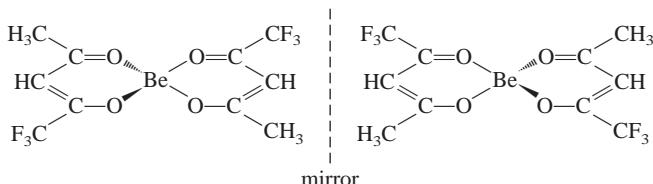
**15.20**  $CN^-$  is a strong-field ligand. Absorbs near UV (blue) so appears yellow. **15.22** (a) Orange. (b)  $255 \text{ kJ mol}^{-1}$ .

**15.24**  $[Co(NH_3)_4Cl_2]Cl$ . Two moles. **15.26** Use  $^{14}CN^-$  label (in  $NaCN$ ). **15.28** First  $Cu(CN)_2$  (white) is formed. It redissolves as  $Cu(CN)_4^{2-}$ . **15.30**  $1.4 \times 10^2$ . **15.32**  $Mn^{3+}$ .  $3d^5$  ( $Cr^{3+}$ ) is a stable electron configuration. **15.34** Ti: +3; Fe: +3. **15.36** Four Fe atoms per hemoglobin molecule.  $1.6 \times 10^4 \text{ g mol}^{-1}$ .

**15.38** (a)  $[Cr(H_2O)_6]Cl_3$ . (b)  $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ .

(c)  $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ . Compare electrical conductance with solutions of  $NaCl$ ,  $MgCl_2$ , and  $FeCl_3$ . **15.40**  $-1.8 \times 10^2 \text{ kJ mol}^{-1}$ ;  $6 \times 10^{30}$ . **15.42** Iron is more abundant. **15.44**  $Mn(H_2O)_6^{2+}$ .

**15.46** Low temperature and low concentration of  $Cl^-$  ions favor the formation of  $Co(H_2O)_6^{2+}$  ions. Adding  $HCl$  (more  $Cl^-$  ions) favors the formation of  $CoCl_4^{2-}$ . This reaction decreases  $[Cl^-]$ , so the pink color is restored. **15.48**  $Fe^{3+}$  is nearly colorless, so it must be light yellow in color. **15.50** The Be complex exhibits optical isomerism. The Cu complex exhibits geometric isomerism.

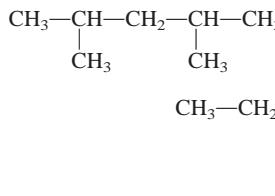
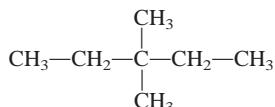
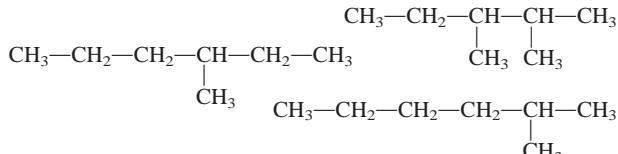


**15.52** Isomer I must be the *cis* isomer. The chlorines must be *cis* to each other for one oxalate ion to complex with Pt; Isomer II must be the *trans* isomer. With the chlorines on opposite sides of the molecule, each Cl is replaced with a hydrogen oxalate ion.

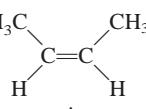
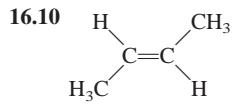
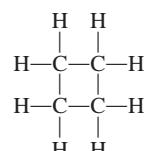
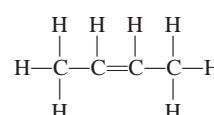
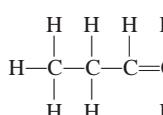
**15.54** (a) If the bonds are along the  $z$ -axis, the  $d_{z^2}$  orbital will have the highest energy. The  $d_{x^2-y^2}$  and  $d_{xy}$  orbitals will have the lowest energy. (b) If the trigonal plane is in the  $xy$ -plane, then the  $d_{x^2-y^2}$  and  $d_{xy}$  orbitals will have the highest energy, and  $d_{z^2}$  will have the lowest energy. (c) If the axial positions are along the  $z$ -axis, the  $d_{z^2}$  orbital will have the highest energy. The trigonal plane will be in the  $xy$ -plane, and thus the  $d_{x^2-y^2}$  and  $d_{xy}$  orbitals will be next highest in energy. **15.56** (a) Second equation. (b) Second equation.

