12. From the solubility data given, calculate K_{sp} for each compound.

a. AgI: 2.89×10^{-7} g/100 mL

b. SrF_2: 1.22×10^{-2} g/100 mL

c. $Pb(OH)_2$: 78 mg/500 mL

d. $BiAsO_4$: 14.4 mg/2.0 L

13. From the solubility data given, calculate K_{sp} for each compound.

a. $BaCO_3$: 10.0 mg/500 mL

b. CaF_2: 3.50 mg/200 mL

c. $Mn(OH)_2$: 6.30×10^{-4} g/300 mL

d. Ag_2S: 1.60×10^{-13} mg/100 mL

14. Given the following solubilities, calculate K_{sp} for each compound.

a. $BaCO_3$: 7.00×10^{-5} mol/L

b. CaF_2: 1.70 mg/100 mL

c. $Pb(IO_3)_2$: 2.30 mg/100 mL

d. SrC_2O_4: 1.58×10^{-7}mol/L

15. Given the following solubilities, calculate K_{sp} for each compound.

a. Ag_2SO_4: 4.2×10^{-1} g/100 mL

b. $SrSO_4$: 1.5×10^{-3} g/100 mL

c. CdC_2O_4: 6.0×10^{-3} g/100 mL

d. $Ba(IO_3)_2$: 3.96×10^{-2} g/100 mL

16. The K_{sp} of the phosphate fertilizer $CaHPO_4 \cdot 2H_2O$ is 2.7×10^{-7} at 25°C. What is the molar concentration of a saturated solution? What mass of this compound will dissolve in 3.0 L of water at this temperature?

17. The K_{sp} of zinc carbonate monohydrate is 5.5×10^{-11} at 25°C. What is the molar concentration of a saturated solution? What mass of this compound will dissolve in 2.0 L of water at this temperature?

18. Silver nitrate eye drops were formerly administered to newborn infants to guard against eye infections contracted during birth. Although silver nitrate is highly water soluble, silver sulfate has a K_{sp} of 1.20×10^{-5} at 25°C. If you add 25.0 mL of 0.015 M $AgNO_3$ to 150 mL of 2.8×10^{-3} M Na_2SO_4, will you get a precipitate? If so, what will its mass be?

19. Use the data in Chapter 26 "Appendix B: Solubility-Product Constants (" to predict whether precipitation will occur when each pair of solutions is mixed.

a. 150 mL of 0.142 M $Ba(NO_3)_2$ with 200 mL of 0.089 M NaF

b. 250 mL of 0.079 M K_2CrO_4 with 175 mL of 0.087 M $CaCl_2$

c. 300 mL of 0.109 M $MgCl_2$ with 230 mL of 0.073 M $Na_2(C_2O_4)$

20. What is the maximum volume of 0.048 M $Pb(NO_3)_2$ that can be added to 250 mL of 0.10 M NaSCN before precipitation occurs? $K_{sp} = 2.0 \times 10^{-5}$ for $Pb(SCN)_2$.

21. Given 300 mL of a solution that is 0.056 M in lithium nitrate, what mass of solid sodium carbonate can be added before precipitation occurs (assuming that the volume of solution does not change after adding the solid)? $K_{sp} = 8.15 \times 10^{-4}$ for Li_2CO_3.

22. Given the information in the following table, calculate the molar solubility of each sparingly soluble salt in 0.95 M $MgCl_2$.

Saturated Solution	K_{sp}
$MgCO_3 \cdot 3H_2O$	2.4×10^{-6}
$Mg(OH)_2$	5.6×10^{-12}
$Mg_3(PO_4)_2$	1.04×10^{-24}

ANSWERS

1.

a. 1.84×10^{-3} M

b. 7.73×10^{-9} M

c. 1.9×10^{-10} M

2.

3. 3.37 g

4.

5.

a. 4.15×10^{-4} M

b. 7.26×10^{-4} M

c. 6.26×10^{-6} M

d. 6.54×10^{-5} M

e. 5.86×10^{-4} M

6.

7. 22.4 mg; a secondary reaction occurs, where OH^- from the dissociation of the salt reacts with H^+ from the dissociation of water. This reaction causes further dissociation of the salt (Le Châtelier's principle).

8.

9. 1.2×10^{-10}

10.

11. 1.70×10^{-5}

12.

13.

14.

15.

a. 8.8×10^{-6}

b. 6.7×10^{-9}

c. 9.0×10^{-8}

d. 2.16×10^{-9}

16.

17. 7.4×10^{-6} M; 2.1 mg

18.

19. Precipitation will occur in all cases.

20.

21. 8.27 g

[1] As you will discover in Section 17.4 "Solubility and pH" and in more advanced chemistry courses, basic anions, such as S^{2-}, PO_4^{3-}, and CO_3^{2-}, react with water to produce OH^- and the corresponding protonated anion. Consequently, their calculated molarities, assuming no protonation in aqueous solution, are only approximate.

[2] The exceptions generally involve the formation of complex ions, which is discussed inSection 17.3 "The Formation of Complex Ions".

17.2 Factors That Affect Solubility

LEARNING OBJECTIVE

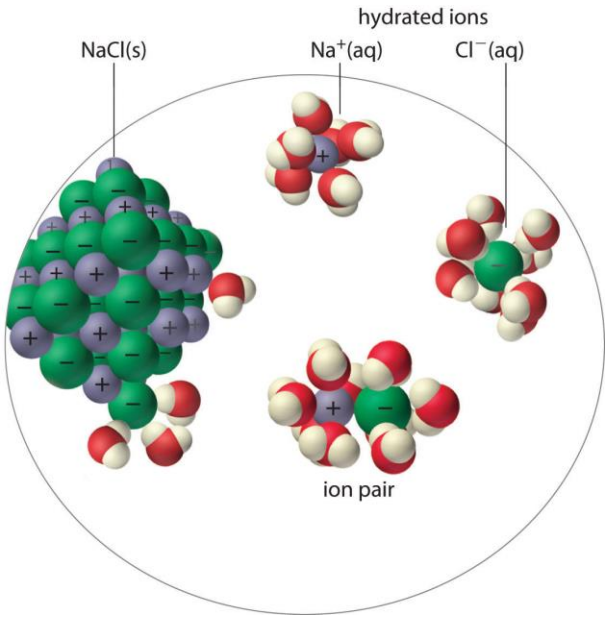
1. To understand the factors that determine the solubility of ionic compounds.

The solubility product of an ionic compound describes the concentrations of *ions* in equilibrium with a solid, but what happens if some of the cations become associated with anions rather than being completely surrounded by solvent? Then predictions of the total solubility of the compound based on the assumption that the solute exists solely as discrete ions would differ substantially from the actual solubility, as would predictions of ionic concentrations. In general, four situations explain why the solubility of a compound may be other than expected: ion pair formation, the incomplete dissociation of molecular solutes, the formation of complex ions, and changes in pH. The first two situations are described in this section, the formation of complex ions is discussed in Section 17.3 "The Formation of Complex Ions", and changes in pH are discussed in Section 17.4 "Solubility and pH".

Ion-Pair Formation

An ion pair consists of a cation and an anion that are in intimate contact in solution, rather than separated by solvent (Figure 17.2 "Ion-Pair Formation"). The ions in an ion pair are held together by the same attractive electrostatic forces that we discussed inChapter 8 "Ionic versus Covalent Bonding" for ionic solids. As a result, the ions in an ion pair migrate as a single unit, whose net charge is the sum of the charges on the ions. In many ways, we can view an ion pair as a species intermediate between the ionic solid (in which each ion participates in many cation–anion interactions that hold the ions in a rigid array) and the completely dissociated ions in solution (where each is fully surrounded by water molecules and free to migrate independently).

Figure 17.2 *Ion-Pair Formation*



In an ion pair, the cation and the anion are in intimate contact in solution and migrate as a single unit. They are not completely dissociated and individually surrounded by solvent molecules, as are the hydrated ions, which are free to migrate independently.

As illustrated for calcium sulfate in the following equation, a second equilibrium must be included to describe the solubility of salts that form ion pairs:

Equation 17.3

$$CaSO4(s) \rightleftharpoons Ca2+ SO42- \ ion\ pair(aq) \rightleftharpoons Ca2+(aq) + SO42-(aq)$$

The ion pair is represented by the symbols of the individual ions separated by a dot, which indicates that they are associated in solution. The formation of an ion pair is a dynamic process, just like any other equilibrium, so a particular ion pair may exist only briefly before dissociating into the free ions, each of which may later associate briefly with other ions.

Ion-pair formation can have a major effect on the measured solubility of a salt. For example, the measured K_{sp} for calcium sulfate is 4.93×10^{-5} at 25°C. The solubility of $CaSO_4$ should be 7.02×10^{-3} M if the only equilibrium involved were as follows:

Equation 17.4

$$CaSO4(s) \rightleftharpoons Ca2+(aq) + SO42-(aq)$$

In fact, the experimentally measured solubility of calcium sulfate at 25°C is 1.6×10^{-2}M, almost twice the value predicted from its K_{sp}. The reason for the discrepancy is that the concentration of ion pairs in a saturated $CaSO_4$ solution is almost as high as the concentration of the hydrated ions. Recall that the

magnitude of attractive electrostatic interactions is greatest for small, highly charged ions. Hence ion pair formation is most important for salts that contain M^{2+} and M^{3+} ions, such as Ca^{2+} and La^{3+}, and is relatively unimportant for salts that contain monopositive cations, except for the smallest, Li^{+}. We therefore expect a saturated solution of $CaSO_4$ to contain a high concentration of ion pairs and its solubility to be greater than predicted from its K_{sp}.

Note the Pattern

The formation of ion pairs increases the solubility of a salt.

Incomplete Dissociation

A molecular solute may also be more soluble than predicted by the measured concentrations of ions in solution due to *incomplete dissociation*. This is particularly common with weak organic acids. (For more information about weak organic acids, see Chapter 16 "Aqueous Acid–Base Equilibriums"). Although strong acids (HA) dissociate completely into their constituent ions (H^{+} and A^{-}) in water, weak acids such as carboxylic acids do not ($K_a = 1.5 \times 10^{-5}$). However, the molecular (undissociated) form of a weak acid (HA) is often quite soluble in water; for example, acetic acid (CH_3CO_2H) is completely miscible with water. Many carboxylic acids, however, have only limited solubility in water, such as benzoic acid ($C_6H_5CO_2H$), with $K_a = 6.25 \times 10^{-5}$. Just as with calcium sulfate, we need to include an additional equilibrium to describe the solubility of benzoic acid:

Equation 17.5

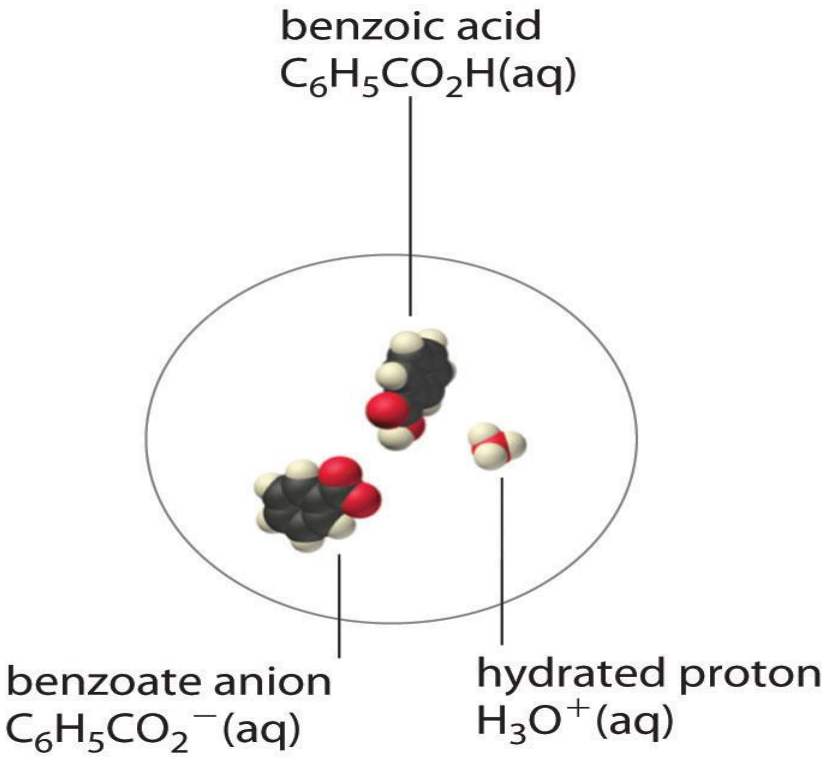
$$C6H5CO2H(s) \square \; C6H5CO2H(aq) \square \; C6H5CO2-(aq) + H+(aq)$$

In a case like this, measuring only the concentration of the ions grossly underestimates the total concentration of the organic acid in solution. In the case of benzoic acid, for example, the pH of a saturated solution at 25°C is 2.85, corresponding to $[H^{+}] = [C_6H_5CO_2^{-}] = 1.4 \times 10^{-3}$ M. The total concentration of benzoic acid in the solution, however, is 2.8×10^{-2} M. Thus approximately 95% of the benzoic acid in solution is in the form of hydrated neutral molecules—$C_6H_5CO_2H(aq)$—and only about 5% is present as the dissociated ions (Figure 17.3 "Incomplete Dissociation of a Molecular Solute").

Note the Pattern

Incomplete dissociation of a molecular solute that is miscible with water can increase the solubility of the solute.

Figure 17.3 *Incomplete Dissociation of a Molecular Solute*



In a saturated solution of benzoic acid in water at 25°C, only about 5% of the dissolved benzoic acid molecules are dissociated to form benzoate anions and hydrated protons. The remaining 95% exists in solution in the form of hydrated neutral molecules. (H_2O molecules are omitted for clarity.)

Although ion pairs, such as $Ca^{2+}{\cdot}SO_4^{2-}$, and undissociated electrolytes, such as $C_6H_5CO_2H$, are both electrically neutral, there is a major difference in the forces responsible for their formation. Simple electrostatic attractive forces between the cation and the anion hold the ion pair together, whereas a polar covalent O–H bond holds together the undissociated electrolyte.

Summary

There are four explanations why the solubility of a compound can differ from the solubility indicated by the concentrations of ions: (1) **ion pair** formation, in which an anion and a cation are in intimate contact in solution and not separated by solvent, (2) the incomplete dissociation of molecular solutes, (3) the formation of complex ions, and (4) changes in pH. An ion pair is held together by electrostatic attractive forces between the cation and the anion, whereas incomplete dissociation results from intramolecular forces, such as polar covalent O–H bonds.

KEY TAKEAWAY

- Ion-pair formation, the incomplete dissociation of molecular solutes, the formation of complex ions, and changes in pH all affect solubility.

CONCEPTUAL PROBLEMS

1. Do you expect the actual molar solubility of $LaPO_4$ to be greater than, the same as, or less than the value calculated from its K_{sp}? Explain your reasoning.
2. Do you expect the difference between the calculated molar solubility and the actual molar solubility of $Ca_3(PO_4)_2$ to be greater than or less than the difference in the solubilities of $Mg_3(PO_4)_2$? Why?
3. Write chemical equations to describe the interactions in a solution that contains $Mg(OH)_2$, which forms ion pairs, and in one that contains propanoic acid ($CH_3CH_2CO_2H$), which forms a hydrated neutral molecule.
4. Draw representations of $Ca(IO_3)_2$ in solution

a. as an ionic solid.

b. in the form of ion pairs.

c. as discrete ions.

NUMERICAL PROBLEM

1. Ferric phosphate has a molar solubility of 5.44×10^{-16} in 1.82 M Na_3PO_4. Predict itsK_{sp}. The actual K_{sp} is 1.3×10^{-22}. Explain this discrepancy.

ANSWER

1. $9.90 \times 10^{-16;}$ the solubility is much higher than predicted by K_{sp} due to the formation of ion pairs (and/or phosphate complexes) in the sodium phosphate solution.

17.3 The Formation of Complex Ions

LEARNING OBJECTIVE

1. To describe the formation of complex ions quantitatively.

In Chapter 4 "Reactions in Aqueous Solution", you learned that metal ions in aqueous solution are *hydrated*—that is, surrounded by a shell of usually four or six water molecules. A hydrated ion is one kind of a complex ion (or, simply, *complex*), a species formed between a central metal ion and one or more surrounding ligands, molecules or ions that contain at least one lone pair of electrons, such as the $[Al(H_2O)_6]^{3+}$ ion in Figure 16.12 "Effect of a Metal Ion on the Acidity of Water".

A complex ion forms from a metal ion and a ligand because of a Lewis acid–base interaction. The positively charged metal ion acts as a Lewis acid, and the ligand, with one or more lone pairs of electrons, acts as a Lewis base. Small, highly charged metal ions, such as Cu^{2+} or Ru^{3+}, have the greatest tendency to act as Lewis acids, and consequently, they have the greatest tendency to form complex ions.

As an example of the formation of complex ions, consider the addition of ammonia to an aqueous solution of the hydrated Cu^{2+} ion {$[Cu(H_2O)_6]^{2+}$}. Because it is a stronger base than H_2O, ammonia replaces the water molecules in the hydrated ion to form the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion. Formation of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex is accompanied by a dramatic color change, as shown in Figure 17.4 "The Formation of Complex Ions". The solution changes from the light blue of $[Cu(H_2O)_6]^{2+}$ to the blue-violet characteristic of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion.

The Formation Constant

The replacement of water molecules from $[Cu(H_2O)_6]^{2+}$ by ammonia occurs in sequential steps. Omitting the water molecules bound to Cu^{2+} for simplicity, we can write the equilibrium reactions as follows:

Equation 17.6

$$Cu2+(aq)+NH3(aq)[Cu(NH3)]2+(aq)+NH3(aq)[Cu(NH3)2]2+(aq)$$
$$+NH3(aq)[Cu(NH3)3]2+(aq)+NH3(aq)\square\ [Cu(NH3)]2+(aq$$
$$)\square\ [Cu(NH3)2]2+(aq)\square\ [Cu(NH3)3]2+(aq)\square\ [Cu(NH3)4]2+(aq)K1K2K3K4$$

The sum of the stepwise reactions is the overall equation for the formation of the complex ion:[1]

Equation 17.7

$$Cu2+(aq)+4NH3(aq)\square\ [Cu(NH3)4]2+(aq$$

The equilibrium constant for the formation of the complex ion from the hydrated ion is called the formation constant (K_f). The equilibrium constant expression for K_f has the same general form as any other equilibrium constant expression. In this case, the expression is as follows:

Equation 17.8

$$Kf=[[Cu(NH3)4]2+][Cu2+][NH3]4=2.1´1013=K1K2K3K4$$

Note the Pattern

The formation constant (K_f) has the same general form as any other equilibrium constant expression.

Water, a pure liquid, does not appear explicitly in the equilibrium constant expression, and the hydrated $Cu^{2+}(aq)$ ion is represented as Cu^{2+} for simplicity. As for any equilibrium, the larger the value of the equilibrium constant (in this case, K_f), the more stable the product. With $K_f = 2.1 \times 10^{13}$, the

$[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion is very stable. The formation constants for some common complex ions are listed in Table 17.2 "Formation Constants for Selected Complex Ions in Aqueous Solution*".

Table 17.2 Formation Constants for Selected Complex Ions in Aqueous Solution*

	Complex Ion	Equilibrium Equation	K_f
Ammonia Complexes	$[Ag(NH_3)_2]^+$	$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$	1.1×10^7
	$[Cu(NH_3)_4]^{2+}$	$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	2.1×10^{13}
	$[Ni(NH_3)_6]^{2+}$	$Ni^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}$	5.5×10^8
Cyanide Complexes	$[Ag(CN)_2]^-$	$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$	1.1×10^{18}
	$[Ni(CN)_4]^{2-}$	$Ni^{2+} + 4CN^- \rightleftharpoons [Ni(CN)_4]^{2-}$	2.2×10^{31}
	$[Fe(CN)_6]^{3-}$	$Fe^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-}$	1×10^{42}
Hydroxide Complexes	$[Zn(OH)_4]^{2-}$	$Zn^{2+} + 4OH^- \rightleftharpoons [Zn(OH)_4]^{2-}$	4.6×10^{17}
	$[Cr(OH)_4]^-$	$Cr^{3+} + 4OH^- \rightleftharpoons [Cr(OH)_4]^-$	8.0×10^{29}
Halide Complexes	$[HgCl_4]^{2-}$	$Hg^{2+} + 4Cl^- \rightleftharpoons [HgCl_4]^{2-}$	1.2×10^{15}
	$[CdI_4]^{2-}$	$Cd^{2+} + 4I^- \rightleftharpoons [CdI_4]^{2-}$	2.6×10^5
	$[AlF_6]^{3-}$	$Al^{3+} + 6F^- \rightleftharpoons [AlF_6]^{3-}$	6.9×10^{19}
Other Complexes	$[Ag(S_2O_3)_2]^{3-}$	$Ag^+ + 2S_2O_3^{2-} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}$	2.9×10^{13}
	$[Fe(C_2O_4)_3]^{3-}$	$Fe^{3+} + 3C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-}$	2.0×10^{20}
***Reported values are overall formation constants.**			

Source: Data from *Lange's Handbook of Chemistry*, 15th ed. (1999).

EXAMPLE 5

If 12.5 g of $Cu(NO_3)_2 \cdot 6H_2O$ is added to 500 mL of 1.00 M aqueous ammonia, what is the equilibrium concentration of $Cu^{2+}(aq)$?

Given: mass of Cu^{2+} salt and volume and concentration of ammonia solution

Asked for: equilibrium concentration of $Cu^{2+}(aq)$

Strategy:

A Calculate the initial concentration of Cu^{2+} due to the addition of copper(II) nitrate hexahydrate. Use the stoichiometry of the reaction shown in Equation 17.7 to construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations of all species in solution.

B Substitute the final concentrations into the expression for the formation constant (Equation 17.8) to calculate the equilibrium concentration of $Cu^{2+}(aq)$.

Solution:

Adding an ionic compound that contains Cu^{2+} to an aqueous ammonia solution will result in the formation of $[Cu(NH_3)_4]^{2+}(aq)$, as shown in Equation 17.7. We assume that the volume change caused by adding solid copper(II) nitrate to aqueous ammonia is negligible.

A The initial concentration of Cu^{2+} from the amount of added copper nitrate prior to any reaction is as follows:

$$12.5\ g\ Cu(NO3)2 \setminus 6H2O(1\ mol295.65\ g)$$
$$(1500\ mL)[\{1000\ mL1\ L\}] = 0.0846\ M$$

Because the stoichiometry of the reaction is four NH_3 to one Cu^{2+}, the amount of NH_3required to react completely with the Cu^{2+} is 4(0.0846) = 0.338 M. The concentration of ammonia after complete reaction is 1.00 M − 0.338 M = 0.66 M. These results are summarized in the first two lines of the following table. Because the equilibrium constant for the reaction is large (2.1×10^{13}), the equilibrium will lie far to the right. Thus we will assume that the formation of $[Cu(NH_3)_4]^{2+}$ in the first step is complete and allow some of it to dissociate into Cu^{2+} and NH_3 until equilibrium has been reached. If we define *x* as the amount of Cu^{2+} produced by the dissociation reaction, then the stoichiometry of the reaction tells us that the change in the concentration of $[Cu(NH_3)_4]^{2+}$ is −*x*, and the change in the concentration of ammonia is +4*x*, as indicated in the table. The final concentrations of all species (in the bottom row of the table) are the sums of the concentrations after complete reaction and the changes in concentrations.

$Cu2+ +4NH3 \square\ [Cu(NH3)4]2+$			
	$[Cu^{2+}]$	$[NH_3]$	$[[Cu(NH_3)_4]^{2+}]$
initial	0.0846	1.00	0
after complete reaction	0	0.66	0.0846
change	+*x*	+4*x*	−*x*
final	*x*	0.66 + 4*x*	0.0846 − *x*

B Substituting the final concentrations into the expression for the formation constant (Equation 17.8) and assuming that *x* << 0.0846, which allows us to remove *x* from the sum and difference,

$$Kfx = [[Cu(NH3)4]2+][Cu2+][NH3]4$$
$$= 0.0846 - xx(0.66 + 4x)4 \gg 0.0846x(0.66)4 = 2.1\acute{}\ 1013 = 2.1\acute{}\ 10 - 14$$

The value of *x* indicates that our assumption was justified. The equilibrium concentration of $Cu^{2+}(aq)$ in a 1.00 M ammonia solution is therefore 2.1×10^{-14} M.

Exercise

The ferrocyanide ion $\{[Fe(CN)_6]^{4-}\}$ is very stable, with a K_f of 1×10^{35}. Calculate the concentration of cyanide ion in equilibrium with a 0.65 M solution of $K_4[Fe(CN)_6]$.

Answer: 2×10^{-6} M

The Effect of the Formation of Complex Ions on Solubility

What happens to the solubility of a sparingly soluble salt if a ligand that forms a stable complex ion is added to the solution? One such example occurs in conventional black-and-white photography, which was discussed briefly in Chapter 4 "Reactions in Aqueous Solution".

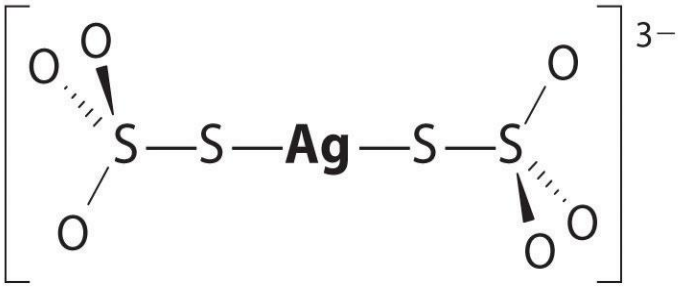
Recall that black-and-white photographic film contains light-sensitive microcrystals of AgBr, or mixtures of AgBr and other silver halides. AgBr is a sparingly soluble salt, with a K_{sp} of 5.35×10^{-13} at 25°C. When the shutter of the camera opens, the light from the object being photographed strikes some of the crystals on the film and initiates a photochemical reaction that converts AgBr to black Ag metal. Well-formed, stable negative images appear in tones of gray, corresponding to the number of grains of AgBr converted, with the areas exposed to the most light being darkest. To fix the image and prevent more AgBr crystals from being converted to Ag metal during processing of the film, the unreacted AgBr on the film is removed using a complexation reaction to dissolve the sparingly soluble salt.

The reaction for the dissolution of silver bromide is as follows:

Equation 17.9

$$AgBr(s) \square \quad Ag+(aq) + Br-(aq) Ksp = 5.35 \acute{} 10 - 13 \; at \; 25°C$$

The equilibrium lies far to the left, and the equilibrium concentrations of Ag^+ and Br^- ions are very low (7.31×10^{-7} M). As a result, removing unreacted AgBr from even a single roll of film using pure water would require tens of thousands of liters of water and a great deal of time. Le Châtelier's principle tells us, however, that we can drive the reaction to the right by removing one of the products, which will cause more AgBr to dissolve. Bromide ion is difficult to remove chemically, but silver ion forms a variety of stable two-coordinate complexes with neutral ligands, such as ammonia, or with anionic ligands, such as cyanide or thiosulfate ($S_2O_3^{2-}$). In photographic processing, excess AgBr is dissolved using a concentrated solution of sodium thiosulfate.



thiosulfate complex of Ag^+

The reaction of Ag^+ with thiosulfate is as follows:

Equation 17.10

$$Ag+(aq)+2S2O32-(aq) \square [Ag(S2O3)2]3-(aq)Kf=2.9\acute{}1013$$

The magnitude of the equilibrium constant indicates that almost all Ag^+ ions in solution will be immediately complexed by thiosulfate to form $[Ag(S_2O_3)_2]^{3-}$. We can see the effect of thiosulfate on the solubility of AgBr by writing the appropriate reactions and adding them together:

Equation 17.11

$$AgBr(s) \square Ag+(aq)+Br-(aq)Ag+(aq)+2S2O32-(aq)$$
$$\square [Ag(S2O3)2]3-(aq)AgBr(s)+2S2O32-(aq) \square [Ag(S2O3)2]3-(aq)+Br-(aq)KspKfK=5.35\acute{}10-13=2.9\acute{}1013=KspKf=15$$

Comparing K with K_{sp} shows that the formation of the complex ion increases the solubility of AgBr by approximately 3×10^{13}. The dramatic increase in solubility combined with the low cost and the low toxicity explains why sodium thiosulfate is almost universally used for developing black-and-white film. If desired, the silver can be recovered from the thiosulfate solution using any of several methods and recycled.

Note the Pattern

If a complex ion has a large K_f, the formation of a complex ion can dramatically increase the solubility of sparingly soluble salts.

EXAMPLE 6

Due to the common ion effect, we might expect a salt such as AgCl to be much less soluble in a concentrated solution of KCl than in water. Such an assumption would be incorrect, however, because it ignores the fact that silver ion tends to form a two-coordinate complex with chloride ions ($AgCl_2^-$). Calculate the solubility of AgCl in each situation:

a. in pure water

b. in 1.0 M KCl solution, ignoring the formation of any complex ions

c. the same solution as in part (b) except taking the formation of complex ions into account, assuming that $AgCl_2^-$ is the only Ag^+ complex that forms in significant concentrations

At 25°C, $K_{sp} = 1.77 \times 10^{-10}$ for AgCl and $K_f = 1.1 \times 10^5$ for $AgCl_2^-$.

Given: K_{sp} of AgCl, K_f of $AgCl_2^-$, and KCl concentration

Asked for: solubility of AgCl in water and in KCl solution with and without the formation of complex ions

Strategy:

A Write the solubility product expression for AgCl and calculate the concentration of Ag^+ and Cl^- in water.

B Calculate the concentration of Ag^+ in the KCl solution.

C Write balanced chemical equations for the dissolution of AgCl and for the formation of the $AgCl_2^-$ complex. Add the two equations and calculate the equilibrium constant for the overall equilibrium.

D Write the equilibrium constant expression for the overall reaction. Solve for the concentration of the complex ion.

Solution:

a. **A** If we let x equal the solubility of AgCl, then at equilibrium $[Ag^+] = [Cl^-] = x$ M. Substituting this value into the solubility product expression,

$$Ksp = [Ag+][Cl-]x = (x)(x) = x2 = 1.77 ´ 10 - 10 = 1.33 ´ 10 - 5$$ Thus the solubility of AgCl in pure water at 25°C is 1.33×10^{-5} M.

b. **B** If x equals the solubility of AgCl in the KCl solution, then at equilibrium $[Ag^+] = x$ M and $[Cl^-] =$ (1.0 + x) M. Substituting these values into the solubility product expression and assuming that $x << 1.0$,

c. $$Ksp = [Ag+][Cl-] = (x)(1.0 + x) » x(1.0) = 1.77 ´ 10 - 10 = x$$

$$AgCl(s) \square Ag + (aq) + Cl - (aq) Ag + (aq) + 2Cl -$$

$$\square [AgCl2] - AgCl(s) + Cl - \square [AgCl2] - KspKfK$$

$$= 1.77 ´ 10 - 10 = 1.1 ´ 105 = KspKf = 1.$$

If the common ion effect were the only important factor, we would predict that AgCl is approximately five orders of magnitude less soluble in a 1.0 M KCl solution than in water.