## Chapter 16

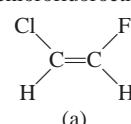
**16.4**  $CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$



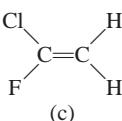
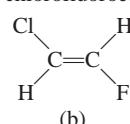
**16.6**



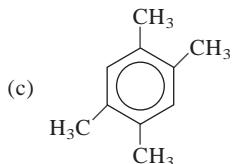
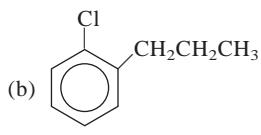
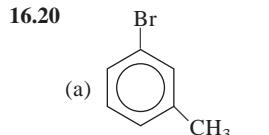
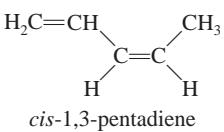
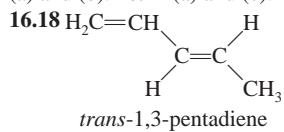
**16.12** *cis*-chlorofluoroethylene



1,1-chlorofluoroethylene

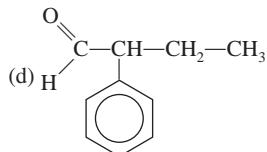
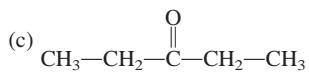
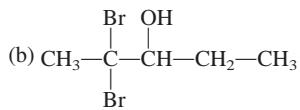
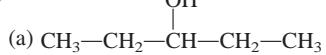


(a) and (b) are geometric isomers. (c) is a structural isomer of both  
 (a) and (b). **16.14** (a) and (c).



**16.22**  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  is an alkane and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$  is an alkene. Only an alkene would react with a hydrogen halide and hydrogen. **16.24**  $-633.1 \text{ kJ mol}^{-1}$ . **16.28** (a) Ether. (b) Amine. (c) Aldehyde. (d) Ketone. (e) Carboxylic acid. (f) Alcohol. (g) Amino acid.

**16.30**



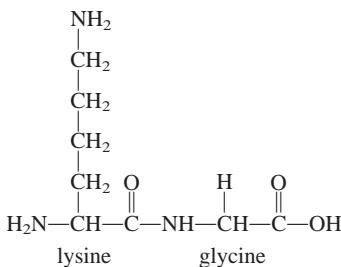
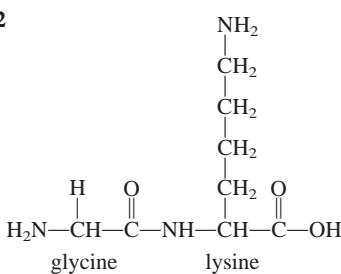
**16.32** (a) methoxyethane. (b) ethanamine. (c) propanal.  
 (d) 2-butanone. (e) methanoic acid. (f) 1-propanol.

**16.34**  $\text{HCOOH} + \text{CH}_3\text{OH} \longrightarrow \text{HCOOCH}_3 + \text{H}_2\text{O}$ . Methyl formate. **16.36**  $(\text{CH}_3)_2\text{CH}-\text{O}-\text{CH}_3$ . **16.38** (a) Ketone. (b) Ester.  
 (c) Ether. **16.40** osmotic pressure.

**16.42**  $-\text{CH}_2-\text{CHCl}-\text{CH}_2-\text{CCl}_2-$ . **16.44** By an addition reaction involving styrene monomers.

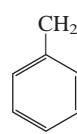
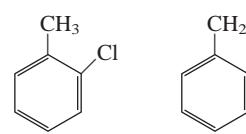
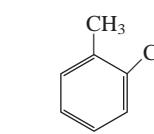
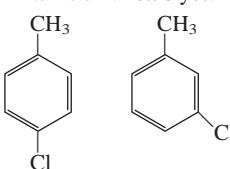
**16.46** (a)  $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$ . (b)  $\text{HO}_2\text{C}(\text{CH}_2)_6\text{NH}_2$ .

**16.52**



**16.56** 11 turns  $\text{s}^{-1}$ . **16.58** yes.

**16.60**



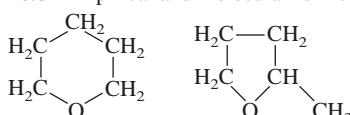
**16.62** (a) Cyclopropane because of the strained bond angles. (The C—C—C angle is  $60^\circ$  instead of  $109.5^\circ$ ). (b) Ethylene because of the C=C bond. (c) Acetaldehyde (susceptible to oxidation).

**16.64** (a) HCF. (b) No. (c)  $\text{C}_2\text{H}_2\text{F}_2$ . (d) tetrahedral. (e) *trans*-difluoroethylene. **16.66**  $8.4 \times 10^3 \text{ L air}$ . **16.68** (a) Six. (b) Four.

(c) Seven. **16.72** Proteins are made of 20 amino acids. Nucleic acids are made of four building blocks (purines, pyrimidines, sugar, phosphate group) only. **16.74** C-G base pairs have three hydrogen bonds and higher boiling point; A-T base pairs have two hydrogen bonds. **16.76** Leg muscles are active, have a high metabolic rate and hence a high concentration of myoglobin. The iron content in Mb makes the meat look dark. **16.78** Insects have blood that contains no hemoglobin. It is unlikely that a human-sized insect could obtain sufficient oxygen for metabolism by diffusion. **16.80** There are four Fe atoms per hemoglobin molecule;  $1.6 \times 10^4 \text{ g mol}^{-1}$ .

**16.82** Gly-Ala-Phe-Glu-His-Gly-Ala-Leu-Val.

**16.84** Empirical and molecular formula:  $\text{C}_5\text{H}_{10}\text{O}$ ; 88.7 g/mol.

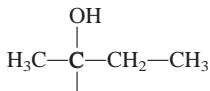


**16.86** The C atoms bonded to the methyl group and the amino group and the H atom. (b) The C atoms bonded to Br.

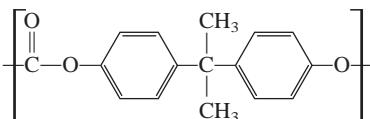
**16.88**  $\text{CH}_3\text{CH}_2\text{CHO}$ . **16.90** (a) Alcohol. (b) Ether. (c) Aldehyde. (d) Carboxylic acid. (e) Amine. **16.92** The acids in lemon juice convert the amines to the ammonium salts, which have very low vapor pressures. **16.94** Methane ( $\text{CH}_4$ ), ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), methanol ( $\text{CH}_3\text{OH}$ ), isopropanol ( $\text{C}_3\text{H}_7\text{OH}$ ), ethylene glycol ( $\text{CH}_2\text{OHCH}_2\text{O}$ ), naphthalene ( $\text{C}_{10}\text{H}_8$ ), acetic acid ( $\text{CH}_3\text{COOH}$ ).

**16.96** (a) 1. (b) 2. (c) 5. **16.98**  $\text{Br}_2$  dissociates into Br atoms, which react with  $\text{CH}_4$  to form  $\text{CH}_3\text{Br}$  and HBr.

**16.100**  $1.0 \times 10^3$  Hz.

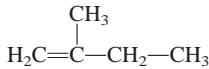
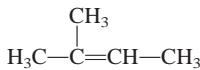
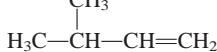


**16.104** (a) . The compound is chiral.  
(b) the product is a racemic mixture. **16.106** (a) 53. (c) 27.

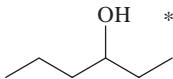
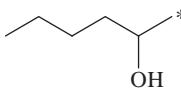


**16.112** (a) The  $-\text{COOH}$  group. (b) pH = 1.0: The valine is in the fully protonated form. pH = 7.0: Only the  $-\text{COOH}$  group is ionized. pH = 12.0: Both groups are ionized.

**16.114**



**16.116**



\*Chiral

## Chapter 17

**17.2** (a)  $-_1^0\beta$ . (b)  $^{40}\text{Ca}$ . (c)  $^4_2\alpha$ . (d)  $^1_0\text{n}$ . **17.4** (a)  $^{235}\text{U} \rightarrow ^{231}\text{Th} + ^4_2\alpha$ .  
(b)  $^{15}_8\text{O} \rightarrow ^{15}_7\text{N} + ^0_1\beta$ . (c)  $^4_1\text{Be} \rightarrow ^{11}_5\text{B} + ^0_1\beta$ .  
(d)  $^{235}_9\text{U} \rightarrow ^{235}_{93}\text{Np} + ^0_1\beta$ . **17.6** (a) Lithium-9. (b) Sodium-25.  
(c) Scandium-48. **17.8** (a) Neon-17. (b) Calcium-45.  
(c) Technetium. (d) Mercury-195. (e) Curium.