C To account for the effects of the formation of complex ions, we must first write the equilibrium equations for both the dissolution and the formation of complex ions. Adding the equations corresponding to $K_{sp}$and K_f gives us an equation that describes the dissolution of AgCl in a KCl solution. The equilibrium constant for the reaction is therefore the product of K_{sp} and K_f:

$$9 \times 10^{-5}$$

D If we let x equal the solubility of AgCl in the KCl solution, then at equilibrium $[AgCl_2^-] = x$ and $[Cl^-] = 1.0 - x$. Substituting these quantities into the equilibrium constant expression for the net reaction and assuming that x << 1.0,

$$K = [AgCl2^-][Cl^-] = x(1.0 - x) \approx 1.9 \times 10^{-5} = x$$

That is, AgCl dissolves in 1.0 M KCl to produce a 1.9×10^{-5} M solution of the $AgCl_2^-$ complex ion. Thus we predict that AgCl has approximately the same solubility in a 1.0 M KCl solution as it does in pure water, which is 10^5 times greater than that predicted based on the common ion effect. (In fact, the measured solubility of AgCl in 1.0 M KCl is almost a factor of 10 *greater* than that in pure water, largely due to the formation of other chloride-containing complexes.)

xercise

Calculate the solubility of mercury(II) iodide (HgI_2) in each situation:

a. pure water

b. a 3.0 M solution of NaI, assuming $[HgI_4]^{2-}$ is the only Hg-containing species present in significant amounts

$K_{sp} = 2.9 \times 10^{-29}$ for HgI_2 and $K_f = 6.8 \times 10^{29}$ for $[HgI_4]^{2-}$.

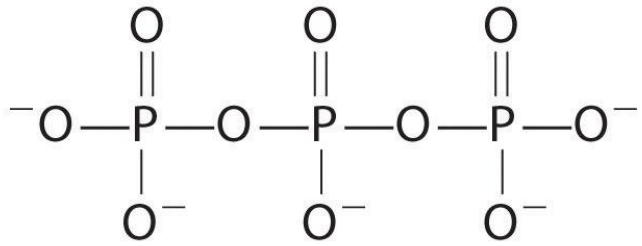
Answer:

a. 1.9×10^{-10} M

b. 1.4 M

Complexing agents, molecules or ions that increase the solubility of metal salts by forming soluble metal complexes, are common components of laundry detergents. Long-chain carboxylic acids, the major components of soaps, form insoluble salts with Ca^{2+} and Mg^{2+}, which are present in high concentrations in "hard" water. The precipitation of these salts produces a bathtub ring and gives a gray tinge to clothing. Adding a complexing agent such as pyrophosphate ($O_3POPO_3^{4-}$, or $P_2O_7^{4-}$) or triphosphate ($P_3O_{10}^{5-}$) to

detergents prevents the magnesium and calcium salts from precipitating because the equilibrium constant for complex-ion formation is large:

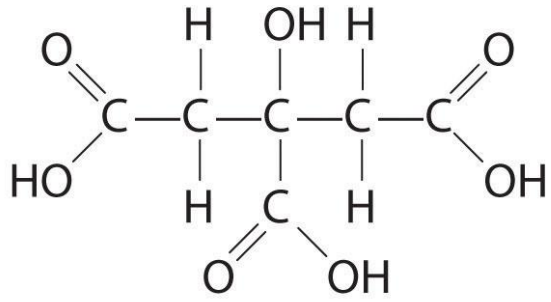


triphosphate

Equation 17.12

$$Ca2+(aq)+O3POPO34-(aq) \square [Ca(O3POPO3)]2-(aq) Kf = 4 \acute{} 104$$

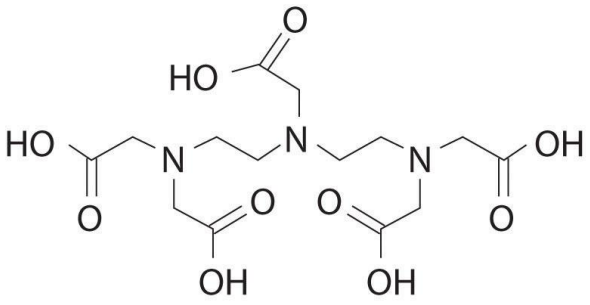
However, phosphates can cause environmental damage by promoting *eutrophication*, the growth of excessive amounts of algae in a body of water, which can eventually lead to large decreases in levels of dissolved oxygen that kill fish and other aquatic organisms. Consequently, many states in the United States have banned the use of phosphate-containing detergents, and France has banned their use beginning in 2007. “Phosphate-free” detergents contain different kinds of complexing agents, such as derivatives of acetic acid or other carboxylic acids. The development of phosphate substitutes is an area of intense research.



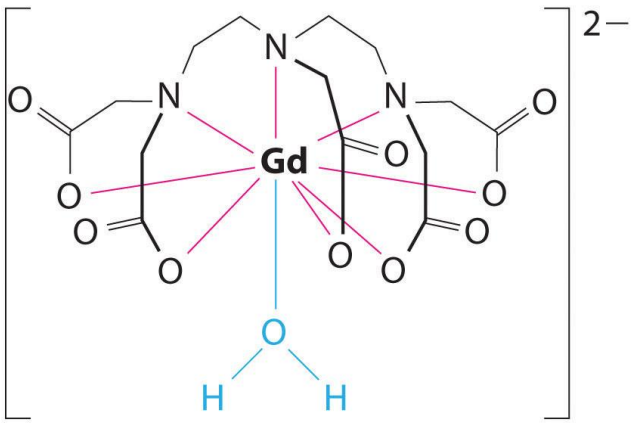
Citric acid,
a hydroxy polycarboxylic acid

Commercial water softeners also use a complexing agent to treat hard water by passing the water over ion-exchange resins, which are complex sodium salts. When water flows over the resin, sodium ion is dissolved, and insoluble salts precipitate onto the resin surface. Water treated in this way has a saltier taste due to the presence of Na^+, but it contains fewer dissolved minerals.

Another application of complexing agents is found in medicine. Unlike x-rays, magnetic resonance imaging (MRI) can give relatively good images of soft tissues such as internal organs. MRI is based on the magnetic properties of the ^{1}H nucleus of hydrogen atoms in water, which is a major component of soft tissues. Because the properties of water do not depend very much on whether it is inside a cell or in the blood, it is hard to get detailed images of these tissues that have good contrast. To solve this problem, scientists have developed a class of metal complexes known as "MRI contrast agents." Injecting an MRI contrast agent into a patient selectively affects the magnetic properties of water in cells of normal tissues, in tumors, or in blood vessels and allows doctors to "see" each of these separately (Figure 17.5 "An MRI Image of the Heart, Arteries, and Veins"). One of the most important metal ions for this application is Gd^{3+}, which with seven unpaired electrons is highly paramagnetic. Because $Gd^{3+}(aq)$ is quite toxic, it must be administered as a very stable complex that does not dissociate in the body and can be excreted intact by the kidneys. The complexing agents used for gadolinium are ligands such as $DTPA^{5-}$ (diethylene triamine pentaacetic acid), whose fully protonated form is shown here.



DTPA (diethylenetriaminepentaacetic acid)



gadolinium-DTPA complex, $[Gd(DTPA{\cdot}H_2O)]^{2-}$

Figure 17.5 *An MRI Image of the Heart, Arteries, and Veins*

Summary

A **complex ion** is a species formed between a central metal ion and one or more surrounding **ligands**, molecules or ions that contain at least one lone pair of electrons. Small, highly charged metal ions have the greatest tendency to act as Lewis acids and form complex ions. The equilibrium constant for the formation of the complex ion is the **formation constant (*K*f)**. The formation of a complex ion by adding a *complexing agent* increases the solubility of a compound.

KEY TAKEAWAY

- The formation of complex ions can substantially increase the solubility of sparingly soluble salts if the complex ion has a large K_f.

CONCEPTUAL PROBLEMS

1. What is the difference between K_{eq} and K_f?
2. Which would you expect to have the greater tendency to form a complex ion: Mg^{2+} or Ba^{2+}? Why?
3. How can a ligand be used to affect the concentration of hydrated metal ions in solution? How is K_{sp} affected? Explain your answer.
4. Co(II) forms a complex ion with pyridine (C_5H_5N). Which is the Lewis acid, and which is the Lewis base? Use Lewis electron structures to justify your answer.

NUMERICAL PROBLEMS

1. Fe(II) forms the complex ion $[Fe(OH)_4]^{2-}$ through equilibrium reactions in which hydroxide replaces water in a stepwise manner. If log K_1 = 5.56, log K_2 = 4.21, log K_3 = −0.10, and log K_4 = −1.09, what is K_f? Write the equilibrium equation that corresponds to each stepwise equilibrium constant. Do you expect the $[Fe(OH)_4]^{2-}$ complex to be stable? Explain your reasoning.
2. Zn(II) forms the complex ion $[Zn(NH_3)_4]^{2+}$ through equilibrium reactions in which ammonia replaces coordinated water molecules in a stepwise manner. If log K_1 = 2.37, log K_2 = 2.44, log K_3 = 2.50, and log K_4 = 2.15, what is the overall K_f? Write the equilibrium equation that corresponds to each stepwise equilibrium constant. Do you expect the $[Zn(NH_3)_4]^{2+}$ complex to be stable? Explain your reasoning.
3. Although thallium has limited commercial applications because it is toxic to humans (10 mg/kg body weight is fatal to children), it is used as a substitute for mercury in industrial switches. The complex ion $[TlBr_6]^{3-}$ is

highly stable, with log K_f = 31.6. What is the concentration of Tl(III)(aq) in equilibrium with a 1.12 M solution of $Na_3[TlBr_6]$?

ANSWER

1.

$$[Fe(H2O)6]2+(aq)+OH-(aq)$$
$$\square\ [Fe(H2O(aq))5(OH)]+(aq)+H2OlogK1=5.56$$
$$[Fe(H2O)5(OH)]+(aq)+OH-(aq)$$
$$\square\ [Fe(H2O)4(OH)2](aq)+H2O(aq)logK2=9.77$$
$$[Fe(H2O)4(OH)2](aq)+OH-(aq)$$
$$\square\ [Fe(H2O)3(OH)3]-(aq)+H2O(aq)logK3=9.67$$
$$[Fe(H2O)3(OH)3]-(aq)+OH-(aq)$$
$$\square\ [Fe(OH)4]2-(aq)+3H2O(l)logK4=8.58$$

$$[Fe(H2O)6]2+(aq)+4OH-(aq)logKf$$
$$\square\ [Fe(OH)4]2-(aq)+6H2O(l)=logK1+logK2+logK2+logK4=33.58$$

Thus, K_f = 3.8×10^{33}. Because $[Fe(OH)_4]^{2-}$ has a very large value of K_f, it should be stable in the presence of excess OH^-.

[1] The hydrated Cu^{2+} ion contains six H_2O ligands, but the complex ion that is produced contains only four NH_3 ligands, not six. The reasons for this apparently unusual behavior will be discussed in Chapter 23 "The ".

17.4 Solubility and pH

LEARNING OBJECTIVE

1. To understand why the solubility of many compounds depends on pH.

The solubility of many compounds depends strongly on the pH of the solution. For example, the anion in many sparingly soluble salts is the conjugate base of a weak acid that may become protonated in solution. In addition, the solubility of simple binary compounds such as oxides and sulfides, both strong bases, is often dependent on pH. In this section, we discuss the relationship between the solubility of these classes of compounds and pH.

The Effect of Acid–Base Equilibriums on the Solubility of Salts

We begin our discussion by examining the effect of pH on the solubility of a representative salt, M^+A^-, where A^- is the conjugate base of the weak acid HA. When the salt dissolves in water, the following reaction occurs:

Equation 17.13

$$MA(s) \rightleftharpoons M+(aq)+A-(aq) \quad Ksp=[M+][A-]$$

The anion can also react with water in a hydrolysis reaction:

Equation 17.14

$$A-(aq)+H2O(l) \rightleftharpoons OH-(aq)+HA(aq)$$

Because of the reaction described in Equation 17.14, the predicted solubility of a sparingly soluble salt that has a basic anion such as S^{2-}, PO_4^{3-}, or CO_3^{2-} is increased, as described in Section 17.1 "Determining the Solubility of Ionic Compounds". If instead a strong acid is added to the solution, the added H^+ will react essentially completely with A^- to form HA. This reaction decreases $[A^-]$, which decreases the magnitude of the ion product ($Q = [M^+][A^-]$). According to Le Châtelier's principle, more MA will dissolve until $Q = K_{sp}$. Hence *an acidic pH dramatically increases the solubility of virtually all sparingly soluble salts whose anion is the conjugate base of a weak acid*. In contrast, pH has little to no effect on the solubility of salts whose anion is the conjugate base of a stronger weak acid or a *strong* acid, respectively (e.g., chlorides, bromides, iodides, and sulfates). For example, the hydroxide salt $Mg(OH)_2$ is relatively insoluble in water:

Equation 17.15

$$Mg(OH)2(s) \rightleftharpoons Mg2+(aq)+2OH-(aq) \quad Ksp=5.61\times 10-12$$

When acid is added to a saturated solution that contains excess solid $Mg(OH)_2$, the following reaction occurs, removing OH^- from solution:

Equation 17.16

$$H+(aq)+OH-(aq) \rightarrow H2O(l)$$

The overall equation for the reaction of $Mg(OH)_2$ with acid is thus

Equation 17.17

$$Mg(OH)2(s)+2H+(aq) \rightleftharpoons Mg2+(aq)+2H2O(l)$$

As more acid is added to a suspension of $Mg(OH)_2$, the equilibrium shown in Equation 17.17 is driven to the right, so more $Mg(OH)_2$ dissolves.

Such pH-dependent solubility is not restricted to salts that contain anions derived from water. For example, CaF_2 is a sparingly soluble salt:

Equation 17.18

$$CaF2(s) \rightleftharpoons Ca2+(aq)+2F-(aq) \quad Ksp=3.45\times 10-11$$

When strong acid is added to a saturated solution of CaF_2, the following reaction occurs:

Equation 17.19

$$H+(aq)+F-(aq) \square \quad HF(aq)$$

Because the forward reaction decreases the fluoride ion concentration, more CaF_2dissolves to relieve the stress on the system. The net reaction of CaF_2 with strong acid is thus

Equation 17.20

$CaF_2(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + 2HF(aq)$

Example 7 shows how to calculate the solubility effect of adding a strong acid to a solution of a sparingly soluble salt.

Note the Pattern

Sparingly soluble salts derived from weak acids tend to be more soluble in an acidic solution.

EXAMPLE 7

Lead oxalate (PbC_2O_4), lead iodide (PbI_2), and lead sulfate ($PbSO_4$) are all rather insoluble, with K_{sp} values of 4.8×10^{-10}, 9.8×10^{-9}, and 2.53×10^{-8}, respectively. What effect does adding a strong acid, such as perchloric acid, have on their relative solubilities?

Given: K_{sp} values for three compounds

Asked for: relative solubilities in acid solution

Strategy:

Write the balanced chemical equation for the dissolution of each salt. Because the strongest conjugate base will be most affected by the addition of strong acid, determine the relative solubilities from the relative basicity of the anions.

Solution:

The solubility equilibriums for the three salts are as follows:

$$PbC2O4(s) \square \quad Pb2+(aq)+C2O42-(aq) PbI2(s)$$

$$\square \quad Pb2+(aq)+2I-(aq) PbSO4(s) \square \quad Pb2+(aq)+SO42-(aq)$$

The addition of a strong acid will have the greatest effect on the solubility of a salt that contains the conjugate base of a weak acid as the anion. Because HI is a strong acid, we predict that adding a strong acid to a saturated solution of PbI_2 will not greatly affect its solubility; the acid will simply dissociate to form H^+(aq) and the corresponding anion. In contrast, oxalate is the fully deprotonated form of oxalic acid

(HO_2CCO_2H), which is a weak diprotic acid (pK_{a1} = 1.23 and pK_{a2} = 4.19). Consequently, the oxalate ion has a significant affinity for one proton and a lower affinity for a second proton. Adding a strong acid to a saturated solution of lead oxalate will result in the following reactions:

$$C2O42\text{-}(aq)+H+(aq)\rightarrow HO2CCO2$$

$$\text{-}(aq)HO2CCO2\text{-}(aq)+H+(aq)\rightarrow HO2CCO2H(aq)$$

These reactions will decrease [$C_2O_4^{2-}$], causing more lead oxalate to dissolve to relieve the stress on the system.The pK_a of HSO_4^- (1.99) is similar in magnitude to the pK_{a1} of oxalic acid, so adding a strong acid to a saturated solution of $PbSO_4$ will result in the following reaction:

$$SO_4^{2-}(aq) + H^+(aq) \rightleftharpoons HSO_4^-(aq)$$

Because HSO_4^- has a pKa of 1.99, this reaction will lie largely to the left as written. Consequently, we predict that the effect of added strong acid on the solubility of $PbSO_4$ will be significantly less than for PbC_2O_4.

Exercise

Which of the following insoluble salts—AgCl, Ag_2CO_3, Ag_3PO_4, and/or AgBr—will be substantially more soluble in 1.0 M HNO_3 than in pure water?

Answer: Ag_2CO_3 and Ag_3PO_4

Caves and their associated pinnacles and spires of stone provide one of the most impressive examples of pH-dependent solubility equilibriums (part (a) in Figure 17.6 "The Chemistry of Cave Formation"). Perhaps the most familiar caves are formed from limestone, such as Carlsbad Caverns in New Mexico, Mammoth Cave in Kentucky, and Luray Caverns in Virginia. The primary reactions that are responsible for the formation of limestone caves are as follows:

Equation 17.21

$$CO2(aq)+H2O(l)\square\ \ H+(aq)+HCO3\text{-}(aq)$$

Equation 17.22

$$HCO3\text{-}(aq)\square\ \ H+(aq)+CO32\text{-}(aq)$$

Equation 17.23

$$Ca2+(aq)+CO32\text{-}(aq)\square\ \ CaCO3(s)$$

Limestone deposits that form caves consist primarily of $CaCO_3$ from the remains of living creatures such as clams and corals, which used it for making structures such as shells. When a saturated solution of $CaCO_3$ in CO_2-rich water rises toward Earth's surface or is otherwise heated, CO_2 gas is released as the water warms. $CaCO_3$ then precipitates from the solution according to the following equation (part (b) in Figure 17.6 "The Chemistry of Cave Formation"):

Equation 17.24

$$Ca2+(aq)+2HCO3-(aq) \rightleftharpoons CaCO3(s)+CO2(g)+H2O(l)$$

The forward direction is the same reaction that produces the solid called *scale* in teapots, coffee makers, water heaters, boilers, and other places where hard water is repeatedly heated.

When groundwater-containing atmospheric CO_2 (Equation 17.21 and Equation 17.22) finds its way into microscopic cracks in the limestone deposits, $CaCO_3$ dissolves in the acidic solution in the reverse direction of Equation 17.24. The cracks gradually enlarge from 10–50 μm to 5–10 mm, a process that can take as long as 10,000 yr. Eventually, after about another 10,000 yr, a cave forms. Groundwater from the surface seeps into the cave and clings to the ceiling, where the water evaporates and causes the equilibrium in Equation 17.24 to shift to the right. A circular layer of solid $CaCO_3$ is deposited, which eventually produces a long, hollow spire of limestone called a*stalactite* that grows down from the ceiling. Below, where the droplets land when they fall from the ceiling, a similar process causes another spire, called a *stalagmite*, to grow up. The same processes that carve out hollows below ground are also at work above ground, in some cases producing fantastically convoluted landscapes like that of Yunnan Province in China (Figure 17.7 "Solubility Equilibriums in the Formation of Karst Landscapes").

Acidic, Basic, and Amphoteric Oxides and Hydroxides

One of the earliest classifications of substances was based on their solubility in acidic versus basic solution, which led to the classification of oxides and hydroxides as being either basic or acidic. Basic oxides and hydroxides either react with water to produce a basic solution or dissolve readily in aqueous acid.Acidic oxides or hydroxides either react with water to produce an acidic solution or are soluble in aqueous base. As shown in Figure 17.8 "Classification of the Oxides of the Main Group Elements According to Their Acidic or Basic Character", there is a clear correlation between the acidic or the basic character of an oxide and the position of the element combined with oxygen in the periodic

table. *Oxides of metallic elements are generally basic oxides, and oxides of nonmetallic elements are acidic oxides*. Compare, for example, the reactions of a typical metal oxide, cesium oxide, and a typical nonmetal oxide, sulfur trioxide, with water:

Equation 17.25

$$Cs2O(s) + H2O(l) \rightarrow 2Cs + (aq) + 2OH - (aq)$$

Equation 17.26

$$SO3(g) + H2O(l) \rightarrow H2SO4(aq)$$

Cesium oxide reacts with water to produce a basic solution of cesium hydroxide, whereas sulfur trioxide reacts with water to produce a solution of sulfuric acid—very different behaviors indeed!

Note the Pattern

Metal oxides generally react with water to produce basic solutions, whereas nonmetal oxides produce acidic solutions.

The difference in reactivity is due to the difference in bonding in the two kinds of oxides. Because of the low electronegativity of the metals at the far left in the periodic table, their oxides are best viewed as containing discrete M^{n+} cations and O^{2-} anions. At the other end of the spectrum are nonmetal oxides; due to their higher electronegativities, nonmetals form oxides with covalent bonds to oxygen. Because of the high electronegativity of oxygen, however, the covalent bond between oxygen and the other atom, E, is usually polarized: $E^{\delta+}$–$O^{\delta-}$. The atom E in these oxides acts as a Lewis acid that reacts with the oxygen atom of water to produce an oxoacid. Oxides of metals in high oxidation states also tend to be acidic oxides for the same reason: they contain covalent bonds to oxygen. An example of an acidic metal oxide is MoO_3, which is insoluble in both water and acid but dissolves in strong base to give solutions of the molybdate ion (MoO_4^{2-}):

Equation 17.27

$$MoO_3(s) + 2OH^-(aq) \rightarrow MoO_4^{2-}(aq) + H_2O(l)$$

As shown in Figure 17.8 "Classification of the Oxides of the Main Group Elements According to Their Acidic or Basic Character", there is a gradual transition from basic metal oxides to acidic nonmetal oxides as we go from the lower left to the upper right in the periodic table, with a broad diagonal band of oxides of intermediate character separating the two extremes. Many of the oxides of the elements in this diagonal region of the periodic table are soluble in both acidic *and* basic solutions; consequently, they are called amphoteric oxides (from the Greek *ampho*, meaning “both,” as in*amphiprotic*, which was defined

in Chapter 16 "Aqueous Acid–Base Equilibriums",Section 16.1 "The Autoionization of Water"). Amphoteric oxides either dissolve in acid to produce water or dissolve in base to produce a soluble complex. As shown in Figure 17.9 "Chromium(III) Hydroxide [Cr(OH)", for example, mixing the amphoteric oxide $Cr(OH)_3$ (also written as $Cr_2O_3 \cdot 3H_2O$) with water gives a muddy, purple-brown suspension. Adding acid causes the $Cr(OH)_3$ to dissolve to give a bright violet solution of $Cr^{3+}(aq)$, which contains the $[Cr(H_2O)_6]^{3+}$ ion, whereas adding strong base gives a green solution of the $[Cr(OH)_4]^-$ ion. The chemical equations for the reactions are as follows:

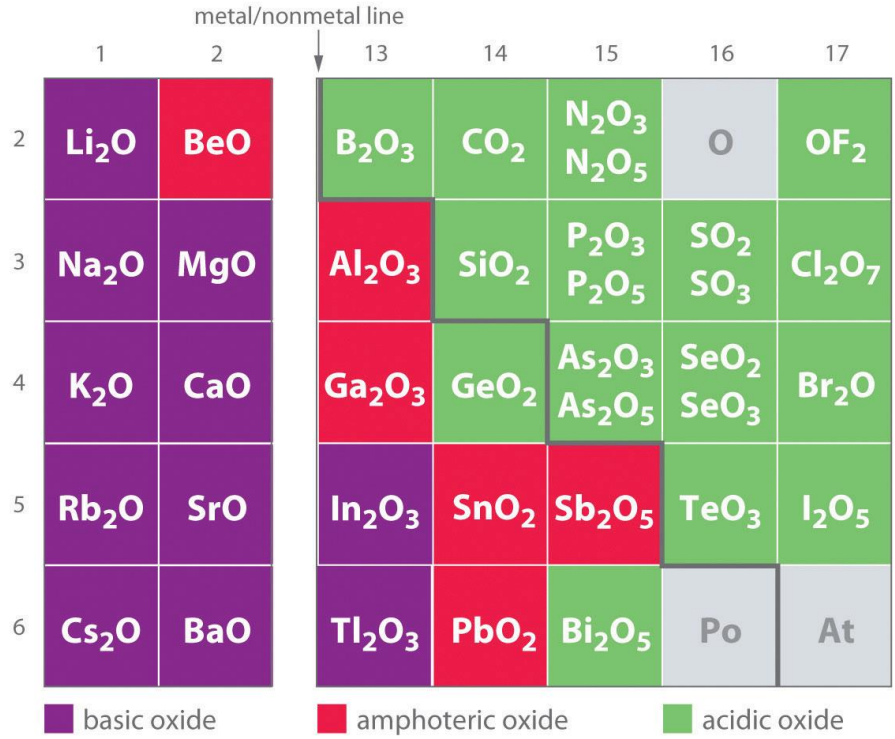
Equation 17.28

$$Cr(OH)3(s)+3H+(aq)\rightarrow Cr3+(aq)\ violet+3H2O(l)$$

Equation 17.29

$$Cr(OH)3(s)+OH\text{ -}(aq)\rightarrow[Cr(OH)4]\text{ -}\ green(aq)$$

Figure 17.8 *Classification of the Oxides of the Main Group Elements According to Their Acidic or Basic Character*



There is a gradual transition from basic oxides to acidic oxides from the lower left to the upper right in the periodic table. Oxides of metallic elements are generally basic oxides, which either react with water to form a basic solution or dissolve in aqueous acid. In contrast, oxides of nonmetallic

elements are acidic oxides, which either react with water to form an acidic solution or are soluble in aqueous base. Oxides of intermediate character, called amphoteric oxides, are located along a diagonal line between the two extremes. Amphoteric oxides either dissolve in acid to produce water or dissolve in base to produce a soluble complex ion. (Radioactive elements are not classified.)
All three beakers originally contained a suspension of brownish purple $Cr(OH)_3(s)$ (center). When concentrated acid (6 M H_2SO_4) was added to the beaker on the left, $Cr(OH)_3$ dissolved to produce violet $[Cr(H_2O)_6]^{3+}$ ions and water. The addition of concentrated base (6 M NaOH) to the beaker on the right caused $Cr(OH)_3$ to dissolve, producing green $[Cr(OH)_4]^-$ ions.

EXAMPLE 8

Aluminum hydroxide, written as either $Al(OH)_3$ or $Al_2O_3 \cdot 3H_2O$, is amphoteric. Write chemical equations to describe the dissolution of aluminum hydroxide in (a) acid and (b) base.

Given: amphoteric compound

Asked for: dissolution reactions in acid and base

Strategy:

Using Equation 17.28 and Equation 17.29 as a guide, write the dissolution reactions in acid and base solutions.

Solution:

a. An acid donates protons to hydroxide to give water and the hydrated metal ion, so aluminum hydroxide, which contains three OH^- ions per Al, needs three H^+ ions:

$$Al(OH)_3(s) + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3H_2O(l)$$

In aqueous solution, Al^{3+} forms the complex ion $[Al(H_2O)_6]^{3+}$.

b. In basic solution, OH^- is added to the compound to produce a soluble and stable poly(hydroxo) complex:

$$Al(OH)_3(s) + OH^-(aq) \rightarrow [Al(OH)_4]^-(aq)$$

Exercise

Copper(II) hydroxide, written as either $Cu(OH)_2$ or $CuO \cdot H_2O$, is amphoteric. Write chemical equations that describe the dissolution of cupric hydroxide both in an acid and in a base.

Answer:

$Cu(OH)_2(s) + 2H^+(aq) \rightarrow Cu^{2+}(aq) + 2H_2O(l) Cu(OH)_2(s) + 2OH^-(aq) \rightarrow [Cu(OH)_4]^{2-}(aq)$

Selective Precipitation Using pH

Many dissolved metal ions can be separated by the selective precipitation of the cations from solution under specific conditions. In this technique, pH is often used to control the concentration of the anion in solution, which controls which cations precipitate.

Note the Pattern

The concentration of anions in solution can often be controlled by adjusting the pH, thereby allowing the selective precipitation of cations.

Suppose, for example, we have a solution that contains 1.0 mM Zn^{2+} and 1.0 mM $Cd^{2+}$and want to separate the two metals by selective precipitation as the insoluble sulfide salts, ZnS and CdS. The relevant solubility equilibriums can be written as follows:

Equation 17.30

$$ZnS(s) \rightleftharpoons Zn2+(aq)+S2-(aq) \quad Ksp = 1.6 \times 10-24$$

Equation 17.31

$$CdS(s) \rightleftharpoons Cd2+(aq)+S2-(aq) \quad Ksp = 8.0 \times 10-27$$

Because the S^{2-} ion is quite basic and reacts extensively with water to give HS^- and OH^-, the solubility equilibriums are more accurately written as $MS(s) \rightleftharpoons M2+(aq)+HS-(aq)+OH-$ rather than $MS(s) \rightleftharpoons M2+(aq)+S2-(aq)$. *Here we use* the simpler form involving S^{2-}, which is justified because we take the reaction of S^{2-} with water into account later in the solution, arriving at the same answer using either equilibrium equation.

The sulfide concentrations needed to cause ZnS and CdS to precipitate are as follows:

Equation 17.32

$$Ksp 1.6 \times 10-24 1.6 \times 10-21\ M = [Zn2+][S2-] = (0.0010\ M)[S2-] = [S2-]$$

Equation 17.33

$$Ksp 8.0 \times 10-27 8.0 \times 10-24\ M = [Cd2+][S2-] = (0.0010\ M)[S2-] = [S2-]$$

Thus sulfide concentrations between 1.6×10^{-21} M and 8.0×10^{-24} M will precipitate CdS from solution but not ZnS. How do we obtain such low concentrations of sulfide? A saturated aqueous solution of H_2S contains 0.10 M H_2S at 20°C. The pK_{a1} for H_2S is 6.97, and pK_{a2} corresponding to the formation of $[S^{2-}]$ is 12.90. The equations for these reactions are as follows:

Equation 17.34

$$H2S(aq) \rightleftharpoons H+(aq)+HS-(aq)HS-(aq) \rightleftharpoons H+(aq)+S2-(aq)pKa1=6.97, pKa2=12.90, Ka1=1.1\times 10-7Ka2=1.3\times 10-13$$

We can show that the concentration of S^{2-} is 1.3×10^{-13} by comparing K_{a1} and K_{a2} and recognizing that the contribution to $[H^+]$ from the dissociation of HS^- is negligible compared with $[H^+]$ from the dissociation of H_2S. Thus substituting 0.10 M in the equation for K_{a1} for the concentration of H_2S, which is essentially constant regardless of the pH, gives the following:

Equation 17.35

$$Ka1=1.1\times 10-7=[H+][HS-][H2S]=x0.10\ Mx=1.1\times 10-4\ M=[H+]=[HS-]$$

Substituting this value for $[H^+]$ and $[HS^-]$ into the equation for K_{a2},

$$Ka2=1.3\times 10-13=$$

$$[H+][S2-][HS-]=(1.1\times 10-4\ M)x1.1\times 10-4\ M=x=[S2-]$$

Although $[S^{2-}]$ in an H_2S solution is very low (1.3×10^{-13} M), bubbling H_2S through the solution until it is saturated would precipitate both metal ions because the concentration of S^{2-} would then be much greater than 1.6×10^{-21} M. Thus we must adjust $[S^{2-}]$ to stay within the desired range. The most direct way to do this is to adjust $[H^+]$ by adding acid to the H_2S solution (recall Le Châtelier's principle), thereby driving the equilibrium in Equation 17.34 to the left. The overall equation for the dissociation of H_2S is as follows:

Equation 17.36

$$H2S(aq) \rightleftharpoons 2H+(aq)+S2-(aq)$$

Now we can use the equilibrium constant K for the overall reaction, which is the product of K_{a1} and K_{a2}, and the concentration of H_2S in a saturated solution to calculate the H^+ concentration needed to produce $[S^{2-}]$ of 1.6×10^{-21} M:

Equation 17.37

$$K=Ka1Ka2=(1.1\times 10-7)(1.3\times 10-13)=1.4\times 10-20=[H+]2[S2-][H2S]$$

Equation 17.38

$$[H+]2=K[H2S][S2-]=(1.4\times 10-20)(0.10\ M)1.6\times 10-21\ M=0.88[H+]=0.94$$

Thus adding a strong acid such as HCl to make the solution 0.94 M in H^+ will prevent the more soluble ZnS from precipitating while ensuring that the less soluble CdS will precipitate when the solution is saturated with H_2S.