**17.10**  $6 \times 10^9 \text{ kg s}^{-1}$ . **17.12** (a)  $1.14 \times 10^{-12} \text{ J/nucleon}$ .  
(b)  $2.36 \times 10^{-10} \text{ J}$ . **17.14**  $\beta^-$  decay increases the n/p ratio, so would be more likely to occur in nuclei that are neutron deficient, such as Neon-19, than in nuclei with a larger n/p ratio, such as Neon-23. **17.16** (a)  $2.489 \times 10^6 \text{ kJ}$ . (b) 278 kg.

**17.18**  $4.89 \times 10^{19}$  atoms. **17.20** Radiative decay of a nucleus does not depend upon collisions with other atoms. Therefore, the mechanism consists of a single “unimolecular” elementary step, which implies pure first-order decay. **17.22** 65.2 yr.

**17.24** (a)  $^{15}_7\text{N} + ^1_0\text{p} \rightarrow ^{12}_6\text{C} + ^4_2\alpha$ ; X is  $^{15}\text{N}$ . (b)  $^{27}_{13}\text{Al} + ^1_0\text{d} \rightarrow ^{25}_{12}\text{Mg} + ^4_2\alpha$ ; X is  $^{25}\text{Mg}$ . (c)  $^{55}_{25}\text{Mn} + ^1_0\text{n} \rightarrow ^{56}_{25}\text{Mn} + \gamma$ ; X is  $^{56}\text{Mn}$ .

**17.26** All you need is a high-intensity alpha particle emitter. Any heavy element like plutonium or curium will do. Place the bismuth-209 sample next to the alpha emitter and wait.

**17.28** The easiest experiment would be to add a small amount of aqueous iodide containing some radioactive iodine to a saturated solution of lead(II) iodide. If the equilibrium is dynamic, radioactive iodine will eventually be detected in the solid lead(II) iodide. **17.30** If one were to dope part of a crystal with a radioactive tracer, one could demonstrate diffusion in the solid

state by detecting the tracer in a different part of the crystal at a later time. This actually happens with many substances.

**17.32** The design and operation of a Geiger counter are discussed in Figure 17.4 of the text. **17.34** 70.5 disintegrations/min.

**17.36** (a)  $^{235}_{92}\text{U} + ^1_0\text{n} \rightarrow ^{140}_{56}\text{Ba} + ^{31}_{0}\text{n} + ^{93}_{36}\text{Kr}$ .

(b)  $^{235}_{92}\text{U} + ^1_0\text{n} \rightarrow ^{144}_{55}\text{Cs} + ^{90}_{37}\text{Rb} + ^2_0\text{n}$ .

(c)  $^{235}_{92}\text{U} + ^1_0\text{n} \rightarrow ^{87}_{35}\text{Br} + ^{146}_{57}\text{La} + ^3_0\text{n}$ .

(d)  $^{235}_{92}\text{U} + ^1_0\text{n} \rightarrow ^{160}_{62}\text{Sm} + ^{72}_{30}\text{Zn} + ^4_0\text{n}$ .

**17.38** (a)  $^3_1\text{H} \rightarrow ^3_2\text{He} + ^0_1\beta$ . (b)  $^{242}_{94}\text{Pu} \rightarrow ^4_2\alpha + ^{238}_{92}\text{U}$ .

(c)  $^{131}_{53}\text{I} \rightarrow ^{131}_{54}\text{Xe} + ^0_1\beta$ . (d)  $^{251}_{98}\text{Cf} \rightarrow ^{247}_{96}\text{Cm} + ^4_2\alpha$ .