EXAMPLE 9

A solution contains 0.010 M Ca^{2+} and 0.010 M La^{3+}. What concentration of HCl is needed to precipitate $La_2(C_2O_4)_3 \cdot 9H_2O$ but not $Ca(C_2O_4) \cdot H_2O$ if the concentration of oxalic acid is 1.0 M? K_{sp} values are 2.32×10^{-9} for $Ca(C_2O_4)$ and 2.5×10^{-27} for $La_2(C_2O_4)_3$; $pK_{a1} = 1.25$ and $pK_{a2} = 3.81$ for oxalic acid.

Given: concentrations of cations, K_{sp} values, and concentration and pK_a values for oxalic acid

Asked for: concentration of HCl needed for selective precipitation of $La_2(C_2O_4)_3$

Strategy:

A Write each solubility product expression and calculate the oxalate concentration needed for precipitation to occur. Determine the concentration range needed for selective precipitation of $La_2(C_2O_4)_3 \cdot 9H_2O$.

B Add the equations for the first and second dissociations of oxalic acid to get an overall equation for the dissociation of oxalic acid to oxalate. Substitute the $[ox^{2-}]$ needed to precipitate $La_2(C_2O_4)_3 \cdot 9H_2O$ into the overall equation for the dissociation of oxalic acid to calculate the required $[H^+]$.

Solution:

A Because the salts have different stoichiometries, we cannot directly compare the magnitudes of the solubility products. Instead, we must use the equilibrium constant expression for each solubility product to calculate the concentration of oxalate needed for precipitation to occur. Using ox^{2-} for oxalate, we write the solubility product expression for calcium oxalate as follows:

$$Ksp = [Ca2+][ox2-][ox2-]$$
$$= (0.010)[ox2-] = 2.32 \times 10-9 = 2.32 \times 10-7\ M$$

The expression for lanthanum oxalate is as follows:

$$Ksp = [La3+]2[ox2-]3[ox2-]$$
$$= (0.010)2[ox2-]3 = 2.5 \times 10-27 = 2.9 \times 10-8\ M$$

Thus lanthanum oxalate is less soluble and will selectively precipitate when the oxalate concentration is between 2.9×10^{-8} M and 2.32×10^{-7} M.

B To prevent Ca^{2+} from precipitating as calcium oxalate, we must add enough H^+ to give a maximum oxalate concentration of 2.32×10^{-7} M. We can calculate the required $[H^+]$ by using the overall equation for the dissociation of oxalic acid to oxalate:

$$HO2CCO2H(aq) \rightleftharpoons 2H+(aq) + C2O42-(aq)$$

$$K = Ka1Ka2 = (10-1.25)(10-3.81) = 10-5.06 = 8.7 \times 10-6$$

Substituting the desired oxalate concentration into the equilibrium constant expression,

$$8.7 \times 10^{-6} = [H^+]^2[ox^{2-}][HO_2CCO_2H][H^+] = [H^+]^2(2.32 \times 10^{-7})1.0 = 6.1\ M$$ Thus adding enough HCl to give $[H^+]$ = 6.1 M will cause only $La_2(C_2O_4)_3 \cdot 9H_2O$ to precipitate from the solution.

Exercise

A solution contains 0.015 M Fe^{2+} and 0.015 M Pb^{2+}. What concentration of acid is needed to ensure that Pb^{2+} precipitates as PbS in a saturated solution of H_2S, but Fe^{2+}does not precipitate as FeS? K_{sp} values are 6.3×10^{-18} for FeS and 8.0×10^{-28} for PbS.

Answer: 0.018 M H^+

Summary

The anion in many sparingly soluble salts is the conjugate base of a weak acid. At low pH, protonation of the anion can dramatically increase the solubility of the salt. Oxides can be classified as acidic oxides or basic oxides. **Acidic oxides**either react with water to give an acidic solution or dissolve in strong base; most acidic oxides are nonmetal oxides or oxides of metals in high oxidation states.**Basic oxides** either react with water to give a basic solution or dissolve in strong acid; most basic oxides are oxides of metallic elements. Oxides or hydroxides that are soluble in both acidic and basic solutions are called **amphoteric oxides**. Most elements whose oxides exhibit amphoteric behavior are located along the diagonal line separating metals and nonmetals in the periodic table. In solutions that contain mixtures of dissolved metal ions, the pH can be used to control the anion concentration needed to selectively precipitate the desired cation.

KEY TAKEAWAY

- The anion in sparingly soluble salts is often the conjugate base of a weak acid that may become protonated in solution, so the solubility of simple oxides and sulfides, both strong bases, often depends on pH.

CONCEPTUAL PROBLEMS

1. Which of the following will show the greatest increase in solubility if 1 M HNO_3 is used instead of distilled water? Explain your reasoning.

a. $CuCl_2$

b. $K[Pb(OH)_3]$

c. $Ba(CH_3CO_2)_2$

d. $CaCO_3$

2. Of the compounds $Sn(CH_3CO_2)_2$ and SnS, one is soluble in dilute HCl and the other is soluble only in hot, concentrated HCl. Which is which? Provide a reasonable explanation.
3. Where in the periodic table do you expect to find elements that form basic oxides? Where do you expect to find elements that form acidic oxides?
4. Because water can autoionize, it reacts with oxides either as a base (as OH^-) or as an acid (as H_3O^+). Do you expect oxides of elements in high oxidation states to be more acidic (reacting with OH^-) or more basic (reacting with H_3O^+) than the corresponding oxides in low oxidation states? Why?
5. Given solid samples of CrO, Cr_2O_3, and CrO_3, which would you expect to be the most acidic (reacts most readily with OH^-)? Which would be the most basic (reacts most readily with H_3O^+)? Why?
6. Which of these elements—Be, B, Al, N, Se, In, Tl, Pb—do you expect to form an amphoteric oxide? Why?

NUMERICAL PROBLEMS

1. A 1.0 L solution contains 1.98 M $Al(NO_3)_3$. What are $[OH^-]$ and $[H^+]$? What pH is required to precipitate the cation as $Al(OH)_3$? $K_{sp} = 1.3 \times 10^{-33}$ and $K_a = 1.05 \times 10^{-5}$ for the hydrated Al^{3+} ion.
2. A 1.0 L solution contains 2.03 M $CoCl_2$. What is $[H^+]$? What pH is required to precipitate the cation as $Co(OH)_2$? $K_{sp} = 5.92 \times 10^{-15}$ and $K_a = 1.26 \times 10^{-9}$ for the hydrated Co^{2+} ion.
3. Given 100 mL of a solution that contains 0.80 mM Ag^+ and 0.80 mM Cu^+, can the two metals be separated by selective precipitation as the insoluble bromide salts by adding 10 mL of an 8.0 mM solution of KBr? K_{sp} values are 6.27×10^{-9} for CuBr and 5.35×10^{-13} for AgBr. What maximum $[Br^-]$ will separate the ions?
4. Given 100 mL of a solution that is 1.5 mM in Tl^+, Zn^{2+}, and Ni^{2+}, which ions can be separated from solution by adding 5.0 mL of a 12.0 mM solution of $Na_2C_2O_4$?

Precipitate	K_{sp}
$Tl_2C_2O_4$	2×10^{-4}
$ZnC_2O_4 \cdot 2H_2O$	1.38×10^{-9}
NiC_2O_4	4×10^{-10}

5. How many milliliters of 12.0 mM $Na_2C_2O_4$ should be added to separate Tl^+ and Zn^{2+} from Ni^{2+}?

ANSWERS

1. $[H^+] = 4.56 \times 10^{-3}$; $[OH^-] = 2.19 \times 10^{-12}$; pH = 2.94

2.

3. No; both metal ions will precipitate; AgBr will precipitate as Br^- is added, and CuBr will begin to precipitate at $[Br^-] = 8.6 \times 10^{-6}$ M.

17.5 Qualitative Analysis Using Selective Precipitation

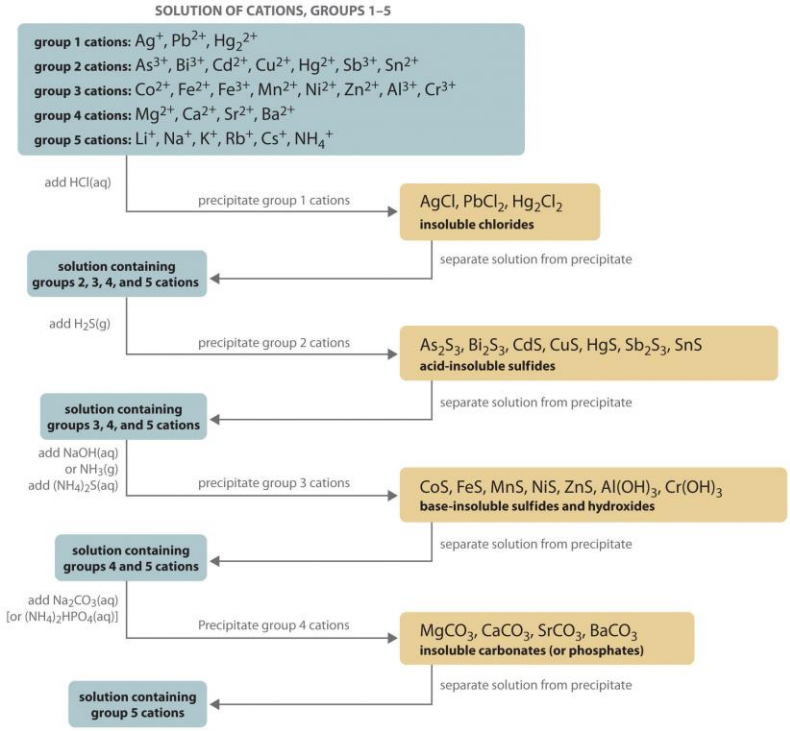
LEARNING OBJECTIVE

1. To know how to separate metal ions by selective precipitation.

The composition of relatively complex mixtures of metal ions can be determined using**qualitative analysis**, a procedure for discovering the *identity* of metal ions present in the mixture (rather than quantitative information about their amounts).

The procedure used to separate and identify more than 20 common metal cations from a single solution consists of selectively precipitating only a few kinds of metal ions at a time under given sets of conditions. Consecutive precipitation steps become progressively *less* selective until almost all of the metal ions are precipitated, as illustrated in Figure 17.10 "Steps in a Typical Qualitative Analysis Scheme for a Solution That Contains Several Metal Ions".

Figure 17.10 *Steps in a Typical Qualitative Analysis Scheme for a Solution That Contains Several Metal Ions*



Group 1: Insoluble Chlorides

Most metal chloride salts are soluble in water; only Ag^+, Pb^{2+}, and Hg_2^{2+} form chlorides that precipitate from water. Thus the first step in a qualitative analysis is to add about 6 M HCl, thereby causing AgCl, $PbCl_2$, and/or Hg_2Cl_2 to precipitate. If no precipitate forms, then these cations are not present in significant amounts. The precipitate can be collected by filtration or centrifugation.

Group 2: Acid-Insoluble Sulfides

Next, the acidic solution is saturated with H_2S gas. Only those metal ions that form very insoluble sulfides, such as As^{3+}, Bi^{3+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Sb^{3+}, and Sn^{2+}, precipitate as their sulfide salts under these acidic conditions. All others, such as $Fe^{2+}$and Zn^{2+}, remain in solution. Once again, the precipitates are collected by filtration or centrifugation.

Group 3: Base-Insoluble Sulfides (and Hydroxides)

Ammonia or NaOH is now added to the solution until it is basic, and then $(NH_4)_2S$ is added. This treatment removes any remaining cations that form insoluble hydroxides or sulfides. The divalent metal ions Co^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+} precipitate as their sulfides, and the trivalent metal ions Al^{3+} and Cr^{3+} precipitate as their hydroxides: $Al(OH)_3$ and $Cr(OH)_3$. If the mixture contains Fe^{3+}, sulfide reduces the cation to Fe^{2+}, which precipitates as FeS.

Group 4: Insoluble Carbonates or Phosphates

The next metal ions to be removed from solution are those that form insoluble carbonates and phosphates. When Na_2CO_3 is added to the basic solution that remains after the precipitated metal ions are removed, insoluble carbonates precipitate and are collected. Alternatively, adding $(NH_4)_2HPO_4$ causes the same metal ions to precipitate as insoluble phosphates.

Group 5: Alkali Metals

At this point, we have removed all the metal ions that form water-insoluble chlorides, sulfides, carbonates, or phosphates. The only common ions that might remain are any alkali metals (Li^+, Na^+, K^+, Rb^+, and Cs^+) and ammonium (NH_4^+). We now take a second sample from the *original* solution and add a small amount of NaOH to neutralize the ammonium ion and produce NH_3. (We cannot use the same sample we used for the first four groups because we added ammonium to that sample in earlier steps.) Any ammonia produced can be detected by either its odor or a litmus paper test. A flame test on another original sample is used to detect sodium, which produces a characteristic bright yellow color. As discussed

in Chapter 6 "The Structure of Atoms", the other alkali metal ions also give characteristic colors in flame tests, which allows them to be identified if only one is present.

Metal ions that precipitate together are separated by various additional techniques, such as forming complex ions, changing the pH of the solution, or increasing the temperature to redissolve some of the solids. For example, the precipitated metal chlorides of group 1 cations, containing Ag^+, Pb^{2+}, and Hg_2^{2+}, are all quite insoluble in water. Because $PbCl_2$ is much more soluble in hot water than are the other two chloride salts, however, adding water to the precipitate and heating the resulting slurry will dissolve any $PbCl_2$ present. Isolating the solution and adding a small amount of Na_2CrO_4 solution to it will produce a bright yellow precipitate of $PbCrO_4$ if Pb^{2+} was in the original sample (Figure 17.11 "The Separation of Metal Ions from Group 1 Using Qualitative Analysis").

As another example, treating the precipitates from group 1 cations with aqueous ammonia will dissolve any AgCl because Ag^+ forms a stable complex with ammonia: $[Ag(NH_3)_2]^+$. In addition, Hg_2Cl_2 *disproportionates* in ammonia ($2Hg_2^{2+} \rightarrow Hg + Hg^{2+}$) to form a black solid that is a mixture of finely divided metallic mercury and an insoluble mercury(II) compound, which is separated from solution:

Equation 17.39

$$Hg_2Cl_2(s) + 2NH_3(aq) \rightarrow Hg(l) + Hg(NH_2)Cl(s) + NH_4^+(aq) + Cl^-(aq)$$

Any silver ion in the solution is then detected by adding HCl, which reverses the reaction and gives a precipitate of white AgCl that slowly darkens when exposed to light:

Equation 17.40

$$[Ag(NH_3)_2]^+(aq) + 2H^+(aq) + Cl^-(aq) \rightarrow AgCl(s) + 2NH_4^+(aq)$$

Similar but slightly more complex reactions are also used to separate and identify the individual components of the other groups.

Summary

In **qualitative analysis**, the identity, not the amount, of metal ions present in a mixture is determined. The technique consists of selectively precipitating only a few kinds of metal ions at a time under given sets of conditions. Consecutive precipitation steps become progressively *less* selective until almost all the metal ions are precipitated. Other additional steps are needed to separate metal ions that precipitate together.

KEY TAKEAWAY

- Several common metal cations can be identified in a solution using selective precipitation.

CONCEPTUAL PROBLEM

1. Given a solution that contains a mixture of NaCl, $CuCl_2$, and $ZnCl_2$, propose a method for separating the metal ions.

17.6 End-of-Chapter Material

APPLICATION PROBLEMS

Problems marked with a ♦ involve multiple concepts.

1. ♦ Gypsum ($CaSO_4 \cdot 2H_2O$) is added to soil to enhance plant growth. It dissolves according to the following equation:

a. $CaSO4 \times 2H2O(s) \square \quad Ca2+(aq)+SO42-(aq)+2H2O(l)$

b. The K_{sp} of gypsum is 3.14×10^{-5}. How much gypsum should you add to your 5.0 L watering can to produce a saturated solution?

c. Gibbsite [$Al(OH)_3$] is a component of clay, found in places such as Molokai, Hawaii. It dissolves according to the following equation
: $Al(OH)3(s) \square \quad Al3+(aq)+3OH-(aq), with$

d. a K_{sp} of 1.3×10^{-33}. You are interested in using gypsum to counteract harmful growth effects of Al^{3+} on plants from dissolved gibbsite, and you have found the pH of your soil to be 8.7. What is the apparent concentration of OH^- in your soil?

2. Egyptian blue, which is difficult to prepare, is a synthetic pigment developed about 4500 yr ago. It was the only blue pigment identified in a study of stocks of dry pigments found in color merchants' shops in Pompeii. The pigment contains 12.9% calcium carbonate (calcite). A major source of $CaCO_3$ is limestone, which also contains $MgCO_3$. Assuming that the masses of $CaCO_3$ and $MgCO_3$ are equal, and that a sample of limestone is dissolved in acidified water to give $[Ca^{2+}] = [Mg^{2+}] = 0.010$ M in 5.0 L of solution, would selective precipitation be a viable method for purifying enough $CaCO_3$ from limestone to produce 1.0 g of pigment? Why?
The K_{sp} values are 3.36×10^{-9} for $CaCO_3$ and 6.8×10^{-6} for $MgCO_3$.

3. One method of mining gold is to extract it through the process of cyanidation. Mined ores are milled and treated with aqueous cyanide solution to produce a gold complex ion {$[Au(CN)_2]^-$} that is very stable. Given a

sample of AuCl, what is the solubility of AuCl in each situation? The K_{sp} of AuCl = 2.0×10^{-13}; log $K_f\{[Au(CN)_2]^-\}$ = 38.3.

a. pure water

b. a 1.68 M solution of NaCN

4. ♦ Almost all barium carbonate is produced synthetically. The compound is used in manufacturing clay tiles and ceramic products as well as in cathode ray tubes and special optical glasses. $BaCO_3$ is synthesized by allowing barium sulfate to react with coal at 1000°C–1200°C in a rotary kiln, followed by treatment of a solution of the product with either CO_2 (reaction 1) or Na_2CO_3 (reaction 2). The reactions are as follows:

$BaSO_4(s) + 4C(s) \rightarrow 4BaS(s) + 4CO(g)$reaction 1. $BaS(s) + CO_2(g) + H_2O(l) \rightarrow BaCO_3(aq) + H_2S(g)$reaction 2. $BaS(s) + Na_2CO_3(aq) \rightleftharpoons BaCO_3(aq) + Na_2S(aq)$

Barium carbonate has a K_{sp} of 2.58×10^{-9}. The pK_a fo $r\ H2S \square\ H++HS-\ is$

6.97, and the pK_a $or\ HS- \square\ H++S2-\ is\ 12$

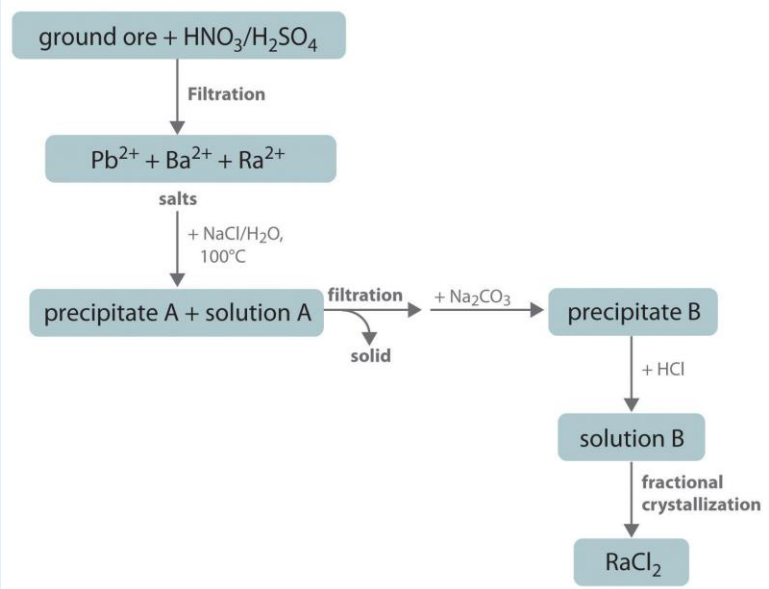
.90. Given this information, answer the following questions:

a. If reaction 1 occurs, what is the pH of the solution if 80.0 g of BaS react with CO_2 in 1.00 L of water?

b. If reaction 2 occurs, how many grams of $BaCO_3$ are produced by the reaction of 80.0 g of BaS with excess Na_2CO_3?

5. A person complaining of chronic indigestion continually consumed antacid tablets containing $Ca(OH)_2$ over a two-week period. A blood test at the end of this period showed that the person had become anemic. Explain the reactions that caused this test result.

6. Although the commercial production of radium has virtually ceased since artificial radionuclides were discovered to have similar properties and lower costs, commercial radium is still isolated using essentially the same procedure developed by Marie Curie, as outlined here. Explain what is happening chemically at each step of the purification process. What is precipitate A? What metal ions are present in solution A? What is precipitate B? What metal ions are present in solution B?



7. In a qualitative analysis laboratory, a student initially treated his sample of metal ions with 6 M HNO_3 instead of 6 M HCl, recognizing his mistake only after the acid-insoluble sulfides had been precipitated. He decided to simply add 6 M HCl to the filtrate from which the sulfides had been removed, but he obtained no precipitate. The student therefore concluded that there were no Ag^+, Hg_2^{2+}, or Pb^{2+} cations in his original sample. Is this conclusion valid?
8. Using qualitative analysis, a student decided to treat her sample with $(NH_4)_2S$ solution directly, skipping the HCl and acidic H_2S treatments because she was running out of time. In a sample that contained Ag^+, Hg_2^{2+}, Cd^{2+}, Sb^{3+}, and Zn^{2+}, which metal ions was she most likely to obtain in the resulting precipitate?

ANSWERS

1.

a. 4.3 g

b. 5×10^{-6} M

2.

3.

a. 4.4×10^{-7} M

b. 0.84 M

4.

5.

6.

7. No; these cations would precipitate as sulfides.
8.

Chapter 18
Chemical Thermodynamics

Chemical reactions obey two fundamental laws. The first of these, the **law of conservation of mass**, states that matter can be neither created nor destroyed. (For more information on matter, see Chapter 1 "Introduction to Chemistry".) The law of conservation of mass is the basis for all the stoichiometry and equilibrium calculations you have learned thus far in chemistry. The second, the **law of conservation of energy**, states that energy can be neither created nor destroyed. (For more information on energy, see Chapter 5 "Energy Changes in Chemical Reactions".) Instead, energy takes various forms that can be converted from one form to another. For example, the energy stored in chemical bonds can be released as heat during a chemical reaction.

In Chapter 5 "Energy Changes in Chemical Reactions", you also learned about*thermochemistry*, the study of energy changes that occur during chemical reactions. Our goal in this chapter is to extend the concepts of thermochemistry to an exploration of thermodynamics (from the Greek *thermo* and *dynamic*, meaning “heat” and “power,” respectively), the study of the interrelationships among heat, work, and the energy content of a system at equilibrium. Thermodynamics tells chemists whether a particular reaction is energetically possible in the direction in which it is written, and it gives the composition of the reaction system at equilibrium. It does not, however, say anything about whether an energetically feasible reaction will *actually* occur as written, and it tells us nothing about the reaction rate or the pathway by which it will occur. The rate of a reaction and its pathway are described by chemical kinetics. (For more information on reaction rates and kinetics, see Chapter 14 "Chemical Kinetics".)

Chemical thermodynamics provides a bridge between the macroscopic properties of a substance and the individual properties of its constituent molecules and atoms. As you will see, thermodynamics explains why graphite can be converted to diamond; how chemical energy stored in molecules can be used to perform work; and why certain processes, such as iron rusting and organisms aging and dying, proceed spontaneously in only one direction, requiring no net input of energy to occur.

18.1 Thermodynamics and Work

LEARNING OBJECTIVES

1. To understand the relationships between work, heat, and energy.
2. To become familiar with the concept of *PV* work.

We begin our discussion of thermodynamics by reviewing some important terms introduced in Chapter 5 "Energy Changes in Chemical Reactions". First, we need to distinguish between a system and its surroundings. A **system** is that part of the universe in which we are interested, such as a mixture of gases in a glass bulb or a solution of substances in a flask. The **surroundings** are everything else—the rest of the *universe*. We can therefore state the following:

Equation 18.1
system + surroundings = universe

A **closed system**, such as the contents of a sealed jar, cannot exchange matter with its surroundings, whereas an **open system** can; in this case, we can convert a closed system (the jar) to an open system by removing the jar's lid.

In Chapter 5 "Energy Changes in Chemical Reactions", we also introduced the concept of a state function, a property of a system that depends on only the present state of the system, not its history. Thus a change in a state function depends on only the difference between the initial and final states, not the pathway used to go from one to the other. To help understand the concept of a state function, imagine a person hiking up a mountain (Figure 18.1 "Altitude Is a State Function"). If the person is well trained and fit, he or she may be able to climb almost vertically to the top (path A), whereas another less athletic person may choose a path that winds gradually to the top (path B). If both hikers start from the same point at the base of the mountain and end up at the same point at the top, their *net change in altitude* will be the same regardless of the path chosen. Hence altitude is a state function. On the other hand, a person may or may not carry a heavy pack and may climb in hot weather or cold. These conditions would influence changes in the hiker's fatigue level, which depends on the path taken and the conditions experienced. Fatigue, therefore, is not a state function. Thermodynamics is generally concerned with state functions and does not deal with how the change between the initial state and final state occurs.

The Connections among Work, Heat, and Energy

The internal energy (E) of a system is the sum of the potential energy and the kinetic energy of all the components; internal energy is a state function. Although a closed system cannot exchange matter with its surroundings, it can exchange energy with its surroundings in two ways: by doing work or by releasing or

absorbing heat—the flow of thermal energy. Work and heat are therefore two distinct ways of changing the internal energy of a system. We defined *work* (*w*) in Chapter 5 "Energy Changes in Chemical Reactions" as a force *F* acting through a distance *d*:

Equation 18.2
$w = Fd$

Because work occurs only when an object, such as a person, or a substance, such as water, moves against an opposing force, work requires that a system and its surroundings be connected. In contrast, the flow of *heat*, the transfer of energy due to differences in temperature between two objects, represents a thermal connection between a system and its surroundings. Thus doing work causes a physical displacement, whereas the flow of heat causes a temperature change. The units of work and heat must be the same because both processes result in the transfer of energy. In the SI system, those units are joules (J), the same unit used for energy. There is no difference between an energy change brought about by doing work on a system and an equal energy change brought about by heating it.

The connections among work, heat, and energy were first described by Benjamin Thompson (1753–1814), an American-born scientist who was also known as Count Rumford. While supervising the manufacture of cannons, Rumford recognized the relationship between the amount of work required to drill out a cannon and the temperature of the water used to cool it during the drilling process (Figure 18.2 "The Relationship between Heat and Work"). At that time, it was generally thought that heat and work were separate and unrelated phenomena. Hence Rumford's ideas were not widely accepted until many years later, after his findings had been corroborated in other laboratories.

In the 1780s, an American scientist named Benjamin Thompson, also known as Count Rumford, was hired by the Elector of Bavaria to supervise the manufacture of cannons. During the manufacturing process, teams of horses harnessed to a large-toothed wheel supplied the power needed to drill a hole several inches in diameter straight down the center of a solid brass or bronze cylinder, which was cooled by water. Based on his observations, Rumford became convinced that heat and work are equivalent ways of transferring energy.

PV Work

As we saw in Chapter 5 "Energy Changes in Chemical Reactions", there are many kinds of work, including mechanical work, electrical work, and work against a gravitational or a magnetic field. Here we will

consider only mechanical work, focusing on the work done during changes in the pressure or the volume of a gas. To describe this *pressure–volume work* (*PV* work), we will use such imaginary oddities as frictionless pistons, which involve no component of resistance, and ideal gases, which have no attractive or repulsive interactions.

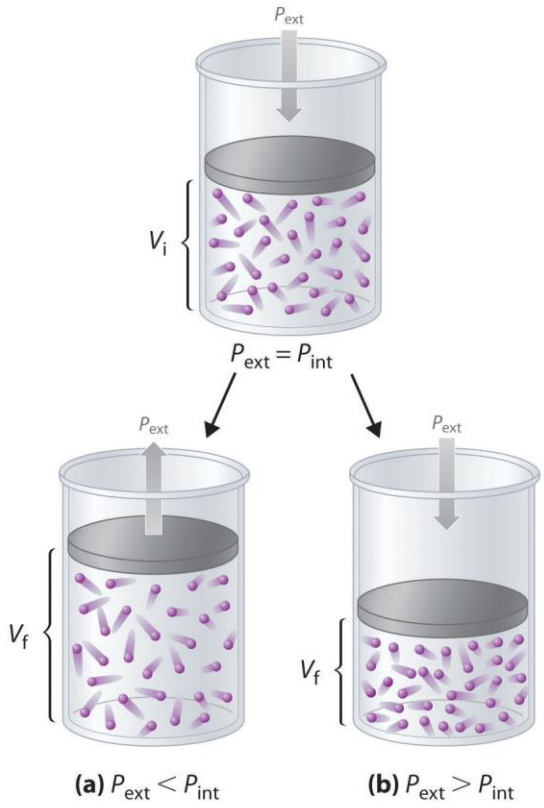
Imagine, for example, an ideal gas, confined by a frictionless piston, with internal pressure P_{int} and initial volume V_i (Figure 18.3). If $P_{ext} = P_{int}$, the system is at equilibrium; the piston does not move, and no work is done. If the external pressure on the piston (P_{ext}) is less than P_{int}, however, then the ideal gas inside the piston will expand, forcing the piston to perform work on its surroundings; that is, the final volume (V_f) will be greater than V_i. If $P_{ext} > P_{int}$, then the gas will be compressed, and the surroundings will perform work on the system.

If the piston has cross-sectional area A, the external pressure exerted by the piston is, by definition, the force per unit area: $P_{ext} = F/A$. The volume of any three-dimensional object with parallel sides (such as a cylinder) is the cross-sectional area times the height ($V = Ah$). Rearranging to give $F = P_{ext}A$ and defining the distance the piston moves (d) as Δh, we can calculate the magnitude of the work performed by the piston by substituting into Equation 18.2:

Equation 18.3

$$w = Fd = P_{ext}A\Delta h$$

Figure 18.3 PV Work



Using a frictionless piston, if the external pressure is less than P_{int} (a), the ideal gas inside the piston will expand, forcing the piston to perform work on its surroundings. The final volume (V_f) will be greater than V_i. Alternatively, if the external pressure is greater than P_{int} (b), the gas will be compressed, and the surroundings will perform work on the system.