**17.40** Because both Ca and Sr belong to Group 2A, radioactive strontium that has been ingested into the human body becomes concentrated in bones (replacing Ca) and can damage blood cell production. **17.42** Normally the human body concentrates iodine in the thyroid gland. The purpose of the large doses of KI is to displace radioactive iodine from the thyroid and allow its excretion from the body. **17.44** (a)  $^{14}_7\text{N} + ^1_0\text{n} \rightarrow ^{15}_7\text{N} + \gamma$ . (b) X-ray analysis only detects shapes, particularly of metal objects. Bombs can be made in a variety of shapes and sizes and can be constructed of “plastic” explosives. Thermal neutron analysis is much more specific than X-ray analysis. **17.46** The neutron-to-proton ratio for tritium equals 2 and is thus outside the belt of stability. In a more elaborate analysis, it can be shown that the decay of tritium to  $^3\text{He}$  is exothermic; thus, the total energy of the products is less than the reactant. **17.48** 0.24%. **17.50** All isotopes of radium are radioactive; therefore, radium is not naturally occurring and would not be found with barium. However, radium is a decay product of uranium-238, so it is found in uranium ores. **17.52** A radioactive isotope with a shorter half-life because more radiation would be emitted over a certain period of time. **17.54** The energy of irradiation is not sufficient to bring about nuclear transmutation.

**17.56** Ds and Rg are transition metals:  $^{208}_{82}\text{Pb} + ^{62}_{28}\text{Ni} \rightarrow ^{270}_{110}\text{Ds}$ ;

$^{209}_{83}\text{Bi} + ^{64}_{28}\text{Ni} \rightarrow ^{273}_{111}\text{Rg}$ . Uub resembles Zn, Cd, and Hg:  $^{208}_{82}\text{Pb} + ^{66}_{30}\text{Zn} \rightarrow ^{274}_{112}\text{Uub}$ . Uuu is in the carbon family:  $^{244}_{94}\text{Pu} + ^{48}_{20}\text{Zn} \rightarrow ^{289}_{114}\text{Uuu}$ .

**17.58** There was radioactive material inside the box.

**17.60** (a)  $6.87 \times 10^{-13} \text{ J}$ . (b) The smaller particle ( $\alpha$ ) will move away at a greater speed due to its lighter mass. **17.62** The  $\alpha$  particles emitted by  $^{241}\text{Am}$  ionize the air molecules between the plates. The voltage from the battery makes one plate positive and the other negative, so each plate attracts ions of opposite charge.

This creates a current in the circuit attached to the plates. The presence of smoke particles between the plates reduces the current, because the ions that collide with smoke particles (or steam) are usually absorbed (and neutralized) by the particles. This drop in current triggers the alarm. **17.64** (a) The nuclear submarine can be submerged for a long period without refueling. (b) Conventional diesel engines receive an input of oxygen. A nuclear reactor does not. **17.66** 53.0 g Zn. **17.68** (a)  $\Delta m$  for neutron decay is  $-1.39 \times 10^{-30} \text{ g}$  (that is, it is exothermic) whereas, for proton decay,  $\Delta m$  is  $+3.22 \times 10^{-30} \text{ g}$  (that is, it is endothermic). Thus, proton decay can only occur with input of energy, which is not readily available to an isolated proton. (b) In a nucleus, energy for proton decay can be supplied by the decrease in the repulsive electrostatic energy due to replacing one proton with a neutron or, if by changing into a neutron, the proton can occupy a lower energy shell.

**17.70** (a)  $^{238}_{94}\text{Pu} \rightarrow ^4_2\text{He} + ^{234}_{92}\text{U}$ . (b)  $t = 10 \text{ yr}: 0.53 \text{ mW}$ .

**17.72** 0.49 rem.



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The screenshot shows a computer window titled "Question 1". The problem statement is: "Certain sunglasses have small crystals of silver chloride (AgCl) incorporated in the lenses. When the lenses are exposed to light of the appropriate wavelength, the following reaction occurs: AgCl → Ag + Cl. The Ag atoms formed produce a uniform gray color that reduces glare. If ΔH for the preceding reaction is about 243 kJ/mol, calculate the maximum wavelength (in nm) of light that will induce this process." Below the question is a numeric input field with a multiplier of  $\times 10^3$ . At the bottom of the window are buttons for "Previous", "View Solution", "Check Answer", and "Submit". To the right of the window, the text "Problem in ARIS" is displayed.

### Chapter Problem in Text

**Interface.** ARIS is built from years of research and testing on how students learn and how instructors want to use online homework programs.

**Content.** Created by market leading authors and instructors, ARIS includes questions derived directly from the textbook's end-of-chapter problems and features robust feedback for students.

**Management.** ARIS allows instructors to build assignments, track student progress, enable mastery features for students, create content, share with colleagues, and more—letting them use as little or as much course management as is needed.

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