The change in the volume of the cylinder (ΔV) as the piston moves a distance d is $\Delta V = A\Delta h$, as shown inFigure 18.4 "Work Performed with a Change in Volume". The work performed is thus

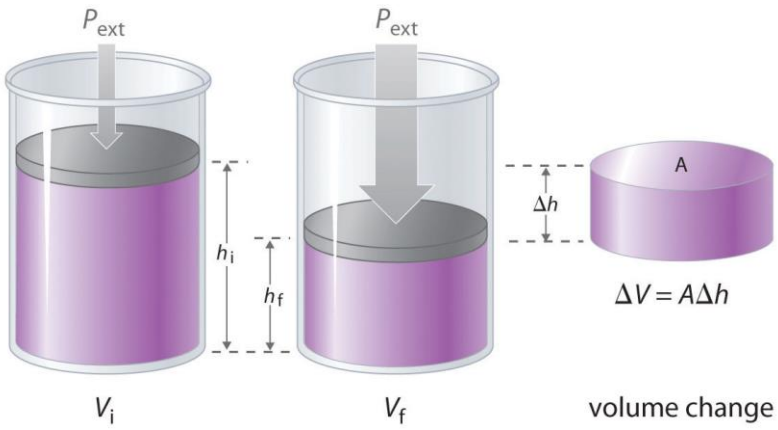
Equation 18.4

$w = P_{ext}\Delta V$

The units of work obtained using this definition are correct for energy: pressure is force per unit area (newton/m^2) and volume has units of cubic meters, so

$$w = (FA)ext(\mathrm{D}V) = newtonm2 \times m3 = newton \cdot m = joule$$

Figure 18.4 Work Performed with a Change in Volume



The change in the volume (ΔV) of the cylinder housing a piston is $\Delta V = A\Delta h$ as the piston moves. The work performed by the surroundings on the system as the piston moves inward is given by $w = P_{ext}\Delta V$.

If we use atmospheres for P and liters for V, we obtain units of L·atm for work. These units correspond to units of energy, as shown in the different values of the ideal gas constant R:

$$R = 0.08206\ L \times atm mol \times K = 8.314\ J mol \times K$$

Thus 0.08206 L·atm = 8.314 J and 1 L·atm = 101.3 J. (For more information on the ideal gas law, see Chapter 10 "Gases".)

Whether work is defined as having a positive sign or a negative sign is a matter of convention. In Chapter 5 "Energy Changes in Chemical Reactions", we defined heat flow *from* a system *to* its surroundings as negative. Using that same sign convention, we define work done *by* a system *on* its surroundings as having a negative sign because it results in a transfer of energy from a system to its surroundings.[1] Because $\Delta V > 0$ for an expansion, Equation 18.4 must be written with a negative sign to describe *PV*work done *by* the system as negative:

Equation 18.5

$$w = -P_{ext}\Delta V$$

The work done by a gas expanding against an external pressure is therefore negative, corresponding to work done *by* a system *on* its surroundings. Conversely, when a gas is compressed by an external pressure, $\Delta V < 0$ and the work is positive because work is being done *on* a system *by* its surroundings. Suppose, for example, that the system under study is a mass of steam heated by the combustion of several hundred pounds of coal and enclosed within a cylinder housing a piston attached to the crankshaft of a large steam engine. The gas is not ideal, and the cylinder is not frictionless. Nonetheless, as steam enters

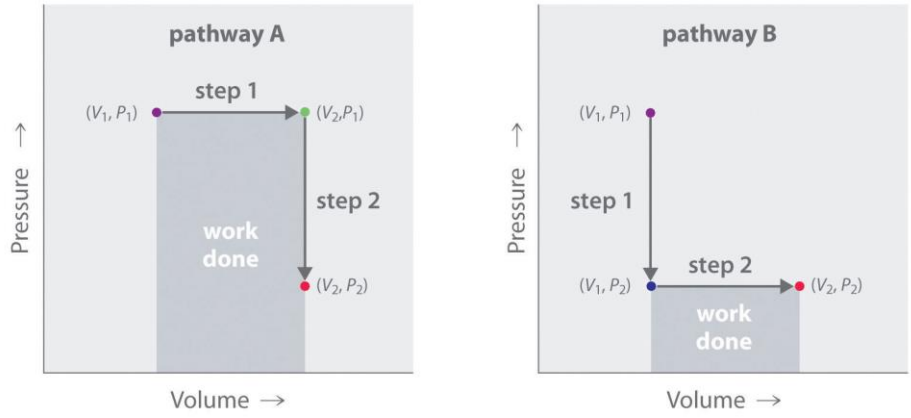
the engine chamber and the expanding gas pushes against the piston, the piston moves, so useful work is performed. In fact, *PV* work launched the Industrial Revolution of the 19th century and powers the internal combustion engine on which most of us still rely for transportation.

In contrast to internal energy, work is not a state function. We can see this by examining Figure 18.5 "Work Is Not a State Function", in which two different, two-step pathways take a gaseous system from an initial state to a final state with corresponding changes in temperature. In pathway A, the volume of a gas is initially increased while its pressure stays constant (step 1); then its pressure is decreased while the volume remains constant (step 2). In pathway B, the order of the steps is reversed. The temperatures, pressures, and volumes of the initial and final states are identical in both cases, but the amount of work done, indicated by the shaded areas in the figure, is substantially different. As we can see, the amount of work done depends on the pathway taken from (V_1, P_1) to (V_2, P_2), which means that work is not a state function.

Note the Pattern

Internal energy is a state function, whereas work is not.

Figure 18.5 *Work Is Not a State Function*



In pathway A, the volume of a gas is initially increased while its pressure stays constant (step 1). Its pressure is then decreased while the volume remains constant (step 2). Pathway B reverses these steps. Although (V_1, P_1) and (V_2, P_2) are identical in both cases, the amount of work done (shaded area) depends on the pathway taken.

EXAMPLE 1

A small high-performance internal combustion engine has six cylinders with a total nominal displacement (volume) of 2.40 L and a 10:1 compression ratio (meaning that the volume of each cylinder decreases by a

factor of 10 when the piston compresses the air–gas mixture inside the cylinder prior to ignition). How much work in joules is done when a gas in one cylinder of the engine expands at constant temperature against an opposing pressure of 40.0 atm during the engine cycle? Assume that the gas is ideal, the piston is frictionless, and no energy is lost as heat.

Given: final volume, compression ratio, and external pressure

Asked for: work done

Strategy:

A Calculate the final volume of gas in a single cylinder. Then compute the initial volume of gas in a single cylinder from the compression ratio.

B Use Equation 18.5 to calculate the work done in liter-atmospheres. Convert from liter-atmospheres to joules.

Solution:

A To calculate the work done, we need to know the initial and final volumes. The final volume is the volume of one of the six cylinders with the piston all the way down: V_f = 2.40 L/6 = 0.400 L. With a 10:1 compression ratio, the volume of the same cylinder with the piston all the way up is V_i = 0.400 L/10 = 0.0400 L. Work is done by the system on its surroundings, so work is negative.

$w = -P_{ext}\Delta V = -(40.0\text{ atm})(0.400\text{ L} - 0.0400\text{ L}) = -14.4\text{ L·atm}$

Converting from liter-atmospheres to joules,

$$w = -(14.4\,L \times atm)[101.3\,J/(L \times atm)] = -1.46 \times 10^3\,J$$

In the following exercise, you will see that the concept of work is not confined to engines and pistons. It is found in other applications as well.

Exercise

Breathing requires work, even if you are unaware of it. The lung volume of a 70 kg man at rest changed from 2200 mL to 2700 mL when he inhaled, while his lungs maintained a pressure of approximately 1.0 atm. How much work in liter-atmospheres and joules was required to take a single breath? During exercise, his lung volume changed from 2200 mL to 5200 mL on each in-breath. How much additional work in joules did he require to take a breath while exercising?

Answer: −0.500 L·atm, or −50.7 J; −304 J; if he takes a breath every three seconds, this corresponds to 1.4 Calories per minute (1.4 kcal).

Summary

Thermodynamics is the study of the interrelationships among heat, work, and the energy content of a system at equilibrium. The sum of the potential energy and the kinetic energy of all the components of a system is the **internal energy (*E*)** of the system, which is a **state function**. When the pressure or the volume of a gas is changed, any mechanical work done is called *PV work*. Work done by a system on its surroundings is given a negative value, whereas work done on a system by its surroundings has a positive value.

KEY TAKEAWAY

- Internal energy is a state function that is the sum of the potential and kinetic energy of the system, whereas work is not a state function.

KEY EQUATION

Definition of *PV* work

Equation 18.5: $w = -P_{ext}\Delta V$

CONCEPTUAL PROBLEMS

1. Thermodynamics focuses on the energetics of the reactants and products and provides information about the composition of the reaction system at equilibrium. What information on reaction systems is not provided by thermodynamics?
2. Given a system in which a substance can produce either of two possible products, A → B or A → C, which of the following can be predicted using chemical thermodynamics?

a. At equilibrium, the concentration of product C is greater than the concentration of product B.

b. Product C forms more quickly than product B.

c. The reaction A → C is exothermic.

d. Low-energy intermediates are formed in the reaction A → B.

e. The reaction A → C is spontaneous.

3. In what two ways can a closed system exchange energy with its surroundings? Are these two processes path dependent or path independent?

4. A microwave oven operates by providing enough energy to rotate water molecules, which produces heat. Can the change in the internal energy of a cup of water heated in a microwave oven be described as a state function? Can the heat produced be described as a state function?

ANSWERS

1. Thermodynamics tells us nothing about the rate at which reactants are converted to products.
2.
3. heat and work; path dependent
4.

NUMERICAL PROBLEMS

1. Calculate the work done in joules in each process.

a. compressing 12.8 L of hydrogen gas at an external pressure of 1.00 atm to 8.4 L at a constant temperature

b. expanding 21.9 L of oxygen gas at an external pressure of 0.71 atm to 23.7 L at a constant temperature

2. How much work in joules is done when oxygen is compressed from a volume of 22.8 L and an external pressure of 1.20 atm to 12.0 L at a constant temperature? Was work done by the system or the surroundings?
3. Champagne is bottled at a CO_2 pressure of about 5 atm. What is the force on the cork if its cross-sectional area is 2.0 cm^2? How much work is done if a 2.0 g cork flies a distance of 8.2 ft straight into the air when the cork is popped? Was work done by the system or the surroundings?
4. One mole of water is converted to steam at 1.00 atm pressure and 100°C. Assuming ideal behavior, what is the change in volume when the water is converted from a liquid to a gas? If this transformation took place in a cylinder with a piston, how much work could be done by vaporizing the water at 1.00 atm? Is work done by the system or the surroundings?
5. Acceleration due to gravity on the earth's surface is 9.8 m/s^2. How much work is done by a 175 lb person going over Niagara Falls (approximately 520 ft high) in a barrel that weighs 145 lb?
6. Recall that force can be expressed as mass times acceleration ($F = ma$). Acceleration due to gravity on the earth's surface is 9.8 m/s^2.

a. What is the gravitational force on a person who weighs 52 kg?

b. How much work is done if the person leaps from a burning building out of a window that is 20 m above the ground?

c. If the person lands on a large rescue cushion fitted with a pressure-release valve that maintains an internal pressure of 1.5 atm, how much air is forced out of the cushion?

7. A gas is allowed to expand from a volume of 2.3 L to a volume of 5.8 L. During the process, 460 J of heat is transferred from the surroundings to the gas.

a. How much work has been done if the gas expands against a vacuum?

b. How much work has been done if the gas expands against a pressure of 1.3 atm?

c. What is the change in the internal energy of the system?

8. One mole of an ideal gas is allowed to expand from an initial volume of 0.62 L to a final volume of 1.00 L at constant temperature against a constant external pressure of 1.0 atm. How much work has been done?

ANSWERS

1.

2.

3.

4.

5. −230 kJ

6.

7.

a. 0 J

b. −460 J

c. 0 J

[1] This is an arbitrary convention and one that is not universally used. Some engineering disciplines are more interested in the work done *on* the surroundings than in the work done*by* the system and therefore use the opposite convention.

18.2 The First Law of Thermodynamics

LEARNING OBJECTIVE

1. To calculate changes in internal energy.

The relationship between the energy change of a system and that of its surroundings is given by the first law of thermodynamics, which states that the *energy of the universe is constant*. Using Equation 18.1, we can express this law mathematically as follows:

Equation 18.6

$$\Delta E_{univ} \Delta E_{sys} = \Delta E_{sys} + \Delta E_{surr} = 0 = -\Delta E_{surr}$$

where the subscripts *univ*, *sys*, and *surr* refer to the universe, the system, and the surroundings, respectively. Thus the change in energy of a system is identical in magnitude but opposite in sign to the change in energy of its surroundings.

An important factor that determines the outcome of a chemical reaction is the tendency of all systems, chemical or otherwise, to move toward the lowest possible overall energy state. As a brick dropped from a rooftop falls, its potential energy is converted to kinetic energy; when it reaches ground level, it has achieved a state of lower potential energy. Anyone nearby will notice that energy is transferred to the surroundings as the noise of the impact reverberates and the dust rises when the brick hits the ground. Similarly, if a spark ignites a mixture of isooctane and oxygen in an internal combustion engine, carbon dioxide and water form spontaneously, while potential energy (in the form of the relative positions of atoms in the molecules) is released to the surroundings as heat and work. The internal energy content of the CO_2/H_2O product mixture is less than that of the isooctane/O_2 reactant mixture. The two cases differ, however, in the form in which the energy is released to the surroundings. In the case of the falling brick, the energy is transferred as work done on whatever happens to be in the path of the brick; in the case of burning isooctane, the energy can be released as solely heat (if the reaction is carried out in an open container) or as a mixture of heat and work (if the reaction is carried out in the cylinder of an internal combustion engine). Because heat and work are the only two ways in which energy can be transferred between a system and its surroundings, any change in the internal energy of the system is the sum of the heat transferred (q) and the work done (w):

Equation 18.7

$$\Delta E_{sys} = q + w$$

Although q and w are not state functions on their own, their sum (ΔE_{sys}) is independent of the path taken and is therefore a state function. A major task for the designers of any machine that converts energy to work is to maximize the amount of work obtained and minimize the amount of energy released to the environment as heat. An example is the combustion of coal to produce electricity. Although the maximum amount of energy available from the process is fixed by the energy content of the reactants and the products, the fraction of that energy that can be used to perform

useful work is not fixed, as discussed in Section 18.5 "Free Energy". Because we focus almost exclusively on the changes in the energy of a system, we will not use “sys” as a subscript unless we need to distinguish explicitly between a system and its surroundings.

Note the Pattern

The tendency of all systems, chemical or otherwise, is to move toward the state with the lowest possible energy.

Note the Pattern

Although q and w are not state functions, their sum (ΔE_{sys}) is independent of the path taken and therefore is a state function.

EXAMPLE 2

A sample of an ideal gas in the cylinder of an engine is compressed from 400 mL to 50.0 mL during the compression stroke against a constant pressure of 8.00 atm. At the same time, 140 J of energy is transferred from the gas to the surroundings as heat. What is the total change in the internal energy (ΔE) of the gas in joules?

Given: initial volume, final volume, external pressure, and quantity of energy transferred as heat

Asked for: total change in internal energy

Strategy:

A Determine the sign of q to use in Equation 18.7.

B From Equation 18.5, calculate w from the values given. Substitute this value intoEquation 18.7 to calculate ΔE.

Solution:

A From Equation 18.7, we know that $\Delta E = q + w$. We are given the magnitude of q(140 J) and need only determine its sign. Because energy is transferred from the system (the gas) to the surroundings, q is negative by convention.

B Because the gas is being compressed, we know that work is being done *on* the system, so w must be positive. From Equation 18.5,

$$w = - PextDV = - 8.00 atm$$
$$(0.0500\ L - 0.400\ L)[(101.3\ JL \cdot atm)] = 284\ J$$

Thus

$\Delta E = q + w = -140\ \text{J} + 284\ \text{J} = 144\ \text{J}$

In this case, although work is done *on* the gas, increasing its internal energy, heat flows *from* the system *to* the surroundings, decreasing its internal energy by 144 J. The work done and the heat transferred can have opposite signs.

Exercise

A sample of an ideal gas is allowed to expand from an initial volume of 0.200 L to a final volume of 3.50 L against a constant external pressure of 0.995 atm. At the same time, 117 J of heat is transferred from the surroundings to the gas. What is the total change in the internal energy (ΔE) of the gas in joules?

Answer: −216 J

Note the Pattern

By convention, both heat flow and work have a negative sign when energy is transferred from a system to its surroundings and vice versa.

Enthalpy

To further understand the relationship between heat flow (q) and the resulting change in internal energy (ΔE), we can look at two sets of limiting conditions: reactions that occur at constant volume and reactions that occur at constant pressure. We will assume that PV work is the only kind of work possible for the system, so we can substitute its definition from Equation 18.5 into Equation 18.7 to obtain the following:

Equation 18.8

$$\Delta E = q - P\Delta V$$

where the subscripts have been deleted.

If the reaction occurs in a closed vessel, the volume of the system is fixed, and ΔV is zero. Under these conditions, the heat flow (often given the symbol q_v to indicate constant volume) must equal ΔE:

Equation 18.9

$$qv = \Delta E \text{constant volume}$$

No PV work can be done, and the change in the internal energy of the system is equal to the amount of heat transferred from the system to the surroundings or vice versa.

Many chemical reactions are not, however, carried out in sealed containers at constant volume but in open containers at a more or less constant pressure of about 1 atm. The heat flow under these conditions is given the symbol q_p to indicate constant pressure. Replacing q in Equation 18.8 by q_p and rearranging to solve for q_p,

Equation 18.10

$$qp = \Delta E + P\Delta V \quad constant\ \ pressure$$

Thus, at constant pressure, the heat flow for any process is equal to the change in the internal energy of the system plus the *PV* work done, as we stated in Chapter 5 "Energy Changes in Chemical Reactions". Because conditions of constant pressure are so important in chemistry, a new state function called enthalpy (*H*) is defined as $H = E + PV$. At constant pressure, the change in the enthalpy of a system is as follows:

Equation 18.11

$$\Delta H = \Delta E + \Delta(PV) = \Delta E + P\Delta V$$

Comparing the previous two equations shows that at constant pressure, the change in the enthalpy of a system is equal to the heat flow: $\Delta H = q_p$. This expression is consistent with our definition of enthalpy in Chapter 5 "Energy Changes in Chemical Reactions", where we stated that enthalpy is the heat absorbed or produced during any process that occurs at constant pressure.

Note the Pattern

At constant pressure, the change in the enthalpy of a system is equal to the heat flow: $\Delta H = q_p$.

EXAMPLE 3

The molar enthalpy of fusion for ice at 0.0°C and a pressure of 1.00 atm is 6.01 kJ, and the molar volumes of ice and water at 0°C are 0.0197 L and 0.0180 L, respectively. Calculate Δ*H* and Δ*E* for the melting of ice at 0.0°C. (For more information on enthalpy, see Chapter 5 "Energy Changes in Chemical Reactions", Section 5.2 "Enthalpy".)

Given: enthalpy of fusion for ice, pressure, and molar volumes of ice and water

Asked for: Δ*H* and Δ*E* for ice melting at 0.0°C

Strategy:

A Determine the sign of *q* and set this value equal to Δ*H*.

B Calculate Δ(*PV*) from the information given.

C Determine Δ*E* by substituting the calculated values into Equation 18.11.

Solution:

A Because 6.01 kJ of heat is absorbed from the surroundings when 1 mol of ice melts, $q = +6.01$ kJ. When the process is carried out at constant pressure, $q = q_p = \Delta H = 6.01$ kJ.

B To find Δ*E* using Equation 18.11, we need to calculate Δ(*PV*). The process is carried out at a constant pressure of 1.00 atm, so

$$\Delta(PV) = P\Delta V = P(Vf - V)$$
$$= (1.00\ atm)(0.0180\ L - 0.0197\ L)$$
$$= (-1.7 \times 10^{-3}\ L \cdot atm)(101.3\ J/L \cdot atm) = -0.0017\ J$$

C Substituting the calculated values of Δ*H* and *P*Δ*V* into Equation 18.11,

Δ*E* = Δ*H* − *P*Δ*V* = 6010 J − (−0.0017 J) = 6010 J = 6.01 kJ

Exercise

At 298 K and 1 atm, the conversion of graphite to diamond requires the input of 1.850 kJ of heat per mole of carbon. The molar volumes of graphite and diamond are 0.00534 L and 0.00342 L, respectively.

Calculate Δ*H* and Δ*E* for the conversion of C (graphite) to C (diamond) under these conditions.

Answer: Δ*H* = 1.85 kJ/mol; Δ*E* = 1.85 kJ/mol

The Relationship between Δ*H* and Δ*E*

If Δ*H* for a reaction is known, we can use the change in the enthalpy of the system (Equation 18.11) to calculate its change in internal energy. When a reaction involves only solids, liquids, liquid solutions, or any combination of these, the volume does not change appreciably (Δ*V* = 0). Under these conditions, we can simplify Equation 18.11to Δ*H* = Δ*E*. If gases are involved, however, Δ*H* and Δ*E* can differ significantly. We can calculate Δ*E* from the measured value of Δ*H* by using the right side of Equation 18.11together with the ideal gas law, *PV* = *nRT*. Recognizing that Δ(*PV*) = Δ(*nRT*), we can rewrite Equation 18.11 as follows:

Equation 18.12
Δ*H* = Δ*E* + Δ(*PV*) = Δ*E* + Δ(*nRT*)

At constant temperature, Δ(*nRT*) = *RT*Δ*n*, where Δ*n* is the difference between the final and initial numbers of moles of gas. Thus

Equation 18.13
Δ*E* = Δ*H* − *RT*Δ*n*

For reactions that result in a net production of gas, Δ*n* > 0, so Δ*E* < Δ*H*. Conversely, endothermic reactions (Δ*H* > 0) that result in a net consumption of gas have Δ*n* < 0 and Δ*E* > Δ*H*. The relationship between Δ*H* and Δ*E* for systems involving gases is illustrated in Example 4.

Note the Pattern

For reactions that result in a net production of gas, $\Delta E < \Delta H$. For endothermic reactions that result in a net consumption of gas, $\Delta E > \Delta H$.

EXAMPLE 4

The combustion of graphite to produce carbon dioxide is described by the equation C (graphite, s) + O_2(g) → CO_2(g). At 298 K and 1.0 atm, ΔH = −393.5 kJ/mol of graphite for this reaction, and the molar volume of graphite is 0.0053 L. What is ΔE for the reaction?

Given: balanced chemical equation, temperature, pressure, ΔH, and molar volume of reactant

Asked for: ΔE

Strategy:

A Use the balanced chemical equation to calculate the change in the number of moles of gas during the reaction.

B Substitute this value and the data given into Equation 18.13 to obtain ΔE.

Solution:

A In this reaction, 1 mol of gas (CO_2) is produced, and 1 mol of gas (O_2) is consumed. Thus $\Delta n = 1 - 1 = 0$.

B Substituting this calculated value and the given values into Equation 18.13,

$$\Delta E = \Delta H - RT\Delta n = (-393.5\ kJ/mol)$$
$$-[8.314\ J/(mol \cdot K)](298\ K)(0) =$$
$$(-393.5\ kJ/mol) - (0\ J/mol) = -393.5\ kJ/mol$$

To understand why only the change in the volume of the gases needs to be considered, notice that the molar volume of graphite is only 0.0053 L. A change in the number of moles of gas corresponds to a volume change of 22.4 L/mol of gas at standard temperature and pressure (STP), so the volume of gas consumed or produced in this case is (1)(22.4 L) = 22.4 L, which is much, much greater than the volume of 1 mol of a solid such as graphite.

Exercise

Calculate ΔE for the conversion of oxygen gas to ozone at 298 K: $3O_2$(g) → $2O_3$(g). The value of ΔH for the reaction is 285.4 kJ.

Answer: 288 kJ

As the exercise in Example 4 illustrates, the magnitudes of ΔH and ΔE for reactions that involve gases are generally rather similar, even when there is a net production or consumption of gases.

Summary

The **first law of thermodynamics** states that the energy of the universe is constant. The change in the internal energy of a system is the sum of the heat transferred and the work done. At constant pressure, heat flow (q) and internal energy (E) are related to the system's **enthalpy (H)**. The heat flow is equal to the change in the internal energy of the system plus the PV work done. When the volume of a system is constant, changes in its internal energy can be calculated by substituting the ideal gas law into the equation for ΔE.

KEY TAKEAWAY

- Enthalpy is a state function, and the change in enthalpy of a system is equal to the sum of the change in the internal energy of the system and the PV work done.

KEY EQUATIONS

Internal energy change

Equation 18.7: $\Delta E_{sys} = q + w$

Enthalpy change

Equation 18.11: $\Delta H = \Delta E + \Delta(PV)$

Relationship between Δ H and Δ E for an ideal gas

Equation 18.13: $\Delta E = \Delta H - RT\Delta n$

CONCEPTUAL PROBLEMS

1. Describe how a swinging pendulum that slows with time illustrates the first law of thermodynamics.
2. When air is pumped into a bicycle tire, the air is compressed. Assuming that the volume is constant, express the change in internal energy in terms of q and w.
3. What is the relationship between enthalpy and internal energy for a reaction that occurs at constant pressure?
4. An intrepid scientist placed an unknown salt in a small amount of water. All the salt dissolved in the water, and the temperature of the solution dropped several degrees.

a. What is the sign of the enthalpy change for this reaction?

b. Assuming the heat capacity of the solution is the same as that of pure water, how would the scientist calculate the molar enthalpy change?

c. Propose an explanation for the decrease in temperature.

5. For years, chemists and physicists focused on enthalpy changes as a way to measure the spontaneity of a reaction. What arguments would you use to convince them not to use this method?

6. What is the relationship between enthalpy and internal energy for a reaction that occurs at constant volume?

7. The *enthalpy of combustion* (ΔH_{comb}) is defined thermodynamically as the enthalpy change for complete oxidation. The complete oxidation of hydrocarbons is represented by the following general equation: hydrocarbon + $O_2(g) \rightarrow CO_2(g) + H_2O(g)$. Enthalpies of combustion from reactions like this one can be measured experimentally with a high degree of precision. It has been found that the less stable the reactant, the more heat is evolved, so the more negative the value of ΔH_{comb}. In each pair of hydrocarbons, which member do you expect to have the greater (more negative) heat of combustion? Justify your answers.

a. cyclopropane or cyclopentane

b. butane or 2-methylpropane

c. hexane or cyclohexane

8. Using a structural argument, explain why the *trans* isomer of 2-butene is more stable than the *cis* isomer. The enthalpies of formation of *cis*- and *trans*-2-butene are −7.1 kJ/mol and −11.4 kJ/mol, respectively.

9. Using structural arguments, explain why cyclopropane has a positive $\Delta H°_f$ (12.7 kJ/mol), whereas cyclopentane has a negative $\Delta H°_f$ (−18.4 kJ/mol). (Hint: consider bond angles.)

ANSWERS

1.

2.

3. At constant pressure, $\Delta H = \Delta E + P\Delta V$.

4.

5.

6.

7.

8.

9. With bond angles of 60°, cyclopropane is highly strained, causing it to be less stable than cyclopentane, which has nearly ideal tetrahedral geometry at each carbon atom.

NUMERICAL PROBLEMS

1. A block of CO_2 weighing 15 g evaporates in a 5.0 L container at 25°C. How much work has been done if the gas is allowed to expand against an external pressure of 0.98 atm under isothermal conditions? The enthalpy of sublimation of CO_2 is 25.1 kJ/mol. What is the change in internal energy (kJ/mol) for the sublimation of CO_2 under these conditions?
2. Zinc and HCl react according to the following equation:

   $Zn(s) + 2HCl(aq) \rightarrow Zn^{2+}(aq) + 2Cl^{-}(aq) + H_2(g)$

   When 3.00 g of zinc metal is added to a dilute HCl solution at 1.00 atm and 25°C, and this reaction is allowed to go to completion at constant pressure, 6.99 kJ of heat must be removed to return the final solution to its original temperature. What are the values of *q*and *w*, and what is the change in internal energy?
3. Acetylene torches, used industrially to cut and weld metals, reach flame temperatures as high as 3000°C. The combustion reaction is as follows:

   $$2C2H2(g) + 5O2(g) \rightarrow 4CO2(g) + 2H2O(l)$$
   $$DH = -2599\ kJ$$

18.3 The Second Law of Thermodynamics

LEARNING OBJECTIVE

1. To understand the relationship between internal energy and entropy.

The first law of thermodynamics governs changes in the state function we have called internal energy (E). According to Section 18.2 "The First Law of Thermodynamics", changes in the internal energy (ΔE) are closely related to changes in the enthalpy (ΔH), which is a measure of the heat flow between a system and its surroundings at constant pressure. You also learned in Chapter 5 "Energy Changes in Chemical Reactions" that the enthalpy change for a chemical reaction can be calculated using tabulated values of enthalpies of formation. This information, however, does not tell us whether a particular process or reaction will occur spontaneously.

Let's consider a familiar example of spontaneous change. If a hot frying pan that has just been removed from the stove is allowed to come into contact with a cooler object, such as cold water in a sink, heat will flow from the hotter object to the cooler one, in this case usually releasing steam. Eventually both objects will reach the same temperature,

at a value between the initial temperatures of the two objects. This transfer of heat from a hot object to a cooler one obeys the first law of thermodynamics: energy is conserved.

Now consider the same process in reverse. Suppose that a hot frying pan in a sink of cold water were to become hotter while the water became cooler. As long as the same amount of thermal energy was gained by the frying pan and lost by the water, the first law of thermodynamics would be satisfied. Yet we all know that such a process cannot occur: heat always flows from a hot object to a cold one, never in the reverse direction. That is, *by itself* the magnitude of the heat flow associated with a process does not predict whether the process will occur spontaneously.

For many years, chemists and physicists tried to identify a single measurable quantity that would enable them to predict whether a particular process or reaction would occur spontaneously. Initially, many of them focused on enthalpy changes and hypothesized that an exothermic process would always be spontaneous. But although it is true that many, if not most, spontaneous processes are exothermic, there are also many spontaneous processes that are *not* exothermic. For example, at a pressure of 1 atm, ice melts spontaneously at temperatures greater than 0°C, yet this is an endothermic process because heat is absorbed. Similarly, many salts (such as NH_4NO_3, NaCl, and KBr) dissolve spontaneously in water even though they absorb heat from the surroundings as they dissolve (i.e., $\Delta H_{soln} > 0$). Reactions can also be both spontaneous and highly endothermic, like the reaction of barium hydroxide with ammonium thiocyanate shown in Figure 18.6 "An Endothermic Reaction".

The reaction of barium hydroxide with ammonium thiocyanate is spontaneous but highly endothermic, so water, one product of the reaction, quickly freezes into slush. When water is placed on a block of wood under the flask, the highly endothermic reaction that takes place in the flask freezes water that has been placed under the beaker, so the flask becomes frozen to the wood.

Thus enthalpy is not the only factor that determines whether a process is spontaneous. For example, after a cube of sugar has dissolved in a glass of water so that the sucrose molecules are uniformly dispersed in a dilute solution, they never spontaneously come back together in solution to form a sugar cube. Moreover, the molecules of a gas remain evenly distributed throughout the entire volume of a glass bulb and never spontaneously assemble in only one portion of the available volume. To help explain why these phenomena proceed spontaneously in only one direction requires an additional state function called entropy (S), a thermodynamic property of all substances that is proportional to their degree of disorder. In Chapter 13 "Solutions", we introduced the concept of entropy in relation to solution formation. Here we further explore the nature of this state function and define it mathematically.

Entropy

Chemical and physical changes in a system may be accompanied by either an increase or a decrease in the disorder of the system, corresponding to an increase in entropy ($\Delta S > 0$) or a decrease in entropy ($\Delta S < 0$), respectively. As with any other state function, the change in entropy is defined as the difference between the entropies of the final and initial states: $\Delta S = S_f - S_i$.

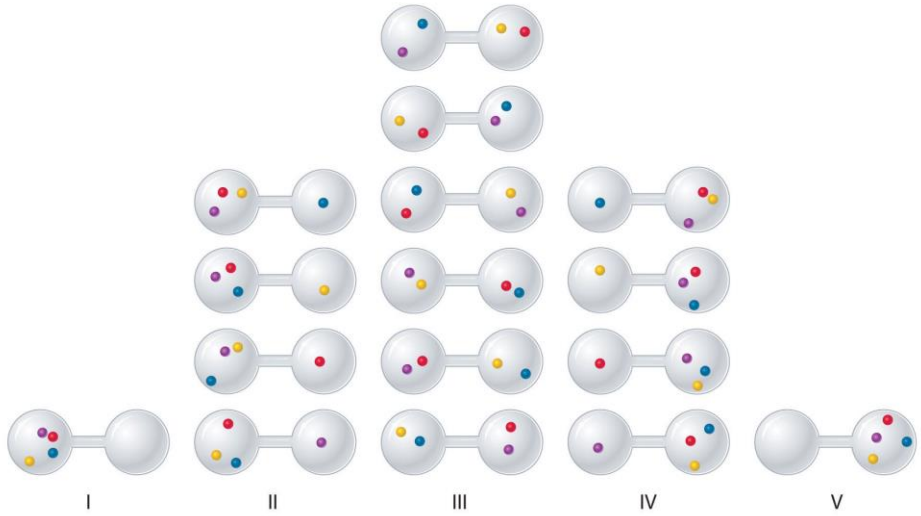
When a gas expands into a vacuum, its entropy increases because the increased volume allows for greater atomic or molecular disorder. The greater the number of atoms or molecules in the gas, the greater the disorder. The magnitude of the entropy of a system depends on the number of microscopic states, or *microstates*, associated with it (in this case, the number of atoms or molecules); that is, the greater the number of microstates, the greater the entropy.

We can illustrate the concepts of microstates and entropy using a deck of playing cards, as shown in Figure 18.7 "Illustrating Low- and High-Entropy States with a Deck of Playing Cards". In any new deck, the 52 cards are arranged by four suits, with each suit arranged in descending order. If the cards are shuffled, however, there are approximately 10^{68} different ways they might be arranged, which corresponds to 10^{68}different microscopic states. The entropy of an ordered new deck of cards is therefore low, whereas the entropy of a randomly shuffled deck is high. Card games assign a higher value to a hand that has a low degree of disorder. In games such as five-card poker, only 4 of the 2,598,960 different possible hands, or microstates, contain the highly ordered and valued arrangement of cards called a royal flush, almost 1.1 million hands contain one pair, and more than 1.3 million hands are completely disordered and therefore have no value. Because the last two arrangements are far more probable than the first, the value of a poker hand is inversely proportional to its entropy.

We can see how to calculate these kinds of probabilities for a chemical system by considering the possible arrangements of a sample of four gas molecules in a two-bulb container (Figure 18.8 "The Possible Microstates for a Sample of Four Gas Molecules in Two Bulbs of Equal Volume"). There are five possible arrangements: all four molecules in the left bulb (I); three molecules in the left bulb and one in the right bulb (II); two molecules in each bulb (III); one molecule in the left bulb and three molecules in the right bulb (IV); and four molecules in the right bulb (V). If we assign a different color to each molecule to keep track of it for this discussion (remember, however, that in reality the molecules are indistinguishable from one another), we can see that there are 16 different ways the four molecules can be distributed in the bulbs, each corresponding to a particular microstate. As shown in Figure 18.8 "The Possible Microstates

for a Sample of Four Gas Molecules in Two Bulbs of Equal Volume", arrangement I is associated with a single microstate, as is arrangement V, so each arrangement has a probability of 1/16. Arrangements II and IV each have a probability of 4/16 because each can exist in four microstates. Similarly, six different microstates can occur as arrangement III, making the probability of this arrangement 6/16. Thus the arrangement that we would expect to encounter, with half the gas molecules in each bulb, is the *most probable* arrangement. The others are not impossible but simply less likely.

Figure 18.8 *The Possible Microstates for a Sample of Four Gas Molecules in Two Bulbs of Equal Volume*



There are 16 different ways to distribute four gas molecules between the bulbs, with each distribution corresponding to a particular microstate. Arrangements I and V each produce a single microstate with a probability of 1/16. This particular arrangement is so improbable that it is likely not observed. Arrangements II and IV each produce four microstates, with a probability of 4/16. Arrangement III, with half the gas molecules in each bulb, has a probability of 6/16. It is the one encompassing the most microstates, so it is the most probable.

Instead of four molecules of gas, let's now consider 1 L of an ideal gas at standard temperature and pressure (STP), which contains 2.69×10^{22} molecules (6.022×10^{23}molecules/22.4 L). If we allow the sample of gas to expand into a second 1 L container, the probability of finding all 2.69×10^{22} molecules in one container and none in the other at any given time is extremely small,

*approximately*22.69´ 1022.

The probability of such an occurrence is effectively zero. Although

nothing prevents the molecules in the gas sample from occupying only one of the two bulbs, that particular arrangement is so improbable that it is never actually observed. The probability of arrangements with essentially equal numbers of molecules in each bulb is quite high, however, because there are *many* equivalent microstates in which the molecules are distributed equally. Hence a macroscopic sample of a gas occupies all of the space available to it, simply because this is the most probable arrangement.

A disordered system has a greater number of possible microstates than does an ordered system, so it has a higher entropy. This is most clearly seen in the entropy changes that accompany phase transitions, such as solid to liquid or liquid to gas. As you know fromChapter 11 "Liquids", Chapter 12 "Solids", and Chapter 13 "Solutions", a crystalline solid is composed of an ordered array of molecules, ions, or atoms that occupy fixed positions in a lattice, whereas the molecules in a liquid are free to move and tumble within the volume of the liquid; molecules in a gas have even more freedom to move than those in a liquid. Each degree of motion increases the number of available microstates, resulting in a higher entropy. Thus the entropy of a system must increase during melting ($\Delta S_{fus} > 0$). Similarly, when a liquid is converted to a vapor, the greater freedom of motion of the molecules in the gas phase means that $\Delta S_{vap} > 0$. Conversely, the reverse processes (condensing a vapor to form a liquid or freezing a liquid to form a solid) must be accompanied by a decrease in the entropy of the system: $\Delta S < 0$.

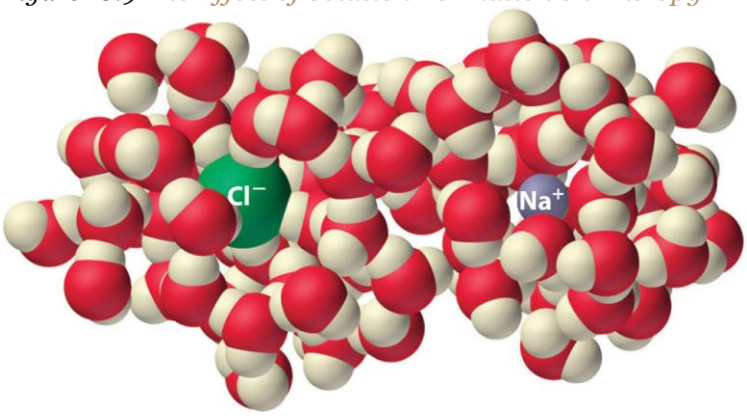
Note the Pattern

Entropy (S) is a thermodynamic property of all substances that is proportional to their degree of disorder. The greater the number of possible microstates for a system, the greater the disorder and the higher the entropy.

Experiments show that the magnitude of ΔS_{vap} is 80–90 J/(mol·K) for a wide variety of liquids with different boiling points. However, liquids that have highly ordered structures due to hydrogen bonding or other intermolecular interactions tend to have significantly higher values of ΔS_{vap}. For instance, ΔS_{vap} for water is 102 J/(mol·K). Another process that is accompanied by entropy changes is the formation of a solution. As illustrated in Figure 18.9 "The Effect of Solution Formation on Entropy", the formation of a liquid solution from a crystalline solid (the solute) and a liquid solvent is expected to result in an increase in the number of available microstates of the system and hence its entropy. Indeed, dissolving a substance such as NaCl in water disrupts both the ordered crystal lattice of NaCl and the ordered hydrogen-bonded

structure of water, leading to an increase in the entropy of the system. At the same time, however, each dissolved Na^+ ion becomes hydrated by an ordered arrangement of at least six water molecules, and the Cl^- ions also cause the water to adopt a particular local structure. Both of these effects *increase* the order of the system, leading to a *decrease* in entropy. The overall entropy change for the formation of a solution therefore depends on the relative magnitudes of these opposing factors. In the case of an NaCl solution, disruption of the crystalline NaCl structure and the hydrogen-bonded interactions in water is quantitatively more important, so $\Delta S_{soln} > 0$.

Figure 18.9 *The Effect of Solution Formation on Entropy*



Dissolving NaCl in water results in an increase in the entropy of the system. Each hydrated ion, however, forms an ordered arrangement with water molecules, which decreases the entropy of the system. The magnitude of the increase is greater than the magnitude of the decrease, so the overall entropy change for the formation of an NaCl solution is positive.

EXAMPLE 5

Predict which substance in each pair has the higher entropy and justify your answer.

a. 1 mol of $NH_3(g)$ or 1 mol of He(g), both at 25°C

b. 1 mol of Pb(s) at 25°C or 1 mol of Pb(l) at 800°C

Given: amounts of substances and temperature

Asked for: higher entropy

Strategy:

From the number of atoms present and the phase of each substance, predict which has the greater number of available microstates and hence the higher entropy.

Solution:

a. Both substances are gases at 25°C, but one consists of He atoms and the other consists of NH_3 molecules. With four atoms instead of one, the NH_3 molecules have more motions available, leading to a greater number of microstates. Hence we predict that the NH_3 sample will have the higher entropy.

b. The nature of the atomic species is the same in both cases, but the phase is different: one sample is a solid, and one is a liquid. Based on the greater freedom of motion available to atoms in a liquid, we predict that the liquid sample will have the higher entropy.

Exercise

Predict which substance in each pair has the higher entropy and justify your answer.

a. 1 mol of He(g) at 10 K and 1 atm pressure or 1 mol of He(g) at 250°C and 0.2 atm

b. a mixture of 3 mol of H_2(g) and 1 mol of N_2(g) at 25°C and 1 atm or a sample of 2 mol of NH_3(g) at 25°C and 1 atm

Answer:

a. 1 mol of He(g) at 250°C and 0.2 atm (higher temperature and lower pressure indicate greater volume and more microstates)

b. a mixture of 3 mol of H_2(g) and 1 mol of N_2(g) at 25°C and 1 atm (more molecules of gas are present)

Reversible and Irreversible Changes

Changes in entropy (ΔS), together with changes in enthalpy (ΔH), enable us to predict in which direction a chemical or physical change will occur spontaneously. Before discussing how to do so, however, we must understand the difference between a reversible process and an irreversible one. In a reversible process, every intermediate state between the extremes is an equilibrium state, regardless of the direction of the change. In contrast, an irreversible process is one in which the intermediate states are not equilibrium states, so change occurs spontaneously in only one direction. As a result, *a reversible process can change direction at any time, whereas an irreversible process cannot*. When a gas expands reversibly against an external pressure such as a piston, for example, the expansion can be reversed at any time by reversing the motion of the piston; once the gas is compressed, it can be allowed to expand again, and the process

can continue indefinitely. In contrast, the expansion of a gas into a vacuum ($P_{ext} = 0$) is irreversible because the external pressure is measurably less than the internal pressure of the gas. No equilibrium states exist, and the gas expands irreversibly. When gas escapes from a microscopic hole in a balloon into a vacuum, for example, the process is irreversible; the direction of airflow cannot change.

Because work done during the expansion of a gas depends on the opposing external pressure ($w = P_{ext}\Delta V$), *work done in a reversible process is always equal to or greater than work done in a corresponding irreversible process*: $w_{rev} \geq w_{irrev}$. Whether a process is reversible or irreversible, $\Delta E = q + w$. Because E is a state function, the magnitude of ΔE does *not* depend on reversibility and is independent of the path taken. So

Equation 18.14

$$\Delta E = q_{rev} + w_{rev} = q_{irrev} + w_{irrev}$$

Note the Pattern

Work done in a reversible process is always equal to or greater than work done in a corresponding irreversible process: $w_{rev} \geq w_{irrev}$.

In other words, ΔE for a process is the same whether that process is carried out in a reversible manner or an irreversible one. We now return to our earlier definition of entropy, using the magnitude of the heat flow for a reversible process (q_{rev}) to define entropy quantitatively.

The Relationship between Internal Energy and Entropy

Because the quantity of heat transferred (q_{rev}) is directly proportional to the absolute temperature of an object (T) ($q_{rev} \propto T$), the hotter the object, the greater the amount of heat transferred. Moreover, adding heat to a system increases the kinetic energy of the component atoms and molecules and hence their disorder ($\Delta S \propto q_{rev}$). Combining these relationships for any reversible process,

Equation 18.15

$$qrev = T\,\mathrm{D}Sand\mathrm{D}S = qrevT$$

Because the numerator (q_{rev}) is expressed in units of energy (joules), the units of ΔS are joules/kelvin (J/K). Recognizing that the work done in a reversible process at constant pressure is $w_{rev} = -P\Delta V$, we can express Equation 18.14 as follows:

Equation 18.16

$$\Delta E = q_{rev} + w_{rev} = T\Delta S - P\Delta V$$

Thus the change in the internal energy of the system is related to the change in entropy, the absolute temperature, and the *PV* work done.

To illustrate the use of Equation 18.15 and Equation 18.16, we consider two reversible processes before turning to an irreversible process. When a sample of an ideal gas is allowed to expand reversibly at constant temperature, heat must be added to the gas during expansion to keep its T constant (Figure 18.10 "Expansion of Gas at Constant Temperature"). The internal energy of the gas does not change because the temperature of the gas does not change; that is, $\Delta E = 0$ and $q_{rev} = -w_{rev}$. During expansion, $\Delta V > 0$, so the gas performs work on its surroundings: $w_{rev} = -P\Delta V < 0$. According to Equation 18.16, this means that q_{rev} must increase during expansion; that is, the gas must absorb heat from the surroundings during expansion, and the surroundings must give up that same amount of heat. The entropy change of the system is therefore $\Delta S_{sys} = +q_{rev}/T$, and the entropy change of the surroundings is $\Delta S_{surr} = -q_{rev}/T$. The corresponding change in entropy of the universe is then as follows:

Equation 18.17

$$DSuniv = DSsys + DSsurr = qrevT + (- qrevT) = 0$$

Thus no change in ΔS_{univ} has occurred.

Figure 18.10 *Expansion of Gas at Constant Temperature*

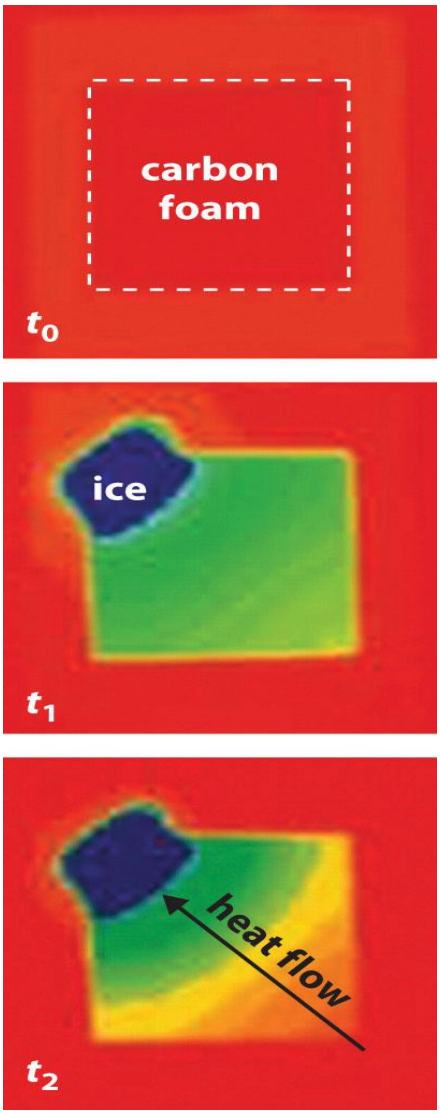
In the initial state (top), the temperatures of a gas and the surroundings are the same. During the reversible expansion of the gas, heat must be added to the gas to maintain a constant temperature. Thus the internal energy of the gas does not change, but work is performed on the surroundings. In the final state (bottom), the temperature of the surroundings is lower because the gas has absorbed heat from the surroundings during expansion.

Now consider the reversible melting of a sample of ice at 0°C and 1 atm. The enthalpy of fusion of ice is 6.01 kJ/mol, which means that 6.01 kJ of heat are absorbed reversibly from the surroundings when 1 mol of ice melts at 0°C, as illustrated in Figure 18.11 "Thermograms Showing That Heat Is Absorbed from the Surroundings When Ice Melts at 0°C". The surroundings constitute a sample of low-density carbon foam that is thermally conductive, and the system is the ice cube that has been placed on it. The direction of heat flow along the resulting temperature gradient is indicated with an arrow. From Equation 18.15, we see that the entropy of fusion of ice can be written as follows:

Equation 18.18

$$\Delta S_{fus} = q_{rev}/T = \Delta H_{fus}/T$$

Figure 18.11 *Thermograms Showing That Heat Is Absorbed from the Surroundings When Ice Melts at 0°C*



By convention, a thermogram shows cold regions in blue, warm regions in red, and thermally intermediate regions in green. When an ice cube (the system, dark blue) is placed on the corner of a square sample of low-density carbon foam with very high thermal conductivity, the temperature of the foam is lowered (going from red to green). As the ice melts, a temperature gradient appears, ranging from warm to very cold. An arrow indicates the direction of heat flow from the surroundings (red and green) to the ice cube. The amount of heat lost by the surroundings is the same as the amount gained by the ice, so the entropy of the universe does not change.

In this case, ΔS_{fus} = (6.01 kJ/mol)/(273 K) = 22.0 J/(mol·K) = ΔS_{sys}. The amount of heat lost by the surroundings is the same as the amount gained by the ice, so $\Delta S_{surr} = q_{rev}/T$ = −(6.01 kJ/mol)/(273 K) = −22.0 J/(mol·K). Once again, we see that the entropy of the universe does not change:
$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$ = 22.0 J/(mol·K) − 22.0 J/(mol·K) = 0

In these two examples of reversible processes, the entropy of the universe is unchanged. This is true of all reversible processes and constitutes part of thesecond law of thermodynamics: *the entropy of the universe remains constant in a reversible process, whereas the entropy of the universe increases in an irreversible (spontaneous) process*.

Note the Pattern

The entropy of the universe increases during a spontaneous process.

As an example of an irreversible process, consider the entropy changes that accompany the spontaneous and irreversible transfer of heat from a hot object to a cold one, as occurs when lava spewed from a volcano flows into cold ocean water. The cold substance, the water, gains heat ($q > 0$), so the change in the entropy of the water can be written as $\Delta S_{cold} = q/T_{cold}$. Similarly, the hot substance, the lava, loses heat ($q < 0$), so its entropy change can be written as $\Delta S_{hot} = -q/T_{hot}$, where T_{cold} and T_{hot} are the temperatures of the cold and hot substances, respectively. The total entropy change of the universe accompanying this process is therefore

Equation 18.19

$$\Delta S_{univ} = \Delta S_{cold} + \Delta S_{hot} = \frac{q}{T_{cold}} + \left(-\frac{q}{T_{hot}}\right)$$

The numerators on the right side of Equation 18.19 are the same in magnitude but opposite in sign. Whether ΔS_{univ} is positive or negative depends on the relative magnitudes of the denominators. By definition, $T_{hot} > T_{cold}$, so $-q/T_{hot}$ must be less than q/T_{cold}, and ΔS_{univ} must be positive. As predicted by the second law of thermodynamics, the entropy of the universe increases during this irreversible process. Any process for which ΔS_{univ} is positive is, by definition, a spontaneous one that will occur as written. Conversely, any process for which ΔS_{univ} approaches zero will not occur spontaneously as written but will occur spontaneously in the reverse direction. We see, therefore, that heat is spontaneously transferred from a hot substance, the lava, to a cold substance, the ocean water. In fact, if the lava is hot enough (e.g., if it is molten), so much heat can be transferred that the water is converted to steam (Figure 18.12 "Spontaneous Transfer of Heat from a Hot Substance to a Cold Substance").

EXAMPLE 6

Tin has two allotropes with different structures. Gray tin (α-tin) has a structure similar to that of diamond, whereas white tin (β-tin) is denser, with a unit cell structure that is based on a rectangular prism. At temperatures greater than 13.2°C, white tin is the more stable phase, but below that temperature, it slowly converts reversibly to the less dense, powdery gray phase. This phenomenon plagued Napoleon's army during his ill-fated invasion of Russia in 1812: the buttons on his soldiers' uniforms were made of tin and disintegrated during the Russian winter, adversely affecting the soldiers' health (and morale). The conversion of white tin to gray tin is exothermic, with $\Delta H = -2.1$ kJ/mol at 13.2°C.

a. What is ΔS for this process?

b. Which is the more highly ordered form of tin—white or gray?

Given: ΔH and temperature

Asked for: ΔS and relative degree of order

Strategy:

Use Equation 18.15 to calculate the change in entropy for the reversible phase transition. From the calculated value of ΔS, predict which allotrope has the more highly ordered structure.

Solution:

a. We know from Equation 18.15 that the entropy change for any reversible process is the heat transferred (in joules) divided by the temperature at which the process occurs. Because the conversion occurs at constant pressure, and ΔH and ΔE are essentially equal for reactions that involve only solids, we can calculate the change in entropy for the reversible phase transition where $q_{rev} = \Delta H$. Substituting the given values for ΔH and temperature in kelvins (in this case, T = 13.2°C = 286.4 K),

a. $$\Delta S = qrevT = (-2.1\ kJ/mol)(1000\ J/kJ)286.4\ K = -7.3\ J/(mol \cdot K)$$

b. The fact that $\Delta S < 0$ means that entropy decreases when white tin is converted to gray tin. Thus gray tin must be the more highly ordered structure.

Exercise

Elemental sulfur exists in two forms: an orthorhombic form (S_α), which is stable below 95.3°C, and a monoclinic form (S_β), which is stable above 95.3°C. The conversion of orthorhombic sulfur to monoclinic sulfur is endothermic, with ΔH = 0.401 kJ/mol at 1 atm.

a. What is ΔS for this process?

b. Which is the more highly ordered form of sulfur—S_α or S_β?

Answer:

a. 1.09 J/(mol·K)

b. S_α

Summary

A measure of the disorder of a system is its **entropy (*S*)**, a state function whose value increases with an increase in the number of available microstates. A**reversible process** is one for which all intermediate states between extremes are equilibrium states; it can change direction at any time. In contrast, an**irreversible process** occurs in one direction only. The change in entropy of the system or the surroundings is the quantity of heat transferred divided by the temperature. The **second law of thermodynamics** states that in a reversible process, the entropy of the universe is constant, whereas in an irreversible process, such as the transfer of heat from a hot object to a cold object, the entropy of the universe increases.

KEY TAKEAWAYS

- For a given system, the greater the number of microstates, the higher the entropy.
- During a spontaneous process, the entropy of the universe increases.

KEY EQUATION

Entropy change

Equation 18.15: $\Delta S = q_{rev}T$

CONCEPTUAL PROBLEMS

1. A Russian space vehicle developed a leak, which resulted in an internal pressure drop from 1 atm to 0.85 atm. Is this an example of a reversible expansion? Has work been done?
2. Which member of each pair do you expect to have a higher entropy? Why?

a. solid phenol or liquid phenol

b. 1-butanol or butane

c. cyclohexane or cyclohexanol

d. 1 mol of N_2 mixed with 2 mol of O_2 or 2 mol of NO_2

e. 1 mol of O_2 or 1 mol of O_3

f. 1 mol of propane at 1 atm or 1 mol of propane at 2 atm

3. Determine whether each process is reversible or irreversible.

a. ice melting at 0°C

b. salt crystallizing from a saline solution

c. evaporation of a liquid in equilibrium with its vapor in a sealed flask

d. a neutralization reaction

4. Determine whether each process is reversible or irreversible.

a. cooking spaghetti

b. the reaction between sodium metal and water

c. oxygen uptake by hemoglobin

d. evaporation of water at its boiling point

5. Explain why increasing the temperature of a gas increases its entropy. What effect does this have on the internal energy of the gas?

6. For a series of related compounds, does ΔS_{vap} increase or decrease with an increase in the strength of intermolecular interactions in the liquid state? Why?

7. Is the change in the enthalpy of reaction or the change in entropy of reaction more sensitive to changes in temperature? Explain your reasoning.

8. Solid potassium chloride has a highly ordered lattice structure. Do you expect ΔS_{soln} to be greater or less than zero? Why? What opposing factors must be considered in making your prediction?

9. Aniline ($C_6H_5NH_2$) is an oily liquid at 25°C that darkens on exposure to air and light. It is used in dying fabrics and in staining wood black. One gram of aniline dissolves in 28.6 mL of water, but aniline is completely miscible with ethanol. Do you expect ΔS_{soln} in H_2O to be greater than, less than, or equal to ΔS_{soln} in CH_3CH_2OH? Why?

ANSWERS

1. No, it is irreversible; no work is done because the external pressure is effectively zero.

2.

3.

a. reversible

b. irreversible

c. reversible

d. irreversible

4.

5.

6.

7.

8.

9. Water has a highly ordered, hydrogen-bonded structure that must reorganize to accommodate hydrophobic solutes like aniline. In contrast, we expect that aniline will be able to disperse randomly throughout ethanol, which has a significantly less ordered structure. We therefore predict that ΔS_{soln} in ethanol will be more positive than ΔS_{soln}in water.

NUMERICAL PROBLEMS

1. Liquid nitrogen, which has a boiling point of −195.79°C, is used as a coolant and as a preservative for biological tissues. Is the entropy of nitrogen higher or lower at −200°C than at −190°C? Explain your answer. Liquid nitrogen freezes to a white solid at −210.00°C, with an enthalpy of fusion of 0.71 kJ/mol. What is its entropy of fusion? Is freezing biological tissue in liquid nitrogen an example of a reversible process or an irreversible process?
2. Using the second law of thermodynamics, explain why heat flows from a hot body to a cold body but not from a cold body to a hot body.
3. One test of the spontaneity of a reaction is whether the entropy of the universe increases: $\Delta S_{univ} > 0$. Using an entropic argument, show that the following reaction is spontaneous at 25°C:

$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$

Why does the entropy of the universe increase in this reaction even though gaseous molecules, which have a high entropy, are consumed?

4. Calculate the missing data in the following table.

Compound	ΔH_{fus} (kJ/mol)	ΔS_{fus} [J/(mol·K)]	Melting Point (°C)
acetic acid	11.7		16.6
CH_3CN	8.2	35.9	

Compound	ΔH_{fus} (kJ/mol)	ΔS_{fus} [J/(mol·K)]	Melting Point (°C)
CH_4	0.94		−182.5
CH_3OH		18.2	−97.7
formic acid	12.7	45.1	

5. Based on this table, can you conclude that entropy is related to the nature of functional groups? Explain your reasoning.
6. Calculate the missing data in the following table.

Compound	ΔH_{vap} (kJ/mol)	ΔS_{vap} [J/(mol·K)]	Boiling Point (°C)
hexanoic acid	71.1		105.7
hexane	28.9	85.5	
formic acid		60.7	100.8
1-hexanol	44.5		157.5

7. The text states that the magnitude of ΔS_{vap} tends to be similar for a wide variety of compounds. Based on the values in the table, do you agree?

alculate the amount of work done against a pressure of 1.0 atm when 4.0 mol of acetylene are allowed to react with 10 mol of O_2 at 1.0 atm at 20°C. What is the change in internal energy for the reaction?

4. When iron dissolves in 1.00 M aqueous HCl, the products are $FeCl_2$(aq) and hydrogen gas. Calculate the work done if 30 g of Fe react with excess hydrochloric acid in a closed vessel at 20°C. How much work is done if the reaction takes place in an open vessel with an external pressure of 1.0 atm?

ANSWER

1. −350 J; 8.2 kJ

18.4 Entropy Changes and the Third Law of Thermodynamics

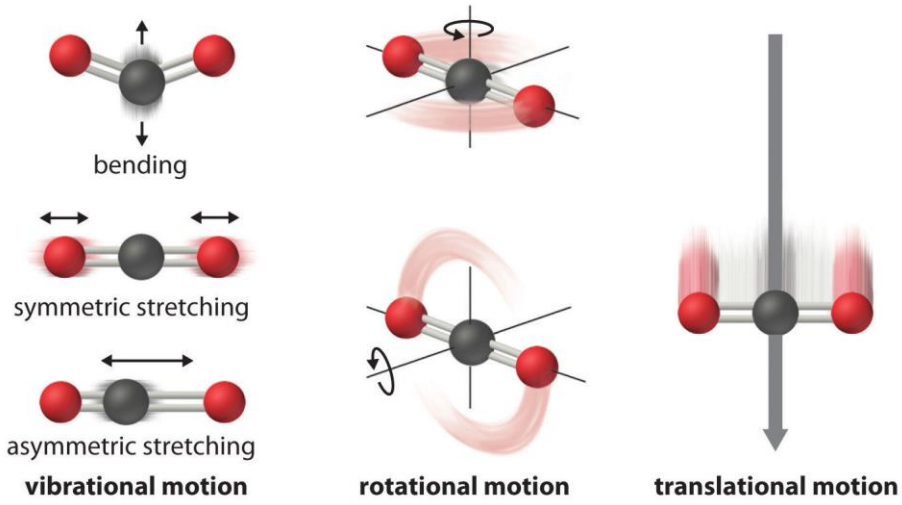
LEARNING OBJECTIVE

1. To use thermodynamic cycles to calculate changes in entropy.

The atoms, molecules, or ions that compose a chemical system can undergo several types of molecular motion, including translation, rotation, and vibration (Figure 18.13 "Molecular Motions"). The greater the molecular motion of a system, the greater the number of possible microstates and the higher the entropy. A perfectly ordered system with only a single microstate available to it would have an entropy of zero. The

only system that meets this criterion is a perfect crystal at a temperature of absolute zero (0 K), in which each component atom, molecule, or ion is fixed in place within a crystal lattice and exhibits no motion. Such a state of perfect order (or, conversely, zero disorder) corresponds to zero entropy. In practice, absolute zero is an ideal temperature that is unobtainable, and a perfect single crystal is also an ideal that cannot be achieved. Nonetheless, the combination of these two ideals constitutes the basis for thethird law of thermodynamics: *the entropy of any perfectly ordered, crystalline substance at absolute zero is zero.*

Figure 18.13 Molecular Motions



Vibrational, rotational, and translational motions of a carbon dioxide molecule are illustrated here. Only a perfectly ordered, crystalline substance at absolute zero would exhibit no molecular motion and have zero entropy. In practice, this is an unattainable ideal.

The third law of thermodynamics has two important consequences: it defines the *sign*of the entropy of any substance at temperatures above absolute zero as positive, and it provides a fixed reference point that allows us to measure the *absolute entropy* of any substance at any temperature.[1] In contrast, other thermodynamic properties, such as internal energy and enthalpy, can be evaluated in only *relative* terms, not absolute terms. In this section, we examine two different ways to calculate ΔS for a reaction or a physical change. The first, based on the definition of absolute entropy provided by the third law of thermodynamics, uses tabulated values of absolute entropies of substances. The second, based on the fact that entropy is a state function, uses a thermodynamic cycle similar to those we first encountered in Chapter 5 "Energy Changes in Chemical Reactions".

Calculating Δ*S* from Standard Molar Entropy Values

One way of calculating Δ*S* for a reaction is to use tabulated values of thestandard molar entropy (*S*°), which is the entropy of 1 mol of a substance at a standard temperature of 298 K; the units of *S*° are J/(mol·K). Unlike enthalpy or internal energy, it is possible to obtain absolute entropy values by measuring the entropy change that occurs between the reference point of 0 K [corresponding to *S* = 0 J/(mol·K)] and 298 K.

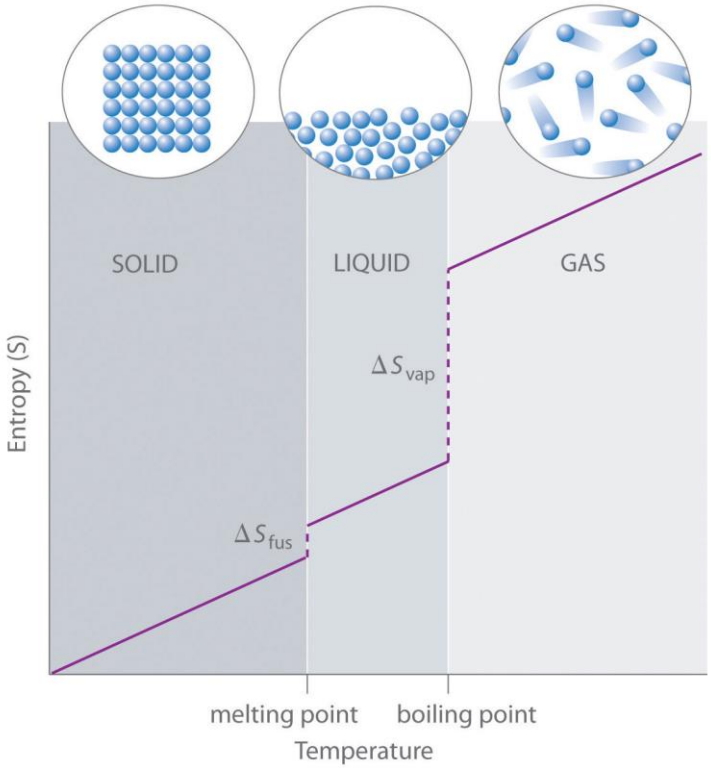
As shown in Table 18.1 "Standard Molar Entropy Values of Selected Substances at 25°C", for substances with approximately the same molar mass and number of atoms,*S*° values fall in the order *S*°(gas) > *S*°(liquid) > *S*°(solid). For instance, *S*° for liquid water is 70.0 J/(mol·K), whereas *S*° for water vapor is 188.8 J/(mol·K). Likewise, *S*° is 260.7 J/(mol·K) for gaseous I_2 and 116.1 J/(mol·K) for solid I_2. This order makes qualitative sense based on the kinds and extents of motion available to atoms and molecules in the three phases. The correlation between physical state and absolute entropy is illustrated in Figure 18.14 "A Generalized Plot of Entropy versus Temperature for a Single Substance", which is a generalized plot of the entropy of a substance versus temperature.

Table 18.1 Standard Molar Entropy Values of Selected Substances at 25°C

Substance	*S*° [J/(mol·K)]
Gases	
He	126.2
H_2	130.7
Ne	146.3
Ar	154.8
Kr	164.1
Xe	169.7
H_2O	188.8
N_2	191.6
O_2	205.2
CO_2	213.8
I_2	260.7
Liquids	
H_2O	70.0

Substance	$S°$ [J/(mol·K)]
CH_3OH	126.8
Br_2	152.2
CH_3CH_2OH	160.7
C_6H_6	173.4
CH_3COCl	200.8
C_6H_{12} (cyclohexane)	204.4
C_8H_{18} (isooctane)	329.3
Solids	
C (diamond)	2.4
C (graphite)	5.7
LiF	35.7
SiO_2 (quartz)	41.5
Ca	41.6
Na	51.3
MgF_2	57.2
K	64.7
NaCl	72.1
KCl	82.6
I_2	116.1

Figure 18.14 *A Generalized Plot of Entropy versus Temperature for a Single Substance*



Absolute entropy increases steadily with increasing temperature until the melting point is reached, where it jumps suddenly as the substance undergoes a phase change from a highly ordered solid to a disordered liquid (ΔS_{fus}). The entropy again increases steadily with increasing temperature until the boiling point is reached, where it jumps suddenly as the liquid undergoes a phase change to a highly disordered gas (ΔS_{vap}).

A closer examination of Table 18.1 "Standard Molar Entropy Values of Selected Substances at 25°C" also reveals that substances with similar molecular structures tend to have similar S° values. Among crystalline materials, those with the lowest entropies tend to be rigid crystals composed of small atoms linked by strong, highly directional bonds, such as diamond [S° = 2.4 J/(mol·K)]. In contrast, graphite, the softer, less rigid allotrope of carbon, has a higher S° [5.7 J/(mol·K)] due to more disorder in the crystal. Soft crystalline substances and those with larger atoms tend to have higher entropies because of increased molecular motion and disorder. Similarly, the absolute entropy of a substance tends to increase with increasing molecular complexity because the number of available microstates increases with molecular complexity. For example, compare the S° values for $CH_3OH(l)$ and $CH_3CH_2OH(l)$. Finally, substances with strong hydrogen bonds have lower values of S°, which reflects a more ordered structure.

To calculate $\Delta S°$ for a chemical reaction from standard molar entropies, we use the familiar "products minus reactants" rule, in which the absolute entropy of each reactant and product is multiplied by its stoichiometric coefficient in the balanced chemical equation. Example 7 illustrates this procedure for the combustion of the liquid hydrocarbon isooctane (C_8H_{18}; 2,2,4-trimethylpentane).

EXAMPLE 7

Use the data in Table 18.1 "Standard Molar Entropy Values of Selected Substances at 25°C" to calculate $\Delta S°$ for the reaction of liquid isooctane with $O_2(g)$ to give $CO_2(g)$ and $H_2O(g)$ at 298 K.

Given: standard molar entropies, reactants, and products

Asked for: $\Delta S°$

Strategy:

Write the balanced chemical equation for the reaction and identify the appropriate quantities in Table 18.1 "Standard Molar Entropy Values of Selected Substances at 25°C". Subtract the sum of the absolute entropies of the reactants from the sum of the absolute entropies of the products, each multiplied by their appropriate stoichiometric coefficients, to obtain $\Delta S°$ for the reaction.

Solution:

The balanced chemical equation for the complete combustion of isooctane (C_8H_{18}) is as follows:

$$C8H18(l) + 252O2(g) \rightarrow 8CO2(g) + 9H2O(g)$$

We calculate $\Delta S°$ for the reaction using the "products minus reactants" rule, where *m* and *n* are the stoichiometric coefficients of each product and each reactant:

$$DS°rxn = \sum mS°(products) - \sum nS°(reactants)$$
$$= [8S°(CO2) + 9S°(H2O)] - [S°(C8H18) + 252S°(O2)]$$
$$= \{[8\ mol\ CO2 \times 213.8\ J/(mol \cdot K)] + [9\ mol\ H2O' 188.8\ J/(mol \times K)]\} - \{[1mol\ C8H18' 329.3\ J/(mol \times K)] + [252mol\ O2' 205.2\ J/(mol \times K)]\} = 515.3\ J/K$$

$\Delta S°$ is positive, as expected for a combustion reaction in which one large hydrocarbon molecule is converted to many molecules of gaseous products.

Exercise

Use the data in Table 18.1 "Standard Molar Entropy Values of Selected Substances at 25°C" to calculate $\Delta S°$ for the reaction of $H_2(g)$ with liquid benzene (C_6H_6) to give cyclohexane (C_6H_{12}).

Answer: −361.1 J/K

Note the Pattern

Entropy increases with softer, less rigid solids, solids that contain larger atoms, and solids with complex molecular structures.

Note the Pattern

$\Delta S°$ for a reaction can be calculated from absolute entropy values using the same "products minus reactants" rule used to calculate $\Delta H°$.

Calculating Δ*S* from Thermodynamic Cycles

We can also calculate a change in entropy using a thermodynamic cycle. As you learned in Chapter 5 "Energy Changes in Chemical Reactions", the molar heat capacity (C_p) is the amount of heat needed to raise the temperature of 1 mol of a substance by 1°C at constant pressure. Similarly, C_v is the amount of heat needed to raise the temperature of 1 mol of a substance by 1°C at constant volume. The increase in entropy with increasing temperature in Figure 18.14 "A Generalized Plot of Entropy versus Temperature for a Single Substance" is approximately proportional to the heat capacity of the substance.

Recall that the entropy change (ΔS) is related to heat flow (q_{rev}) by $\Delta S = q_{rev}/T$. Because $q_{rev} = nC_p\Delta T$ at constant pressure or $nC_v\Delta T$ at constant volume, where n is the number of moles of substance present, the change in entropy for a substance whose temperature changes $from\ T_1\ to\ T_2\ is\ as\ follows$:

$$DS = qrevT = nCpDTT \quad (constant\ \ pressure)$$

As you will discover in more advanced math courses than is required here, it can be shown that this is equal to the following: [2]

Equation 18.20

$$DS = qrevT = nCpDTT \quad (constant\ \ pressure)$$

Similarly,

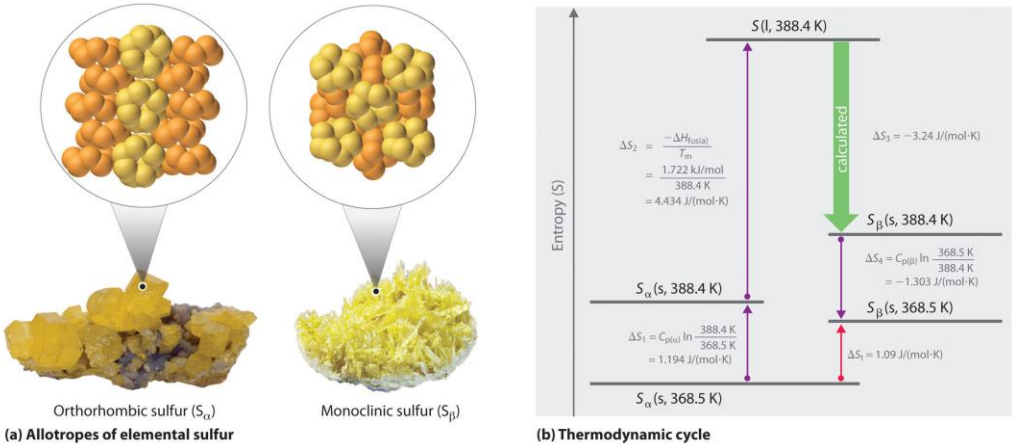
Equation 18.21

$$DS = nCvln\ T2T1 \quad (constant\ \ volume)$$

Thus we can use a combination of heat capacity measurements (Equation 18.20 orEquation 18.21) and experimentally measured values of enthalpies of fusion or vaporization if a phase change is involved (Equation 18.18) to calculate the entropy change corresponding to a change in the temperature of a sample.

We can use a thermodynamic cycle to calculate the entropy change when the phase change for a substance such as sulfur cannot be measured directly. As noted in the exercise in Example 6, elemental sulfur exists in two forms (part (a) in Figure 18.15 "Two Forms of Elemental Sulfur and a Thermodynamic Cycle Showing the Transition from One to the Other"): an orthorhombic form with a highly ordered structure (S_α) and a less-ordered monoclinic form (S_β). The orthorhombic (α) form is more stable at room temperature but undergoes a phase transition to the monoclinic (β) form at temperatures greater than 95.3°C (368.5 K). The transition from S_α to S_β can be described by the thermodynamic cycle shown in part (b) in Figure 18.15 "Two Forms of Elemental Sulfur and a Thermodynamic Cycle Showing the Transition from One to the Other", in which liquid sulfur is an intermediate. The change in entropy that accompanies the conversion of liquid sulfur to S_β ($-\Delta S_{fus(\beta)} = \Delta S_3$ in the cycle) cannot be measured directly. Because entropy is a state function, however, ΔS_3 can be calculated from the overall entropy change (ΔS_t) for the S_α–S_β transition, which equals the sum of the ΔS values for the steps in the thermodynamic cycle, using Equation 18.20 and tabulated thermodynamic parameters (the heat capacities of S_α and S_β, $\Delta H_{fus(\omega)}$, and the melting point of S_α.)

Figure 18.15 *Two Forms of Elemental Sulfur and a Thermodynamic Cycle Showing the Transition from One to the Other*



(a) Orthorhombic sulfur (S_α) has a highly ordered structure in which the S_8 rings are stacked in a "crankshaft" arrangement. Monoclinic sulfur (S_β) is also composed of S_8 rings but has a less-ordered structure. (b) At 368.5 K, S_α undergoes a phase transition to S_β. Although ΔS_3 cannot be measured directly, it can be calculated using the values shown in this thermodynamic cycle.

If we know the melting point of S_α (T_m = 115.2°C = 388.4 K) and ΔS_t for the overall phase transition [calculated to be 1.09 J/(mol·K) in the exercise in Example 6], we can calculate ΔS_3 from the values given in part (b) in Figure 18.15 "Two Forms of Elemental Sulfur and a Thermodynamic Cycle Showing the Transition from One to the Other"where $C_{p(\alpha)}$ = 22.70 J/mol·K and $C_{p(\beta)}$ = 24.77 J/mol·K (subscripts on ΔS refer to steps in the cycle):

$$\begin{aligned}
&\Delta St\,1.09\ J/(mol\cdot K)\\
&=\Delta S1+\Delta S2+\Delta S3+\Delta S4\\
&=Cp(a)ln(T2T1)+\Delta HfusTm\\
&+\Delta S3+Cp(b)ln(T4T3)=22.70\ J\\
&/(mol\cdot K)ln(388.4368.5)+(1.722\ kJ\\
&/mol\,388.4\ K\times 1000\ J/kJ)+\Delta S3\\
&+24.77\ J/(mol\cdot K)ln(368.5388.4)=[1.194\ J\\
&/(mol\cdot K)]+[4.434\ J/(mol\cdot K)]+\Delta S3+[-1\\
&.303\ J/(mol\times K)]
\end{aligned}$$

Solving for ΔS_3 gives a value of −3.24 J/(mol·K). As expected for the conversion of a less ordered state (a liquid) to a more ordered one (a crystal), ΔS_3 is negative.

Summary

The **third law of thermodynamics** states that the entropy of any perfectly ordered, crystalline substance at absolute zero is zero. At temperatures greater than absolute zero, entropy has a positive value, which allows us to measure the*absolute entropy* of a substance. Measurements of the heat capacity of a substance and the enthalpies of fusion or vaporization can be used to calculate the changes in entropy that accompany a physical change. The entropy of 1 mol of a substance at a standard temperature of 298 K is its **standard molar entropy ($S°$)**. We can use the "products minus reactants" rule to calculate the standard entropy change ($\Delta S°$) for a reaction using tabulated values of $S°$ for the reactants and the products.

KEY TAKEAWAY

- Entropy changes can be calculated using the “products minus reactants” rule or from a combination of heat capacity measurements and measured values of enthalpies of fusion or vaporization.

KEY EQUATIONS

Temperature dependence of entropy at constant pressure

Equation 18.20: $\Delta S = nC_p \ln \frac{T_2}{T_1}$

Temperature dependence of entropy at constant volume

Equation 18.21: $\Delta S = nC_v \ln \frac{T_2}{T_1}$

CONCEPTUAL PROBLEMS

1. Crystalline $MgCl_2$ has $S°$ = 89.63 J/(mol·K), whereas aqueous $MgCl_2$ has $S°$ = −25.1 J/(mol·K). Is this consistent with the third law of thermodynamics? Explain your answer.
2. Why is it possible to measure absolute entropies but not absolute enthalpies?
3. How many microstates are available to a system at absolute zero? How many are available to a substance in its liquid state?
4. Substance A has a higher heat capacity than substance B. Do you expect the absolute entropy of substance A to be less than, similar to, or greater than that of substance B? Why? As the two substances are heated, for which substance do you predict the entropy to increase more rapidly?
5. Phase transitions must be considered when calculating entropy changes. Why?

NUMERICAL PROBLEMS

1. What is the final temperature of water when 5.20 g of ice at 0.0°C are added to 250 mL of water in an insulated thermos at 30.0°C? The value of ΔH_{fus} for water is 6.01 kJ/mol, and the heat capacity of liquid water is 75.3 J/(mol·°C). What is the entropy change for this process?
2. Calculate the change in both enthalpy and entropy when a 3.0 g block of ice melts at 0.0°C [$\Delta H_{fus}(H_2O)$ = 6.01 kJ/mol]. For the same block of ice, calculate the entropy change for the system when the ice is warmed from 0.0°C to 25°C. The heat capacity of liquid water over this temperature range is 75.3 J/(mol·°C).

3. Use the data in Table 18.1 "Standard Molar Entropy Values of Selected Substances at 25°C" and Chapter 25 "Appendix A: Standard Thermodynamic Quantities for Chemical Substances at 25°C" to calculate $\Delta S°$ for each reaction.

a. $a.\quad H2(g)+12O2(g)\rightarrow H2O(l)$ $CH_3OH(l) + HCl(g) \rightarrow CH_3Cl(g) + H_2O(l)$

b. $H_2(g) + Br_2(l) \rightarrow 2HBr(g)$

c. $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(s) + H_2(g)$

4. Calculate the entropy change (J/K) when 4.35 g of liquid bromine are heated from 30.0°C to 50.0°C if the molar heat capacity (C_p) of liquid bromine is 75.1 kJ/(mol·K).

5. Calculate the molar heat capacity (C_p) of titanium tetrachloride if the change in entropy when a 6.00 g sample of $TiCl_4(l)$ is heated from 25.0°C to 40.0°C is 0.154 J/K.

6. When a 1.00 g sample of lead is heated from 298.2 K to just below its melting temperature of 600.5 K, the change in entropy is 0.0891 J/K. Determine the molar heat capacity (C_p) of lead over this temperature range.

7. Phosphorus oxychloride ($POCl_3$) is a chlorinating agent that is frequently used in organic chemistry to replace oxygen with chlorine. Given ΔS_{vap} = 93.08 J/(mol·K) and ΔH_{vap} = 35.2 kJ/mol, does $POCl_3$ spontaneously convert from a liquid to a gas at 110°C? Does it spontaneously crystallize at 0.0°C if ΔH_{fus} = 34.3 kJ/mol and ΔS_{fus} = 125 J/(mol·K)? Using the information provided, what is the melting point of $POCl_3$?

8. A useful reagent for the fluorination of alcohols, carboxylic acids, and carbonyl compounds is selenium tetrafluoride (SeF_4). One must be careful when using this compound, however, because it is known to attack glass (such as the glass of a reaction vessel).

a. Is SeF_4 a liquid or a gas at 100°C given that ΔH_{vap} = 46.9 kJ/mol and ΔS_{vap} = 124 J/(mol·K)?

b. Determine the boiling point of SeF_4.

c. Would you use SeF_4 for a solution reaction at 0°C if ΔH_{fus} = 46 kJ/mol and ΔS_{fus} = 178 J/(mol·K)?

ANSWERS

1. 27.8°C; 0.85 J.

2.

3.

a. −163.3 J/K

b. −9.1 J/K

c. 114.5 J/K

d. −173.2 J/K

4.

5. 25.0 J/(mol·K)

6.

7. yes; yes; 274 K

8.

[1] In practice, chemists determine the absolute entropy of a substance by measuring the molar heat capacity (C_p) as a function of temperature and then plotting the quantity C_p/T versus T. The *area* under the curve between 0 K and any temperature T is the absolute entropy of the substance at T.

[2] For a review of natural logarithms, see Essential Skills 6 in Chapter 11 "Liquids".

18.5 Free Energy

LEARNING OBJECTIVE

1. To understand the relationship between Gibbs free energy and work.

One of the major goals of chemical thermodynamics is to establish criteria for predicting whether a particular reaction or process will occur spontaneously. We have developed one such criterion, the change in entropy of the universe: if $\Delta S_{univ} > 0$ for a process or a reaction, then the process will occur spontaneously as written. Conversely, if $\Delta S_{univ} < 0$, a process cannot occur spontaneously; if $\Delta S_{univ} = 0$, the system is at equilibrium. The sign of ΔS_{univ} is a universally applicable and infallible indicator of the spontaneity of a reaction. Unfortunately, using ΔS_{univ} requires that we calculate ΔS for*both* a system *and* its surroundings. This is not particularly useful for two reasons: we are normally much more interested in the system than in the surroundings, and it is difficult to make quantitative measurements of the surroundings (i.e., the rest of the universe). A criterion of spontaneity that is based solely on the state functions of a*system* would be much more convenient and is provided by a new state function: the Gibbs free energy.

Gibbs Free Energy and the Direction of Spontaneous Reactions

The Gibbs free energy (G), often called simply *free energy*, was named in honor of J. Willard Gibbs (1838–1903), an American physicist who first developed the concept. It is defined in terms of three other state functions with which you are already familiar: enthalpy, temperature, and entropy:

Equation 18.22
$G = H - TS$

Because it is a combination of state functions, G is also a state function.

J. Willard Gibbs (1839–1903)

Born in Connecticut, Josiah Willard Gibbs attended Yale, as did his father, a professor of sacred literature at Yale, who was involved in the *Amistad* trial. In 1863, Gibbs was awarded the first engineering doctorate granted in the United States. He was appointed professor of mathematical physics at Yale in 1871, the first such professorship in the United States. His series of papers entitled "On the Equilibrium of Heterogeneous Substances" was the foundation of the field of physical chemistry and is considered one of the great achievements of the 19th century. Gibbs, whose work was translated into French by Le Châtelier, lived with his sister and brother-in-law until his death in 1903, shortly before the inauguration of the Nobel Prizes.

The criterion for predicting spontaneity is based on ΔG, the change in G, at constant temperature and pressure. Although very few chemical reactions actually occur under conditions of constant temperature and pressure, most systems can be brought back to the initial temperature and pressure without significantly affecting the value of thermodynamic state functions such as G. At constant temperature and pressure,

Equation 18.23
$\Delta G = \Delta H - T\Delta S$

where all thermodynamic quantities are those of the *system*. Recall that at constant pressure, $\Delta H = q$, whether a process is reversible or irreversible, and $T\Delta S = q_{rev}$. Using these expressions, we can reduce Equation 18.23 to $\Delta G = q - q_{rev}$. Thus ΔG is the difference between the heat released during a process (via a reversible or an irreversible path) and the heat released for the same process occurring in a reversible manner. Under the special condition in which a process occurs reversibly, $q = q_{rev}$ and $\Delta G = 0$. As we shall soon see, if ΔG is zero, the system is at equilibrium, and there will be no net change.

What about processes for which $\Delta G \neq 0$? To understand how the sign of ΔG for a*system* determines the direction in which change is spontaneous, we can rewriteEquation 18.15 (where $q_p = \Delta H$, Equation 18.11) as follows:

Equation 18.24

$$\Delta S_{surr} = -\Delta H_{sys}/T$$

Thus the entropy change of the *surroundings* is related to the enthalpy change of the*system*. We have stated that for a spontaneous reaction, $\Delta S_{univ} > 0$, so substituting we obtain

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0 = \Delta S_{sys} - \Delta H_{sys}/T > 0$$

Multiplying both sides of the inequality by $-T$ reverses the sign of the inequality; rearranging,

$$\Delta H_{sys} - T\Delta S_{sys} < 0$$

which is equal to ΔG (Equation 18.23). We can therefore see that for a spontaneous process, $\Delta G < 0$. The relationship between the entropy change of the *surroundings* and the heat gained or lost by the *system* provides the key connection between the thermodynamic properties of the system and the change in entropy of the universe. The relationship shown in Equation 18.23 allows us to predict spontaneity by focusing exclusively on the thermodynamic properties and temperature of the system. We predict that highly exothermic processes ($\Delta H << 0$) that increase the disorder of a *system* ($\Delta S_{sys} >> 0$) would therefore occur spontaneously. An example of such a process is the decomposition of ammonium nitrate fertilizer. (This substance destroyed Texas City, Texas, in 1947; see Chapter 3 "Chemical Reactions", Section 3.3.1 "Interpreting Chemical Equations".) Ammonium nitrate was also used to destroy the Murrah Federal Building in Oklahoma City, Oklahoma, in 1995. For a system at constant temperature and pressure, we can summarize the following results:

- If $\Delta G < 0$, the process occurs spontaneously.
- If $\Delta G = 0$, the system is at equilibrium.
- If $\Delta G > 0$, the process is not spontaneous as written but occurs spontaneously in the reverse direction.

To further understand how the various components of ΔG dictate whether a process occurs spontaneously, we now look at a simple and familiar physical change: the conversion of liquid water to water vapor. If this process is carried out at 1 atm and the normal boiling point of 100.00°C (373.15 K), we can calculate ΔG from the experimentally measured value of ΔH_{vap} (40.657 kJ/mol). For vaporizing 1 mol

of water, ΔH = 40,657 J, so the process is highly endothermic. From the definition of ΔS(Equation 18.15), we know that for 1 mol of water,

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b} = \frac{40,657\ J}{373.15\ K} = 108.96\ J/K$$

Hence there is an increase in the disorder of the system. At the normal boiling point of water,

$$\Delta G_{100°C} = \Delta H_{100°C} - T\Delta S_{100°C} = 40,657\ J - [(373.15\ K)(108.96\ J/K)] = 0\ J$$

The energy required for vaporization offsets the increase in disorder of the system. Thus ΔG = 0, and the liquid and vapor are in equilibrium, as is true of any liquid at its boiling point under standard conditions. (For more information on standard conditions, seeChapter 11 "Liquids".)

Now suppose we were to superheat 1 mol of liquid water to 110°C. The value of ΔG for the vaporization of 1 mol of water at 110°C, assuming that ΔH and ΔS do not change significantly with temperature, becomes

$$\Delta G_{110°C} = \Delta H - T\Delta S = 40,657\ J - [(383.15\ K)(108.96\ J/K)] = -1091\ J$$

At 110°C, ΔG < 0, and vaporization is predicted to occur spontaneously and irreversibly.

We can also calculate ΔG for the vaporization of 1 mol of water at a temperature below its normal boiling point—for example, 90°C—making the same assumptions:

$$\Delta G_{90°C} = \Delta H - T\Delta S = 40,657\ J - [(363.15\ K)(108.96\ J/K)] = 1088\ J$$

At 90°C, ΔG > 0, and water does not spontaneously convert to water vapor. When using all the digits in the calculator display in carrying out our calculations, $\Delta G_{110°C}$ = 1090 J = $-\Delta G_{90°C}$, as we would predict. (For more information on using a calculator, see Essential Skills 1 in Chapter 1 "Introduction to Chemistry".)

Note the Pattern

ΔG = 0 only if $\Delta H = T\Delta S$.

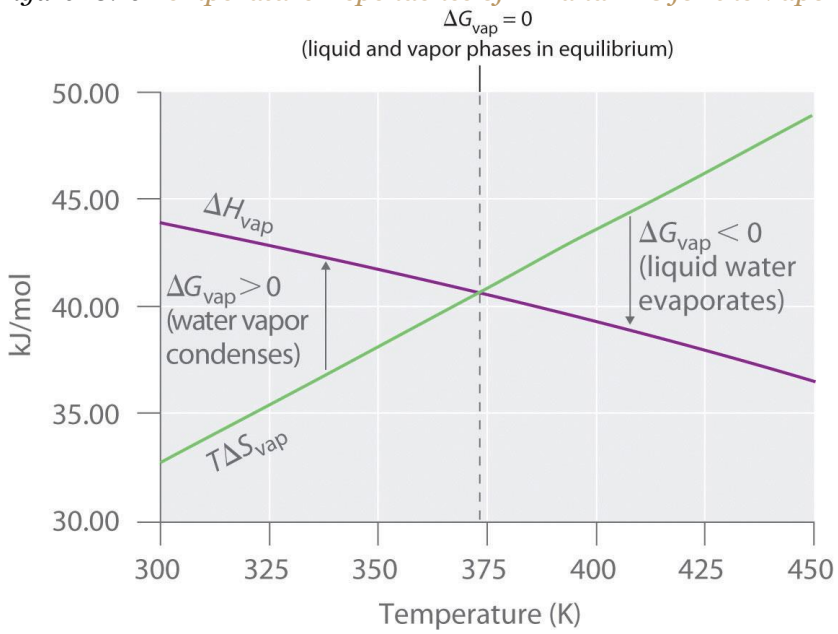
We can also calculate the temperature at which liquid water is in equilibrium with water vapor. Inserting the values of ΔH and ΔS into the definition of ΔG (Equation 18.23), setting ΔG = 0, and solving for T,

$$0\ J = 40,657\ J - T(108.96\ J/K) = 373.15\ K$$

Thus ΔG = 0 at T = 373.15 K and 1 atm, which indicates that liquid water and water vapor are in equilibrium; this temperature is called the *normal boiling point* of water. At temperatures greater than 373.15 K, ΔG is negative, and water evaporates spontaneously and irreversibly. Below 373.15 K, ΔG is positive, and water does not evaporate spontaneously. Instead, water vapor at a temperature less than 373.15 K and 1 atm will spontaneously and irreversibly condense to liquid water. Figure 18.16

"Temperature Dependence of Δ" shows how the Δ*H* and *T*Δ*S* terms vary with temperature for the vaporization of water. When the two lines cross, Δ*G* = 0, and Δ*H* = *T*Δ*S*.

Figure 18.16 *Temperature Dependence of ΔH and TΔS for the Vaporization of Water*



Both ΔH and TΔS are temperature dependent, but the lines have opposite slopes and cross at 373.15 K at 1 atm, where ΔH = TΔS. Because ΔG = ΔH − TΔS, at this temperature ΔG = 0, indicating that the liquid and vapor phases are in equilibrium. The normal boiling point of water is therefore 373.15 K. Above the normal boiling point, the TΔS term is greater than ΔH, making ΔG < 0; hence, liquid water evaporates spontaneously. Below the normal boiling point, the ΔH term is greater than TΔS, making ΔG > 0. Thus liquid water does not evaporate spontaneously, but water vapor spontaneously condenses to liquid.

A similar situation arises in the conversion of liquid egg white to a solid when an egg is boiled. The major component of egg white is a protein called albumin, which is held in a compact, ordered structure by a large number of hydrogen bonds. Breaking them requires an input of energy (Δ*H* > 0), which converts the albumin to a highly disordered structure in which the molecules aggregate as a disorganized solid (Δ*S* > 0). At temperatures greater than 373 K, the *T*Δ*S* term dominates, and Δ*G* < 0, so the conversion of a raw egg to a hard-boiled egg is an irreversible and spontaneous process above 373 K.

The Relationship between Δ*G* and Work

In the previous subsection, we learned that the value of ΔG allows us to predict the spontaneity of a physical or a chemical change. In addition, the magnitude of ΔG for a process provides other important information. The change in free energy (ΔG) is equal to the maximum amount of work that a system can perform on the surroundings while undergoing a spontaneous change (at constant temperature and pressure): $\Delta G = w_{max}$. To see why this is true, let's look again at the relationships among free energy, enthalpy, and entropy expressed in Equation 18.23. We can rearrange this equation as follows:

Equation 18.25

$$\Delta H = \Delta G + T\Delta S$$

This equation tells us that when energy is released during an exothermic process ($\Delta H < 0$), such as during the combustion of a fuel, some of that energy can be used to do work ($\Delta G < 0$), while some is used to increase the entropy of the universe ($T\Delta S > 0$). Only if the process occurs infinitely slowly in a perfectly reversible manner will the entropy of the universe be unchanged. (For more information on entropy and reversibility, seeSection 18.4 "Entropy Changes and the Third Law of Thermodynamics".) Because no real system is perfectly reversible, the entropy of the universe increases during all processes that produce energy. As a result, no process that uses stored energy can ever be 100% efficient; that is, ΔH will never equal ΔG because ΔS has a positive value.

One of the major challenges facing engineers is to maximize the efficiency of converting stored energy to useful work or converting one form of energy to another. As indicated in Table 18.2 "Approximate Thermodynamic Efficiencies of Various Devices", the efficiencies of various energy-converting devices vary widely. For example, an internal combustion engine typically uses only 25%–30% of the energy stored in the hydrocarbon fuel to perform work; the rest of the stored energy is released in an unusable form as heat. In contrast, gas–electric hybrid engines, now used in several models of automobiles, deliver approximately 50% greater fuel efficiency. A large electrical generator is highly efficient (approximately 99%) in converting mechanical to electrical energy, but a typical incandescent light bulb is one of the least efficient devices known (only approximately 5% of the electrical energy is converted to light). In contrast, a mammalian liver cell is a relatively efficient machine and can use fuels such as glucose with an efficiency of 30%–50%.

Table 18.2 Approximate Thermodynamic Efficiencies of Various Devices

Device	Energy Conversion	Approximate Efficiency (%)

Device	Energy Conversion	Approximate Efficiency (%)
large electrical generator	mechanical → electrical	99
chemical battery	chemical → electrical	90
home furnace	chemical → heat	65
small electric tool	electrical → mechanical	60
space shuttle engine	chemical → mechanical	50
mammalian liver cell	chemical → chemical	30–50
spinach cell	light → chemical	30
internal combustion engine	chemical → mechanical	25–30
fluorescent light	electrical → light	20
solar cell	light → electricity	10
incandescent light bulb	electricity → light	5
yeast cell	chemical → chemical	2–4

Standard Free-Energy Change

We have seen that there is no way to measure absolute enthalpies, although we can measure *changes* in enthalpy (ΔH) during a chemical reaction. Because enthalpy is one of the components of Gibbs free energy, we are consequently unable to measure absolute free energies; we can measure only changes in free energy. Thestandard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free-energy change can be calculated from the definition of free energy, if the standard enthalpy and entropy changes are known, using Equation 18.26:

Equation 18.26

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

If ΔS° and ΔH° for a reaction have the same sign, then the sign of ΔG° depends on the relative magnitudes of the ΔH° and $T\Delta S^\circ$ terms. It is important to recognize that a positive value of ΔG° for a reaction does *not* mean that no products will form if the reactants in their standard states are mixed; it means only that at equilibrium the concentrations of the products will be less than the concentrations of the reactants.

Note the Pattern

A positive ΔG° means that the equilibrium constant is less than 1.

EXAMPLE 8

Calculate the standard free-energy change (Δ*G*°) at 25°C for the reaction $H2(g)+O2(g)\rightarrow H2O2(l)$. *At* 25°C, the standard enthalpy change (Δ*H*°) is −187.78 kJ/mol, and the absolute entropies of the products and reactants are *S*°(H_2O_2) = 109.6 J/(mol·K), *S*°(O_2) = 205.2 J/(mol·K), and *S*°(H_2) = 130.7 J/(mol·K). Is the reaction spontaneous as written?

Given: balanced chemical equation, Δ*H*° and *S*° for reactants and products

Asked for: spontaneity of reaction as written

Strategy:

A Calculate Δ*S*° from the absolute molar entropy values given.

B Use Equation 18.26, the calculated value of Δ*S*°, and other data given to calculate Δ*G*° for the reaction. Use the value of Δ*G*° to determine whether the reaction is spontaneous as written.

Solution:

A To calculate Δ*G*° for the reaction, we need to know Δ*H*°, Δ*S*°, and *T*. We are given Δ*H*°, and we know that *T* = 298.15 K. We can calculate Δ*S*° from the absolute molar entropy values provided using the "products minus reactants" rule:

$$\Delta S° = S°(H2O2) - [S°(O2) + S°(H2)] = [1\ mol\ H2O2 \times 109.6\ J/(mol \cdot K)] - \{[1 mol\ H2 \times 130.7\ J/(mol \cdot K)] + [1 mol\ O2 \times 205.2\ J/(mol \cdot K)]\} = -226.3\ J/K\ (per\ mole\ of\ H2O2)$$

As we might expect for a reaction in which 2 mol of gas is converted to 1 mol of a much more ordered liquid, Δ*S*° is very negative for this reaction.

B Substituting the appropriate quantities into Equation 18.26,

$$\Delta G° = \Delta H° - T\Delta S° = -187.78\ kJ/mol - (298.15\ K)[-226.3\ J/(mol \cdot K) \times 1\ kJ/1000\ J] = -187.78\ kJ/mol + 67.47\ kJ/mol = -120.31\ kJ/mol$$

The negative value of Δ*G*° indicates that the reaction is spontaneous as written. Because Δ*S*° and Δ*H*° for this reaction have the same sign, the sign of Δ*G*° depends on the relative magnitudes of the Δ*H*° and *T*Δ*S*° terms. In this particular case, the enthalpy term dominates, indicating that the strength of the bonds formed in the product more than compensates for the unfavorable Δ*S*° term and for the energy needed to break bonds in the reactants.

Exercise

Calculate the standard free-energy change (Δ*G*°) at 25°C for the reactio

$n\ 2H2(g)+N2(g)\ \square\ \ N2H4(l).\ At$

25°C, the standard enthalpy change (Δ*H*°) is 50.6 kJ/mol, and the absolute entropies of the products and reactants are *S*°(N_2H_4) = 121.2 J/(mol·K), *S*°(N_2) = 191.6 J/(mol·K), and *S*°(H_2) = 130.7 J/(mol·K). Is the reaction spontaneous as written?

Answer: 149.5 kJ/mol; no

Tabulated values of standard free energies of formation allow chemists to calculate the values of Δ*G*° for a wide variety of chemical reactions rather than having to measure them in the laboratory.

The standard free energy of formation <math xml:id="averill_1.0-18_m053" display="inline">(ΔGf°)</math xml:id="averill_1.0-18_m053" display="inline"> of a compound is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. By definition, the standard free energy of formation of an element in its standard state is zero at 298.15 K. One mole of Cl_2 gas at 298.15 K, for example, has $(DS\square f)$ = 0. The standard free energy of formation of a compound can be calculated from the standard enthalpy of formation $(DS\square f)$ and the standard entropy of formation $(DS\square f)$ using the definition of free energy:

Equation 18.27

$$DG\square f = DH\square f - TDS\square f$$

Using standard free energies of formation to calculate the standard free energy of a reaction is analogous to calculating standard enthalpy changes from standard enthalpies of formation using the familiar "products minus reactants" rule:

Equation 18.28

$$DG\square rxn = \sum mDG\square f\ (products) - \sum nDG\square f\ (reactants)$$

where *m* and *n* are the stoichiometric coefficients of each product and reactant in the balanced chemical equation. A very large negative Δ*G*° indicates a strong tendency for products to form spontaneously from reactants; *it does not, however, necessarily indicate that the reaction will occur rapidly*. To make this determination, we need to evaluate the kinetics of the reaction. (For more information on chemical kinetics, seeChapter 14 "Chemical Kinetics".)

Note the Pattern

The ΔG° of a reaction can be calculated from tabulated ΔG_f° values using the "products minus reactants" rule.

EXAMPLE 9

Calculate ΔG° for the reaction of isooctane with oxygen gas to give carbon dioxide and water (described in Example 7). Use the following data:

ΔG_f° isooctane) = −353.2 kJ/mol,

ΔG_f° (CO_2) = −394.4 kJ/mol, and

ΔG° (H_2O) = −237.1 kJ/mol. Is the reaction spontaneous as written?

Given: balanced chemical equation and values of ΔG° for isooctane, CO_2, and H_2O

Asked for: spontaneity of reaction as written

Strategy:

Use the "products minus reactants" rule to obtain ΔG°_{rxn}, *remembering that* ΔG_f° *for* an element in its standard state is zero. From the calculated value, determine whether the reaction is spontaneous as written.

Solution:

From Example 7, we know that the balanced chemical equation for the reaction is as follows: $C_8H_{18}(l) + 25_2O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l)$. *We are given* ΔG_f° *values* for all the products and reactants except O_2(g). Because oxygen gas is an element in its standard state, ΔG_f° (O_2) is zero. Using the "products minus reactants" rule,

$$\Delta G^\circ = [8\Delta G_f^\circ(CO_2) + 9\Delta G_f^\circ(H_2O)] - [1\Delta G_f^\circ(C_8H_{18}) + 25_2\Delta G_f^\circ(O_2)] = [(8\ mol)(-394.4\ kJ/mol) + (9\ mol)(-237.1\ kJ/mol)] - [(1\ mol)(-353.2\ kJ/mol) + (25_2 mol)(0\ kJ/mol)]$$

$$= -4935.9\ kJ\ (per\ mol\ of\ C_8H_{18})$$

Because ΔG° is a large negative number, there is a strong tendency for the spontaneous formation of products from reactants (though not necessarily at a rapid rate). Also notice that the magnitude of ΔG° is largely determined by the ΔG_f° of the stable products: water and carbon dioxide.

Exercise

Calculate $\Delta G°$ for the reaction of benzene with hydrogen gas to give cyclohexane using the data $\Delta G_f°$ (benzene) = 124.5 kJ/mol and $\Delta G_f°$ (cyclohexane) = 217.3 kJ/mol. Is the reaction spontaneous as written?

Answer: 92.8 kJ; no

Calculated values of $\Delta G°$ are extremely useful in predicting whether a reaction will occur spontaneously if the reactants and products are mixed under standard conditions. We should note, however, that very few reactions are actually carried out under standard conditions, and calculated values of $\Delta G°$ may not tell us whether a given reaction will occur spontaneously under nonstandard conditions. What determines whether a reaction will occur spontaneously is the free-energy change (ΔG) under the actual experimental conditions, which are usually different from $\Delta G°$. If the ΔH and $T\Delta S$ terms for a reaction have the same sign, for example, then it may be possible to reverse the sign of ΔG by changing the temperature, thereby converting a reaction that is not thermodynamically spontaneous, having $K_{eq} < 1$, to one that is, having a $K_{eq} > 1$, or vice versa. Because ΔH and ΔS usually do not vary greatly with temperature in the absence of a phase change, we can use tabulated values of $\Delta H°$ and $\Delta S°$ to calculate $\Delta G°$ at various temperatures, as long as no phase change occurs over the temperature range being considered.

Note the Pattern

In the absence of a phase change, neither ΔH nor ΔS vary greatly with temperature.

EXAMPLE 10

Calculate (a) $\Delta G°$ and (b) $\Delta G_{300°C}$ for the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, *assuming* that ΔH and ΔS do not change between 25°C and 300°C. Use these data:

$S°(N_2)$ = 191.6 J/(mol·K),

$S°(H_2)$ = 130.7 J/(mol·K),

$S°(NH_3)$ = 192.8 J/(mol·K), and

$\Delta H_f°$ (NH_3) = −45.9 kJ/mol.

Given: balanced chemical equation, temperatures, $S°$ values, and $\Delta H_f°$ for NH_3

Asked for: $\Delta G°$ and ΔG at 300°C

Strategy:

A Convert each temperature to kelvins. Then calculate $\Delta S°$ for the reaction. Calculate $\Delta H°$ for the reaction, recalling that $\Delta H_f°$ for any element in its standard state is zero.

B Substitute the appropriate values into Equation 18.26 to obtain Δ*G*° for the reaction.

C Assuming that Δ*H* and Δ*S* are independent of temperature, substitute values intoEquation 18.23 to obtain Δ*G* for the reaction at 300°C.

olution:

a. **A** To calculate Δ*G*° for the reaction using Equation 18.26, we must know the temperature as well as the values of Δ*S*° and Δ*H*°. At standard conditions, the temperature is 25°C, or 298 K. We can calculate Δ*S*° for the reaction from the absolute molar entropy values given for the reactants and the products using the "products minus reactants" rule:

$$\Delta S°_{rxn} = 2S°(NH_3) - [S°(N_2) + 3S°(H_2)] = [2\,mol\ NH_3 \times 192.8\ J/(mol \cdot K)] - \{[1\,mol\ N_2 \times 191.6\ J/(mol \cdot K)] + [3\,mol\ H_2 \times 130.7\ J/(mol \cdot K)]\}$$

$$= -198.1\ J/K\ (per\ mole\ of\ N_2)$$

We can also calculate Δ*H*° for the reaction using the "products minus reactants" rule. The value of $\Delta H°_f\ (NH_3)\ is\ given,\ and\ \Delta H°_f\ is$ zero for both N_2 and H_2:

$$\Delta H°_{rxn} = 2\Delta H°_f(NH_3) - [\Delta H°_f(N_2) + 3\Delta H°_f(H_2)] = [2 \times (-45.9\ kJ/mol)] - [(1 \times 0\ kJ/mol) + (3 \times 0\ kJ/mol)] = -91.8\ kJ(per\ mole\ of N_2)$$

B Inserting the appropriate values into Equation 18.26,

b. $$\Delta G°_{rxn} = \Delta H° - T\Delta S° = (-91.8\ kJ) - (298\ K)(-198.1\ J/K)(1\ kJ/1000\ J)$$

$$= -32.7\ kJ\ (per\ mole\ of\ N_2)$$

c. **C** To calculate Δ*G* for this reaction at 300°C, we assume that Δ*H* and Δ*S*are independent of temperature (i.e., $\Delta H_{300°C} = H°$ and $\Delta S_{300°C} = \Delta S°$) and insert the appropriate temperature (573 K) into Equation 18.23

c. $$\Delta G300°C = \Delta H300°C - (573\ K)(\Delta S300°C)$$

$$\therefore = \Delta H° - (573\ K)\Delta S° = (-91.8\ kJ) - (573\ K)(-198.1\ J/K)\ mole\ of\ N_2)(1\ kJ/1000\ J) = 21.7\ kJ\ (per\ mole\ of\ N_2)$$

In this example, changing the temperature has a major effect on the thermodynamic spontaneity of the reaction. Under standard conditions, the reaction of nitrogen and hydrogen gas to produce ammonia is

thermodynamically spontaneous, but in practice, it is too slow to be useful industrially. Increasing the temperature in an attempt to make this reaction occur more rapidly also changes the thermodynamics by causing the $-T\Delta S°$ term to dominate, and the reaction is no longer spontaneous at high temperatures; that is, its K_{eq} is less than one. This is a classic example of the conflict encountered in real systems between thermodynamics and kinetics, which is often unavoidable.

Exercise

Calculate (a) $\Delta G°$ and (b) $\Delta G_{750°C}$ for the reaction $2NO(g)+O2(g) \rightarrow 2NO2(g)$, *which* is important in the formation of urban smog. Assume that ΔH and ΔS do not change between 25.0°C and 750°C and use these data:

$S°(NO)$ = 210.8 J/(mol·K),

$S°(O_2)$ = 205.2 J/(mol·K),

$S°(NO_2)$ = 240.1 J/(mol·K),

$\Delta H_f(NO_2)$ = 33.2 kJ/mol, and

$\Delta H_f(NO)$ = 91.3 kJ/mol.

Answer

a. −72.5 kJ/mol of O_2

b. 33.8 kJ/mol of O_2

The effect of temperature on the spontaneity of a reaction, which is an important factor in the design of an experiment or an industrial process, depends on the sign and magnitude of both $\Delta H°$ and $\Delta S°$. The temperature at which a given reaction is at equilibrium can be calculated by setting $\Delta G° = 0$ in Equation 18.26, as illustrated in Example 11.

EXAMPLE 11

As you saw in Example 10, the reaction of nitrogen and hydrogen gas to produce ammonia is one in which $\Delta H°$ and $\Delta S°$ are both negative. Such reactions are predicted to be thermodynamically spontaneous at low temperatures but nonspontaneous at high temperatures. Use the data in Example 10 to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous, assuming that $\Delta H°$ and $\Delta S°$ are independent of temperature.

Given: $\Delta H°$ and $\Delta S°$

Asked for: temperature at which reaction changes from spontaneous to nonspontaneous

Strategy:

Set $\Delta G°$ equal to zero in Equation 18.26 and solve for T, the temperature at which the reaction becomes nonspontaneous.

Solution:

In Example 10, we calculated that $\Delta H°$ is −91.8 kJ/mol of N_2 and $\Delta S°$ is −198.1 J/K per mole of N_2, corresponding to $\Delta G° = -32.7$ kJ/mol of N_2 at 25°C. Thus the reaction is indeed spontaneous at low temperatures, as expected based on the signs of $\Delta H°$ and $\Delta S°$. The temperature at which the reaction becomes nonspontaneous is found by setting $\Delta G°$ equal to zero and rearranging Equation 18.26 to solve for T:

$$\Delta G° \Delta H° T = \Delta H° \Delta S° = \Delta H° - T \Delta S° = 0 = T \Delta S°$$

$$= (-91.8\ kJ)(1000\ J/kJ) - 198.1\ J/K = 463\ K$$

This is a case in which a chemical engineer is severely limited by thermodynamics. Any attempt to increase the rate of reaction of nitrogen with hydrogen by increasing the temperature will cause reactants to be favored over products above 463 K.

Exercise

As you found in the exercise in Example 10, $\Delta H°$ and $\Delta S°$ are both negative for the reaction of nitric oxide and oxygen to form nitrogen dioxide. Use those data to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous.

Answer: 792.6 K

Summary

We can predict whether a reaction will occur spontaneously by combining the entropy, enthalpy, and temperature of a system in a new state function called **Gibbs free energy (G)**. The change in free energy (ΔG) is the difference between the heat released during a process and the heat released for the same process occurring in a reversible manner. If a system is at equilibrium, $\Delta G = 0$. If the process is spontaneous, $\Delta G < 0$. If the process is not spontaneous as written but is spontaneous in the reverse direction, $\Delta G > 0$. At constant temperature and pressure, ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. The **standard free-energy change ($\Delta G°$)** is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The **standard**

free energy of formation $(DG\square f)$, is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. Tabulated values of standard free energies of formation are used to calculate ΔG^{o} for a reaction.

KEY TAKEAWAY

- The change in Gibbs free energy, which is based solely on changes in state functions, is the criterion for predicting the spontaneity of a reaction.

KEY EQUATIONS

Free-energy change

Equation 18.23: $\Delta G = \Delta H - T\Delta S$

Standard free-energy change

Equation 18.26: $\Delta G° = \Delta H° - T\Delta S°$

CONCEPTUAL PROBLEMS

1. How does each example illustrate the fact that no process is 100% efficient?

a. burning a log to stay warm

b. the respiration of glucose to provide energy

c. burning a candle to provide light

2. Neither the change in enthalpy nor the change in entropy is, by itself, sufficient to determine whether a reaction will occur spontaneously. Why?
3. If a system is at equilibrium, what must be the relationship between ΔH and ΔS?
4. The equilibriu $m\ 2AB\square\ \ A2B2\ is\ exothermic$ in the forward direction. Which has the higher entropy—the products or the reactants? Why? Which is favored at high temperatures?
5. Is ΔG a state function that describes a system or its surroundings? Do its components—ΔH and ΔS—describe a system or its surroundings?
6. How can you use ΔG to determine the temperature of a phase transition, such as the boiling point of a liquid or the melting point of a solid?
7. Occasionally, an inventor claims to have invented a “perpetual motion” machine, which requires no additional input of energy once the machine has been put into motion. Using your knowledge of thermodynamics, how would you respond to such a claim? Justify your arguments.

8. Must the entropy of the universe increase in a spontaneous process? If not, why is no process 100% efficient?
9. The reaction of methyl chloride with water produces methanol and hydrogen chloride gas at room temperature, despite the fact that ΔH_{rxn} = 7.3 kcal/mol. Using thermodynamic arguments, propose an explanation as to why methanol forms.

ANSWER

1.
2.
3.
4.
5.
6.
7.
8.
9. In order for the reaction to occur spontaneously, Δ*G* for the reaction must be less than zero. In this case, Δ*S* must be positive, and the *T*Δ*S* term outweighs the positive value of Δ*H*.

NUMERICAL PROBLEMS

1. Use the tables in the text to determine whether each reaction is spontaneous under standard conditions. If a reaction is not spontaneous, write the corresponding spontaneous reaction.

a. $a.\quad H2(g)+12O2(g)\rightarrow H2O(l)$

b. $2H_2(g) + C_2H_2(g) \rightarrow C_2H_6(g)$

c. $(CH_3)_2O(g) + H_2O(g) \rightarrow 2CH_3OH(l)$

d. $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$

2. Use the tables in the text to determine whether each reaction is spontaneous under standard conditions. If a reaction is not spontaneous, write the corresponding spontaneous reaction.

a. $K_2O_2(s) \rightarrow 2K(s) + O_2(g)$

b. $PbCO_3(s) \rightarrow PbO(s) + CO_2(g)$

c. $P_4(s) + 6H_2(g) \rightarrow 4PH_3(g)$

d. $2AgCl(s) + H_2S(g) \rightarrow Ag_2S(s) + 2HCl(g)$

3. Nitrogen fixation is the process by which nitrogen in the atmosphere is reduced to NH_3 for use by organisms. Several reactions are associated with this process; three are listed in the following table. Which of these are spontaneous at 25°C? If a reaction is not spontaneous, at what temperature does it become spontaneous?

Reaction	ΔH_{298} (kcal/mol)	ΔS_{298} [cal/(°·mol)]
$(a)\ 12N2 + O2 \rightarrow NO2$	8.0	−14.4
$(b)\ 12N2 + 12O2 \rightarrow NO$	21.6	2.9
$(c)\ 12N2 + 32H2 \rightarrow NH3$	−11.0	−23.7

4. A student was asked to propose three reactions for the oxidation of carbon or a carbon compound to CO or CO_2. The reactions are listed in the following table. Are any of these reactions spontaneous at 25°C? If a reaction does not occur spontaneously at 25°C, at what temperature does it become spontaneous?

Reaction	ΔH_{298} (kcal/mol)	ΔS_{298} [cal/(°·mol)]
$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$	42	32
$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$	−9.8	−10.1
$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$	49.3	51.3

5. Tungsten trioxide (WO_3) is a dense yellow powder that, because of its bright color, is used as a pigment in oil paints and water colors (although cadmium yellow is more commonly used in artists' paints). Tungsten metal can be isolated by the reaction of WO_3 with H_2 at 1100°C according to the equation $WO_3(s) + 3H_2(g) \rightarrow W(s) + 3H_2O(g)$. What is the lowest temperature at which the reaction occurs spontaneously? $\Delta H°$ = 27.4 kJ/mol and $\Delta S°$ = 29.8 J/K.

6. Sulfur trioxide (SO_3) is produced in large quantities in the industrial synthesis of sulfuric acid. Sulfur dioxide is converted to sulfur trioxide by reaction with oxygen gas.

a. Write a balanced chemical equation for the reaction of SO_2 with $O_2(g)$ and determine its $\Delta G°$.

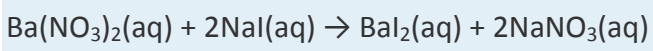
b. What is the value of the equilibrium constant at 600°C?

c. If you had to rely on the equilibrium concentrations alone, would you obtain a higher yield of product at 400°C or at 600°C?

7. Calculate $\Delta G°$ for the general reaction $MCO_3(s) \rightarrow MO(s) + CO_2(g)$ at 25°C, where M is Mg or Ba. At what temperature does each of these reactions become spontaneous?

Compound	ΔH_f° (kJ/mol)	S° [J/(mol·K)]
MCO 3		
Mg	−1111	65.85
Ba	−1213.0	112.1
MO		
Mg	−601.6	27.0
Ba	−548.0	72.1
CO 2	−393.5	213.8

8. The reaction of aqueous solutions of barium nitrate with sodium iodide is described by the following equation:



$$Ba(NO_3)_2(aq) + 2NaI(aq) \rightarrow BaI_2(aq) + 2NaNO_3(aq)$$

You want to determine the absolute entropy of BaI_2, but that information is not listed in your tables. However, you have been able to obtain the following information:

	$Ba(NO_3)_2$	NaI	BaI_2	$NaNO_3$
ΔH_f° (kJ/mol)	−952.36	−295.31	−605.4	−447.5
S° [J/(mol·K)]	302.5	170.3		205.4

You know that ΔG° for the reaction at 25°C is 22.64 kJ/mol. What is ΔH° for this reaction? What is S° for BaI_2?

ANSWERS

1.

a. −237.1 kJ/mol; spontaneous as written

b. −241.9 kJ/mol; spontaneous as written

c. 8.0 kJ/mol; spontaneous in reverse direction.

d. 141.9 kJ/mol; spontaneous in reverse direction.

2.

3.

a. Not spontaneous at any T

b. Not spontaneous at 25°C; spontaneous above 7400 K

c. Spontaneous at 25°C

4.

5. 919 K
6.
7. $MgCO_3$: ΔG° = 63 kJ/mol, spontaneous above 663 K; $BaCO_3$: ΔG° = 220 kJ/mol, spontaneous above 1562 K

18.6 Spontaneity and Equilibrium

LEARNING OBJECTIVE

1. To know the relationship between free energy and the equilibrium constant.

We have identified three criteria for whether a given reaction will occur spontaneously: $\Delta S_{univ} > 0$, $\Delta G_{sys} < 0$, and the relative magnitude of the reaction quotient Q versus the equilibrium constant K. (For more information on the reaction quotient and the equilibrium constant, see Chapter 15 "Chemical Equilibrium".) Recall that if $Q < K$, then the reaction proceeds spontaneously to the right as written, resulting in the net conversion of reactants to products. Conversely, if $Q > K$, then the reaction proceeds spontaneously to the left as written, resulting in the net conversion of products to reactants. If $Q = K$, then the system is at equilibrium, and no net reaction occurs. Table 18.3 "Criteria for the Spontaneity of a Process as Written" summarizes these criteria and their relative values for spontaneous, nonspontaneous, and equilibrium processes. Because all three criteria are assessing the same thing—the spontaneity of the process—it would be most surprising indeed if they were not related. The relationship between ΔS_{univ} and ΔG_{sys} was described in Section 18.5 "Free Energy". In this section, we explore the relationship between the standard free energy of reaction (ΔG°) and the equilibrium constant (K).

Table 18.3 Criteria for the Spontaneity of a Process as Written

Spontaneous	Equilibrium	Nonspontaneous*
$\Delta S_{univ} > 0$	$\Delta S_{univ} = 0$	$\Delta S_{univ} < 0$
$\Delta G_{sys} < 0$	$\Delta G_{sys} = 0$	$\Delta G_{sys} > 0$
$Q < K$	$Q = K$	$Q > K$
***Spontaneous in the *reverse* direction.**		

Free Energy and the Equilibrium Constant

Because ΔH° and ΔS° determine the magnitude of ΔG° (Equation 18.26), and because $K$is a measure of the ratio of the concentrations of products to the concentrations of reactants, we should be able to express K in terms of ΔG° and vice versa. As you learned in Section 18.5 "Free Energy", ΔG is equal to the

maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature, thereby eliminating ΔH from the equation for ΔG. Using higher math, the general relationship can be shown as follows:

Equation 18.29

$$\Delta G = V\Delta P - S\Delta T$$

If a reaction is carried out at constant temperature ($\Delta T = 0$), then Equation 18.29simplifies to

Equation 18.30

$$\Delta G = V\Delta P$$

Under normal conditions, the pressure dependence of free energy is not important for solids and liquids because of their small molar volumes. For reactions that involve gases, however, the effect of pressure on free energy is very important.

Assuming ideal gas behavior, we can replace the V in Equation 18.30 by nRT/P (where$n$ is the number of moles of gas and R is the ideal gas constant) and express ΔG in terms of the initial and final pressures (P_i and P_f, respectively) as in Equation 18.20:

Equation 18.31

$$DG = (nRTP)DP = nRTDPP = nRTln(PfPi)$$

If the initial state is the standard state with $P_i = 1$ atm, then the change in free energy of a substance when going from the standard state to any other state with a pressure P can be written as follows:

$$G - G° = nRT\ln P$$

This can be rearranged as follows:

Equation 18.32

$$G = G° + nRT\ln P$$

As you will soon discover, Equation 18.32 allows us to relate $\Delta G°$ and K_p. Any relationship that is true for K_p must also be true for K because K_p and K are simply different ways of expressing the equilibrium constant using different units.

Let's consider the following hypothetical reaction, in which all the reactants and the products are ideal gases and the lowercase letters correspond to the stoichiometric coefficients for the various species:

Equation 18.33

$$aA + bB \rightleftharpoons cC + dD$$

Because the free-energy change for a reaction is the difference between the sum of the free energies of the products and the reactants, we can write the following expression for ΔG:

Equation 18.34

$$\Delta G = \sum mGproducts - \sum nGreactants = (cGC + dGD) - (aGA + bGB)$$

Substituting Equation 18.32 for each term into Equation 18.34,

$$\Delta G = [(cG°C + cRTln\ PC) + (dG°D + dRTln\ PD)] - [(aG°A + aRTln\ PA) + (bG°B + bRTln\ PB)]$$

Combining terms gives the following relationship between ΔG and the reaction quotient Q:

Equation 18.35

$$\Delta G = \Delta G° + RTln(PcCPdDPaAPbB) = \Delta G° + RTln\ Q$$

where $\Delta G°$ indicates that all reactants and products are in their standard states. In Chapter 15 "Chemical Equilibrium", you learned that for gases $Q = K_p$ at equilibrium, and as you've learned in this chapter, $\Delta G = 0$ for a system at equilibrium. Therefore, we can describe the relationship between $\Delta G°$ and K_p for gases as follows:

Equation 18.36

$$0 \Delta G° = \Delta G° + RTln\ Kp = - RTln\ Kp$$

If the products and reactants are in their standard states and $\Delta G° < 0$, then $K_p > 1$, and products are favored over reactants. Conversely, if $\Delta G° > 0$, then $K_p < 1$, and reactants are favored over products. If $\Delta G° = 0$, then $K_p = 1$, and neither reactants nor products are favored: the system is at equilibrium.

Note the Pattern

For a spontaneous process under standard conditions, K_{eq} and K_p are greater than 1.

EXAMPLE 12

In Example 10, we calculated that $\Delta G° = -32.7$ kJ/mol of N_2 for the reactio

$n\ N2(g) + 3H2(g) \square\ 2NH3(g).\ This$

calculation was for the reaction under standard conditions—that is, with all gases present at a partial pressure of 1 atm and a temperature of 25°C. Calculate ΔG for the same reaction under the following nonstandard conditions: $PN2$ = 2.00 atm, $PH2$ = 7.00 atm, $PNH3$ = 0.021 atm, and T = 100°C. Does the reaction favor products or reactants?

Given: balanced chemical equation, partial pressure of each species, temperature, and $\Delta G°$

Asked for: whether products or reactants are favored

Strategy:

A Using the values given and Equation 18.35, calculate *Q*.

B Substitute the values of Δ*G*° and *Q* into Equation 18.35 to obtain Δ*G* for the reaction under nonstandard conditions.

Solution:

A The relationship between Δ*G*° and Δ*G* under nonstandard conditions is given inEquation 18.35.

Substituting the partial pressures given, we can calculate *Q*:

$$Q = P2NH3PN2P3H2 = (0.021)2(2.00)(7.00)3 = 6.4\acute{}\ 10 - 7$$

B Substituting the values of Δ*G*° and *Q* into

Equation 18.35,

$$DG = DG° + RTln\ Q = - 32.7\ kJ +$$
$$(8.314J / K)(373\ K) / 1\ kJ1000\ J \backslash ln$$
$$(6.4 \times 10 - 7) = - 32.7\ kJ + (- 44\ kJ)$$
$$= - 77\ kJ / mol\ of\ N2$$

Because Δ*G* < 0 and *Q* < 1.0, the reaction is spontaneous to the right as written, so products are favored over reactants.

Exercise

Calculate Δ*G* for the reaction of nitric oxide with oxygen to give nitrogen dioxide under these conditions: T = 50°C, P_{NO} = 0.0100 atm , $PO2 = 0.200\ atm,\ and\ PNO2$ = 1.00 × 10^{-4} atm. The value of Δ*G*° for this reaction is −72.5 kJ/mol of O_2. Are products or reactants favored?

Answer: −92.9 kJ/mol of O_2; the reaction is spontaneous to the right as written, so products are favored.

EXAMPLE 13

Calculate K_p for the reaction of H_2 with N_2 to give NH_3 at 25°C. As calculated in Example 10, Δ*G*° for this reaction is −32.7 kJ/mol of N_2.

Given: balanced chemical equation from Example 10, Δ*G*°, and temperature

Asked for: K_p

Strategy:

Substitute values for Δ*G*° and *T* (in kelvins) into Equation 18.36 to calculate K_p, the equilibrium constant for the formation of ammonia.

Solution:

In Example 10, we used tabulated values $of\ \Delta G\square f\ to$ calculate $\Delta G°$ for this reaction (−32.7 kJ/mol of N_2). For equilibrium conditions, rearranging Equation 18.36,

$$\Delta G° - \Delta G° RT = - RTln\ Kp = ln\ Kp$$

Inserting the value of $\Delta G°$ and the temperature (25°C = 298 K) into this equation,

$$ln\ KpKp = - (- 32.7 kJ)(1000\ J / kJ)$$

$$(8.314\ J / K)(298\ K) = 13.2 = 5.4 \acute{} 105$$

Thus the equilibrium constant for the formation of ammonia at room temperature is favorable. As we saw in Chapter 15 "Chemical Equilibrium", however, the *rate* at which the reaction occurs at room temperature is too slow to be useful.

Exercise

Calculate K_p for the reaction of NO with O_2 to give NO_2 at 25°C. As calculated in the exercise in Example 10, $\Delta G°$ for this reaction is −70.5 kJ/mol of O_2.

Answer: 2.2×10^{12}

Although K_p is defined in terms of the partial pressures of the reactants and the products, the equilibrium constant K is defined in terms of the concentrations of the reactants and the products. We described the relationship between the numerical magnitude of K_p and K in Chapter 15 "Chemical Equilibrium" and showed that they are related:

Equation 18.37

$$K_p = K(RT)^{\Delta n}$$

where Δn is the number of moles of gaseous product minus the number of moles of gaseous reactant. For reactions that involve only solutions, liquids, and solids, $\Delta n = 0$, so $K_p = K$. For all reactions that do not involve a change in the number of moles of gas present, the relationship in Equation 18.36 can be written in a more general form:

Equation 18.38

$$\Delta G° = -RT \ln K$$

Only when a reaction results in a net production or consumption of gases is it necessary to correct Equation 18.38 for the difference between K_p and K.[1]

Combining Equation 18.26 and Equation 18.38 provides insight into how the components of $\Delta G°$ influence the magnitude of the equilibrium constant:

Equation 18.39

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K$

Notice that K becomes larger as ΔS° becomes more positive, indicating that the magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder. Moreover, K increases as ΔH° decreases. Thus the magnitude of the equilibrium constant is also directly influenced by the tendency of a system to seek the lowest energy state possible.

Note the Pattern

The magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder and seek the lowest energy state possible.

Temperature Dependence of the Equilibrium Constant

The fact that ΔG° and K are related provides us with another explanation of why equilibrium constants are temperature dependent. This relationship is shown explicitly in Equation 18.39, which can be rearranged as follows:

Equation 18.40

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

Assuming ΔH° and ΔS° are temperature independent, for an exothermic reaction ($\Delta H^\circ < 0$), the magnitude of K decreases with increasing temperature, whereas for an endothermic reaction ($\Delta H^\circ > 0$), the magnitude of K increases with increasing temperature. The quantitative relationship expressed in Equation 18.40 agrees with the qualitative predictions made by applying Le Châtelier's principle, which we discussed in Chapter 15 "Chemical Equilibrium". Because heat is produced in an exothermic reaction, adding heat (by increasing the temperature) will shift the equilibrium to the left, favoring the reactants and decreasing the magnitude of K. Conversely, because heat is consumed in an endothermic reaction, adding heat will shift the equilibrium to the right, favoring the products and increasing the magnitude of K. Equation 18.40 also shows that the *magnitude* of ΔH° dictates how rapidly K changes as a function of temperature. In contrast, the magnitude and sign of ΔS° affect the magnitude of K but not its temperature dependence.

If we know the value of K at a given temperature and the value of ΔH° for a reaction, we can estimate the value of K at any other temperature, even in the absence of information on ΔS°. Suppose, for example, that K_1 and K_2 are the equilibrium constants for a reaction at temperatures T_1 and T_2, respectively. Applying Equation 18.40 gives the following relationship at each temperature:

$$\ln K1 \ln K2 = -\Delta H^\circ RT1 + \Delta S^\circ R = -\Delta H^\circ RT2 + \Delta S^\circ R$$

Subtracting ln K_1 from ln K_2,

Equation 18.41

$$\ln K2 - \ln K1 = \ln K2K1 = \Delta H^\circ R(1T1 - 1T2)$$

Thus calculating ΔH° from tabulated enthalpies of formation and measuring the equilibrium constant at one temperature (K_1) allow us to calculate the value of the equilibrium constant at any other temperature (K_2), assuming that ΔH° and ΔS° are independent of temperature.

EXAMPLE 14

The equilibrium constant for the formation of NH_3 from H_2 and N_2 at 25°C was calculated to be K_p = 5.4×10^5 in Example 13. What is K_p at 500°C? (Use the data from Example 10.)

Given: balanced chemical equation, ΔH°, initial and final T, and K_p at 25°C

Asked for: K_p at 500°C

Strategy:

Convert the initial and final temperatures to kelvins. Then substitute appropriate values into Equation 18.41 to obtain K_2, the equilibrium constant at the final temperature.

Solution:

The value of ΔH° for the reaction obtained using Hess's law is −91.8 kJ/mol of N_2. If we set T_1 = 25°C = 298.K and T_2 = 500°C = 773 K, then from Equation 18.41 we obtain the following:

$$\ln K2K1K2K1K2 = \Delta H^\circ R(1T1 - 1T2) = (-91.8\ kJ)(1000\ J/kJ)$$
$$8.314\ J/K(1298\ K - 1773\ K) = -22.8 = 1.3 \times 10 - 10 = (5.4 \times 105)(1.\ 3\acute{}\ 10 - 10) = 7.0\acute{}\ 10 - 5$$

Thus at 500°C, the equilibrium strongly favors the reactants over the products.

Exercise

In the exercise in Example 13, you calculated $K_p = 2.2 \times 10^{12}$ for the reaction of NO with O_2 to give NO_2 at 25°C. Use the $\Delta H\square f$ values in the exercise in Example 10 to calculate K_p for this reaction at 1000°C.

Answer: 5.6×10^{-4}

Summary

For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature. If we assume ideal gas behavior, the ideal gas law allows us to express ΔG in terms of the partial pressures of the reactants and products, which gives us a

relationship between ΔG and K_p, the equilibrium constant of a reaction involving gases, or K, the equilibrium constant expressed in terms of concentrations. If $\Delta G^\circ < 0$, then Kor $K_p > 1$, and products are favored over reactants. If $\Delta G^\circ > 0$, then K or $K_p < 1$, and reactants are favored over products. If $\Delta G^\circ = 0$, then K or $K_p = 1$, and the system is at equilibrium. We can use the measured equilibrium constant K at one temperature and ΔH° to estimate the equilibrium constant for a reaction at any other temperature.

KEY TAKEAWAY

- The change in free energy of a reaction can be expressed in terms of the standard free-energy change and the equilibrium constant K or K_p and indicates whether a reaction will occur spontaneously under a given set of conditions.

KEY EQUATIONS

Relationship between standard free-energy change and equilibrium constant

Equation 18.38: $\Delta G^\circ = -RT \ln K$

Temperature dependence of equilibrium constant

Equation 18.40: $ln\ K = - \Delta H^\circ RT + \Delta S^\circ R$ **Calculation of K at second temperature**

Equation 18.41: $ln\ K2K1 = \Delta H^\circ R(1T1 - 1T2)$

CONCEPTUAL PROBLEMS

1. Do you expect products or reactants to dominate at equilibrium in a reaction for which ΔG° is equal to

a. 1.4 kJ/mol?

b. 105 kJ/mol?

c. −34 kJ/mol?

2. The change in free energy enables us to determine whether a reaction will proceed spontaneously. How is this related to the extent to which a reaction proceeds?
3. What happens to the change in free energy of the reaction $N_2(g) + 3F_2(g) \rightarrow 2NF_3(g)$ if the pressure is increased while the temperature remains constant? if the temperature is increased at constant pressure? Why are these effects not so important for reactions that involve liquids and solids?
4. Compare the expressions for the relationship between the change in free energy of a reaction and its equilibrium constant where the reactants are gases versus liquids. What are the differences between these expressions?

NUMERICAL PROBLEMS

1. Carbon monoxide, a toxic product from the incomplete combustion of fossil fuels, reacts with water to form CO_2 and H_2, as shown in the equatio $n\ CO(g)+H2O(g) \rightarrow CO2(g)+H2(g),\ for$

which $\Delta H° = -41.0$ kJ/mol and $\Delta S° = -42.3$ J cal/(mol·K) at 25°C and 1 atm.

a. What is $\Delta G°$ for this reaction?

b. What is ΔG if the gases have the following partial pressures: P_{CO} = 1.3 atm, $PH2O$ = 0.8 atm, $PCO2 = 2.0\ atm,\ and\ PH2$ = 1.3 atm?

c. What is ΔG if the temperature is increased to 150°C assuming no change in pressure?

2. Methane and water react to form carbon monoxide and hydrogen according to the equation $CH4(g)+H2O(g) \rightarrow CO(g)+3H2(g).$

a. What is the standard free energy change for this reaction?

b. What is K_p for this reaction?

c. What is the carbon monoxide pressure if 1.3 atm of methane reacts with 0.8 atm of water, producing 1.8 atm of hydrogen gas?

d. What is the hydrogen gas pressure if 2.0 atm of methane is allowed to react with 1.1 atm of water?

e. At what temperature does the reaction become spontaneous?

3. Calculate the equilibrium constant at 25°C for each equilibrium reaction and comment on the extent of the reaction.

a. $CCl4(g)+6H2O(l) \rightarrow CO2(g)+4HCl(aq);\ \Delta G°$

b. = −377 kJ/mol

c. $Xe(g)+2F2(g) \rightarrow XeF4(s);\ \Delta H° =$

d. −66.3 kJ/mol, $\Delta S° = -102.3$ J/(mol·K)

e. $PCl3(g)+S \rightarrow PSCl3(l);\ \Delta G \rightarrow f(PCl_3) = -272.4\ kJ/mol,\ \Delta G \rightarrow f(PSCl_3)$ = −363.2 kJ/mol

4. Calculate the equilibrium constant at 25°C for each equilibrium reaction and comment on the extent of the reaction.

a. $2KClO3(s) \rightarrow 2KCl(s)+3O2(g);\ \Delta G° =$

b. −225.8 kJ/mol

c. $CoCl2(s)+6H2O(g)\square$
$CoCl2\cdot 6H2O(s); DH\square rxn = -352\ kJ/mol, DS\square rxn = -899$

d. J/(mol·K)

e. $2PCl3(g)+O2(g)\square 2POCl3(g);$
$DG\square f(PCl_3) = -272.4\ kJ/mol, DG\square f(POCl_3$

f.) = −558.5 kJ/mol

5. The gas-phase decomposition of N_2O_4 to NO_2 is an equilibrium reaction with $K_p = 4.66 \times 10^{-3}$. Calculate the standard free-energy change for the equilibrium reaction between N_2O_4 and NO_2.

6. The standard free-energy change for the dissolutio
$n\ K4Fe(CN)6\times H2O(s)\square 4K+(aq)+Fe(CN)64-(aq)+H2O(l)$

7. is 26.1 kJ/mol. What is the equilibrium constant for this process at 25°C?

8. Ammonia reacts with water in liquid ammonia solution (am) according to the equatio
$n\ NH3(g)+H2O(am)\square NH4+(am)+OH-(am).\ The$

9. change in enthalpy for this reaction is 21 kJ/mol, and $\Delta S°$ = −303 J/(mol·K). What is the equilibrium constant for the reaction at the boiling point of liquid ammonia (−31°C)?

10. At 25°C, a saturated solution of barium carbonate is found to have a concentration of $[Ba^{2+}] = [CO_3^{2-}] = 5.08 \times 10^{-5}$ M. Determine $\Delta G°$ for the dissolution of $BaCO_3$.

11. Lead phosphates are believed to play a major role in controlling the overall solubility of lead in acidic soils. One of the dissolution reactions i
$s\ Pb3(PO4)2(s)+4H+(aq)\square$
$3Pb2+(aq)+2H2PO4-(aq),\ for\ which$

12. log K = −1.80. What is $\Delta G°$ for this reaction?

13. The conversion of butane to 2-methylpropane is an equilibrium process with $\Delta H°$ = −2.05 kcal/mol and $\Delta G°$ = −0.89 kcal/mol.

a. What is the change in entropy for this conversion?

b. Based on structural arguments, are the sign and magnitude of the entropy change what you would expect? Why?

c. What is the equilibrium constant for this reaction?

14. The reaction of $CaCO_3$(s) to produce CaO(s) and CO_2(g) has an equilibrium constant at 25°C of 2×10^{-23}. Values $of\ DH\square f\ are$ as follows: $CaCO_3$, −1207.6 kJ/mol; CaO, −634.9 kJ/mol; and CO_2, −393.5 kJ/mol.

a. What is $\Delta G°$ for this reaction?

b. What is the equilibrium constant at 900°C?

c. What is the partial pressure of $CO_2(g)$ in equilibrium with CaO and $CaCO_3$ at this temperature?

d. Are reactants or products favored at the lower temperature? at the higher temperature?

15. In acidic soils, dissolved Al^{3+} undergoes a complex formation reaction with SO_4^{2-} to form $[AlSO_4^{+}]$. The equilibrium constant at 25°C for the reaction $Al3+(aq)+SO42-(aq) \square AlSO4+(aq)$ *is* 1585.

a. What is Δ*G*° for this reaction?

b. How does this value compare with Δ*G*° for the reacti
on $Al3+(aq)+F-(aq) \square AlF2+(aq)$, *for* which $K = 10^7$ at 25°C?

c. Which is the better ligand to use to trap Al^{3+} from the soil?

ANSWERS

1.

a. −28.4 kJ/mol

b. −26.1 kJ/mol

c. −19.9 kJ/mol

2.

3.

a. 1.21×10^{66}; equilibrium lies far to the right.

b. 1.89×10^{6}; equilibrium lies to the right.

c. 5.28×10^{16}; equilibrium lies far to the right.

4.

5. 13.3 kJ/mol

6.

7. 5.1×10^{-21}

8.

9. 10.3 kJ/mol

10.

11.

a. 129.5 kJ/mol

b. 6

c. 6.0 atm

d. Products are favored at high *T*; reactants are favored at low *T*.

12.

[1] Although we typically use concentrations or pressures in our equilibrium calculations, recall that equilibrium constants are generally expressed as unitless numbers because of the use of activities or fugacities in precise thermodynamic work. Systems that contain gases at high pressures or concentrated solutions that deviate substantially from ideal behavior require the use of fugacities or activities, respectively.

18.7 Comparing Thermodynamics and Kinetics

LEARNING OBJECTIVE

1. To understand the differences between the information that thermodynamics and kinetics provide about a system.

Because thermodynamics deals with state functions, it can be used to describe the overall properties, behavior, and equilibrium composition of a system. It is *not* concerned with the particular pathway by which physical or chemical changes occur, however, so it cannot address the *rate* at which a particular process will occur. Although thermodynamics provides a significant constraint on what *can* occur during a reaction process, it does not describe the detailed steps of what *actually* occurs on an atomic or a molecular level.

Note the Pattern

Thermodynamics focuses on the energetics of the products and the reactants, whereas kinetics focuses on the pathway from reactants to products.

Table 18.4 "The Relationship between " gives the numerical values of the equilibrium constant (K) that correspond to various approximate values of ΔG°. Note that $\Delta G^\circ \geq +10$ kJ/mol or $\Delta G^\circ \leq -10$ kJ/mol ensures that an equilibrium lies essentially all the way to the left or to the right, respectively, under standard conditions, corresponding to a reactant-to-product ratio of approximately 10,000:1 (or vice versa). Only if ΔG° is quite small (±10 kJ/mol) are significant amounts of both products and reactants present at equilibrium. Most reactions that we encounter have equilibrium constants substantially greater or less than 1, with the equilibrium strongly favoring either products or reactants. In many cases, we will encounter reactions that are strongly favored by thermodynamics but do not occur at a measurable rate. In contrast, we may encounter reactions that are not thermodynamically favored under standard conditions but nonetheless do occur under certain nonstandard conditions.

Table 18.4 The Relationship between K and ΔG° at 25°C

ΔG° (kJ/mol)	K	Physical Significance
500	3×10^{-88}	For all intents and purposes, the reaction does not proceed in the forward direction: only reactants are present at equilibrium.
100	3×10^{-18}	
10	2×10^{-2}	Both forward and reverse reactions occur: significant amounts of both products and reactants are present at equilibrium.
0	1	
−10	60	
−100	3×10^{17}	For all intents and purposes, the forward reaction proceeds to completion: only products are present at equilibrium.
−500	4×10^{87}	

A typical challenge in industrial processes is a reaction that has a large negative value of ΔG° and hence a large value of K but that is too slow to be practically useful. In such cases, mixing the reactants results in only a physical mixture, not a chemical reaction. An example is the reaction of carbon tetrachloride with water to produce carbon dioxide and hydrochloric acid, for which ΔG° is −232 kJ/mol:

Equation 18.42

$$CCl4(l)+2H2O(l) \square \ CO2(g)+2HCl(g)$$

The value of K for this reaction is 5×10^{40} at 25°C, yet when CCl_4 and water are shaken vigorously at 25°C, nothing happens: the two immiscible liquids form separate layers, with the denser CCl_4 on the bottom. In comparison, the analogous reaction of $SiCl_4$with water to give SiO_2 and HCl, which has a similarly large equilibrium constant, occurs almost explosively. Although the two reactions have comparable thermodynamics, they have very different kinetics! There are also many reactions for which $\Delta G^\circ << 0$ but that do not occur as written because another possible reaction occurs more rapidly. For example, consider the reaction of lead sulfide with hydrogen peroxide. One possible reaction is as follows:

Equation 18.43

$$PbS(s) +4H2O2(l) \square \ PbO2(s)+SO2(g)+4H2O(l)$$

for which ΔG° is −886 kJ/mol and K is 10^{161}. Yet when lead sulfide is mixed with hydrogen peroxide, the ensuing vigorous reaction does *not* produce PbO_2 and SO_2. Instead, the reaction that actually occurs is as follows:

Equation 18.44

$$PbS(s) +4H2O2(l) \square \ PbSO4(s)+4H2O(l)$$

This reaction has a ΔG° value of −1181 kJ/mol, within the same order of magnitude as the reaction in Equation 18.43, but it occurs much more rapidly.

Now consider reactions with $\Delta G^\circ > 0$. Thermodynamically, such reactions do not occur spontaneously under standard conditions. Nonetheless, these reactions can be made to occur under nonstandard conditions. An example is the reduction of chromium(III) chloride by hydrogen gas:

Equation 18.45

$$CrCl3(s) + 12H2(g) \square \quad CrCl2(s) + HCl(g)$$

At 25°C, ΔG° = 35 kJ/mol and $K_p = 7 \times 10^{-7}$. However, at 730°C, ΔG° = −52 kJ/mol and $K_p = 5 \times 10^2$; at this elevated temperature, the reaction is a convenient way of preparing chromium(II) chloride in the laboratory. Moreover, removing HCl gas from the system drives the reaction to completion, as predicted by Le Châtelier's principle. Although the reaction is not thermodynamically spontaneous under standard conditions, it becomes spontaneous under nonstandard conditions.

There are also cases in which a compound whose formation appears to be thermodynamically prohibited can be prepared using a different reaction. The reaction for the preparation of chlorine monoxide from its component elements, for example, is as follows:

Equation 18.46

$$12O2(g) + Cl2(g) \square \quad Cl2O(g)$$

$$h\ DG \square f\ is\ 97.9\ kJ / mol.$$

for whic $The\ large\ positive\ value\ of\ DG \square f\ for\ this$ reaction indicates that mixtures of chlorine and oxygen do not react to any extent to form Cl_2O. Nonetheless, Cl_2O is easily prepared using the reaction

Equation 18.47

$$HgO(s) + 2Cl2(g) \square \quad Cl2O(g) + HgCl2(s)$$

which has a ΔG° of −22.2 kJ/mol and a K_p of approximately 1×10^4.

Finally, the ΔG° values for some reactions are so positive that the only way to make them proceed in the desired direction is to supply external energy, often in the form of electricity. Consider, for example, the formation of metallic lithium from molten lithium chloride:

Equation 18.48

$$LiCl(l) \square \quad Li(l) + 12Cl2(g)$$

Even at 1000°C, ΔG is very positive (324 kJ/mol), and there is no obvious way to obtain lithium metal using a different reaction. Hence in the industrial preparation of metallic lithium, electrical energy is used to drive the reaction to the right, as described inChapter 19 "Electrochemistry".

Note the Pattern

A reaction that does not occur under standard conditions can be made to occur under nonstandard conditions, such as by driving the reaction to completion using Le Châtelier's principle or by providing external energy.

Often reactions that are not thermodynamically spontaneous under standard conditions can be made to occur spontaneously if coupled, or connected, in some way to another reaction for which $\Delta G^\circ << 0$. Because the overall value of ΔG° for a series of reactions is the sum of the ΔG° values for the individual reactions, virtually any unfavorable reaction can be made to occur by chemically coupling it to a sufficiently favorable reaction or reactions. In the preparation of chlorine monoxide from mercuric oxide and chlorine (Equation 18.47), we have already encountered one example of this phenomenon of *coupled reactions*, although we did not describe it as such at the time. We can see how the chemical coupling works if we write Equation 18.47 as the sum of three separate reactions:

$$12O2(g)+Cl2(g)HgO(s)Hg(l)+Cl2(g)HgO(s)+2Cl2(g)\square\ Cl2O(g)$$

$$\square\ Hg(l)+12O2(g)\square\ HgCl2(s)\square\ Cl2O(g)+HgCl2(s)DG°DG$$

$$°DG°DG\square rxn=97.9\ kJ/mol=58.5\ kJ/mol=-178.6\ kJ/mol=-22.2\ kJ/mol(1)(2)(3)$$

Comparing the ΔG° values for the three reactions shows that reaction 3 is so energetically favorable that it more than compensates for the other two energetically unfavorable reactions. Hence the overall reaction is indeed thermodynamically spontaneous as written.

Note the Pattern

By coupling reactions, a reaction that is thermodynamically nonspontaneous can be made spontaneous.

EXAMPLE 15

Bronze Age metallurgists were accomplished practical chemists who unknowingly used coupled reactions to obtain metals from their ores. Realizing that different ores of the same metal required different treatments, they heated copper oxide ore in the presence of charcoal (carbon) to obtain copper metal, whereas they pumped air into the reaction system if the ore was copper ulfide. Assume that a particular copper ore consists of pure cuprous oxide (Cu_2O). Using $the\ DG\square f\ values$ given for each, calculate

a. Δ*G*° and K_p for the decomposition of Cu_2O to metallic copper and oxygen gas [$\Delta G_f^\circ(Cu_2O) = -146.0\ kJ/mol$].

b. Δ*G*° and K_p for the reaction of Cu_2O with carbon to produce metallic copper and carbon monoxide [

Given: reactants and products, ΔG_f° values for Cu_2O and CO, and temperature

Asked for: Δ*G*° and K_p for the formation of metallic copper from Cu_2O in the absence and presence of carbon

Strategy:

A Write the balanced equilibrium equation for each reaction. Using the "products minus reactants" rule, calculate Δ*G*° for the reaction.

B Substitute appropriate values into Equation 18.36 to obtain K_p.

Solution:

a. **A** The chemical equation for the decomposition of cuprous oxide is as follows:

$$Cu_2O(s) \rightarrow 2Cu(s) + \frac{1}{2}O_2(g)$$

The substances on the right side of this equation are pure elements in their standard states, so their ΔG_f° values are zero. Δ*G*° for the reaction is therefore

$$\Delta G^\circ = [2\Delta G_f^\circ(Cu) + \frac{1}{2}\Delta G_f^\circ(O_2)] - \Delta G_f^\circ(Cu_2O)$$

$$= [(2\ mol)(0\ kJ/mol) + (\frac{1}{2}mol)(0\ kJ/mol)] - [(1\ mol)(-146.0\ kJ/mol)] = 146.$$

$$0\ kJ$$

B Rearranging and substituting the appropriate values into Equation 18.36,

$$\ln K_p = -\frac{\Delta G^\circ}{RT} = -\frac{(146.0\ kJ)(1000\ J/kJ)}{(8.314\ J/K)(298.15\ K)} = -58.90 = 2.6 \times 10^{-26}$$

This is a very small number, indicating that Cu_2O does not spontaneously decompose to a significant extent at room temperature.

b. **A** The O_2 produced in the decomposition of Cu_2O can react with carbon to form CO:

$$\frac{1}{2}O_2(g) + C(s) \rightarrow CO(g)$$

Because Δ*G*° for this reaction is equal to ΔG_f° for CO (−137.2 kJ/mol), it is energetically more feasible to produce metallic copper from cuprous oxide by coupling the two reactions:

$$Cu_2O(s) + \frac{1}{2}O_2(g) + C(s) \quad Cu_2O(s) + C(s) \rightarrow 2Cu(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$$

$$\rightarrow 2Cu(s) + CO(g) \quad \Delta G^\circ \quad \Delta G^\circ \quad \Delta G_f^\circ = 146.0\ kJ/mol = -137.2$$

$$kJ/mol = 8.8\ kJ/mol$$

B We can find the corresponding value of K_p:

$$\ln KpKp = - DG°RT = - (8.8kJ)(1000\ J/kJ)$$

$$(8.314\ J/K)(298.15\ K) = - 3.6 = 0.03$$

Although this value is still less than 1, indicating that reactants are favored over products at room temperature, it is about 24 orders of magnitude greater than K_p for the production of copper metal in the absence of carbon. Because both $\Delta H°$ and $\Delta S°$ are positive for this reaction, it becomes thermodynamically feasible at slightly elevated temperatures (greater than about 80°C). At temperatures of a few hundred degrees Celsius, the reaction occurs spontaneously, proceeding smoothly and rapidly to the right as written and producing metallic copper and carbon monoxide from cuprous oxide and carbon.

Exercise

Use the $DG\square f\ values$ given to calculate $\Delta G°$ and K_p for each reaction.

a. the decomposition of cuprous sulfide to copper metal and elemental sulfur $[DG\square f(Cu2S) = - 86.2\ kJ/mol]$

b. the reaction of cuprous sulfide with oxygen gas to produce sulfur dioxide and copper metal $[DG\square f\ [SO_2(g)]\ =\ -\ 300.1\ kJ/mol]$

Answer:

a. $\Delta G° = 86.2$ kJ/mol; $K_p = 7.90 \times 10^{-16}$

b. $\Delta G° = -213.9$ kJ/mol; $K_p = 2.99 \times 10^{37}$

Summary

Thermodynamics describes the overall properties, behavior, and equilibrium composition of a system; kinetics describes the rate at which a particular process will occur and the pathway by which it will occur. Whereas thermodynamics tells us what can occur during a reaction process, kinetics tells us what actually occurs on an atomic or a molecular level. A reaction that is not thermodynamically spontaneous under standard conditions can often be made to occur spontaneously by varying the reaction conditions; using a different reaction to obtain the same product; supplying external energy, such as electricity; or coupling the unfavorable reaction to another reaction for which $\Delta G° << 0$.

KEY TAKEAWAY

- Thermodynamics describes the overall properties, behavior, and equilibrium composition of a system, whereas kinetics describes the particular pathway by which a physical or a chemical change actually occurs.

CONCEPTUAL PROBLEM

1. You are in charge of finding conditions to make the reaction A(l) + B(l) → C(l) + D(g) favorable because it is a critical step in the synthesis of your company's key product. You have calculated that $\Delta G°$ for the reaction is negative, yet the ratio of products to reactants is very small. What have you overlooked in your scheme? What can you do to drive the reaction to increase your product yield?

18.8 Thermodynamics and Life

LEARNING OBJECTIVE

1. To understand the importance of thermodynamics in biochemical systems.

In a thermodynamic sense, a living cell can be viewed as a low-entropy system that is*not* in equilibrium with its surroundings and is capable of replicating itself. A constant input of energy is needed to maintain the cell's highly organized structure, its wide array of precisely folded biomolecules, and its intricate system of thousands of chemical reactions. A cell also needs energy to synthesize complex molecules from simple precursors (e.g., to make proteins from amino acids), create and maintain differences in the concentrations of various substances inside and outside the cell, and do mechanical work (e.g., muscle contraction). In this section, we examine the nature of the energy flow between a cell and its environment as well as some of the chemical strategies cells use to extract energy from their surroundings and store that energy.

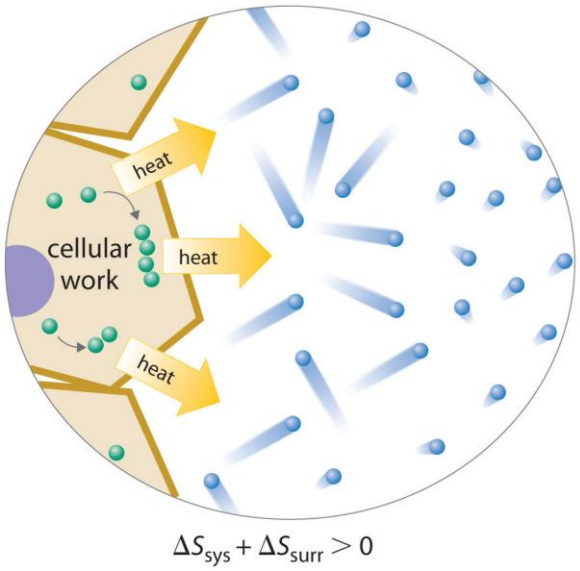
Energy Flow between a Cell and Its Surroundings

One implication of the first and second laws of thermodynamics is that any closed system must eventually reach equilibrium. With no external input, a clock will run down, a battery will lose its charge, and a mixture of an aqueous acid and an aqueous base will achieve a uniform intermediate pH value. In contrast, a cell is an open system that can exchange matter with its surroundings as well as absorb energy from its environment in the form of heat or light. Cells use the energy obtained in these ways to maintain the nonequilibrium state that is essential for life.

Because cells are open systems, they cannot be described using the concepts of classical thermodynamics that we have discussed in this chapter, which have focused on reversible processes occurring in closed chemical systems that can exchange energy—but not matter—with their surroundings. Consequently, a relatively new subdiscipline called *nonequilibrium thermodynamics* has been developed to quantitatively describe open systems such as living cells.

Because a cell cannot violate the second law of thermodynamics, the only way it can maintain a low-entropy, nonequilibrium state characterized by a high degree of structural organization is to increase the entropy of its surroundings. A cell releases some of the energy that it obtains from its environment as heat that is transferred to its surroundings, thereby resulting in an increase in S_{surr} (Figure 18.17 "Life and Entropy"). As long as ΔS_{surr} is positive and greater than ΔS_{sys}, the entropy of the universe increases, so the second law of thermodynamics is not violated. Releasing heat to the surroundings is necessary but not sufficient for life: the release of energy must be coupled to processes that increase the degree of order within a cell. For example, a wood fire releases heat to its surroundings, but unless energy from the burning wood is also used to do work, there is no increase in order of any portion of the universe.

Figure 18.17 *Life and Entropy*



A living cell is in a low-entropy, nonequilibrium state characterized by a high degree of structural organization. To maintain this state, a cell must release some of the energy it obtains from its environment as heat, thereby increasing S_{surr} sufficiently that the second law of thermodynamics is not violated. In this example, the cell combines smaller components into larger, more ordered

structures; the accompanying release of heat increases the entropy of the surrounding environment so that $S_{univ} > 0$.

Note the Pattern

Any organism in equilibrium with its environment is dead.

Extracting Energy from the Environment

Although organisms employ a wide range of specific strategies to obtain the energy they need to live and reproduce, they can generally be divided into two categories: organisms are either *phototrophs* (from the Greek *photos*, meaning "light," and *trophos*, meaning "feeder"), whose energy source is sunlight, or *chemotrophs*, whose energy source is chemical compounds, usually obtained by consuming or breaking down other organisms. Phototrophs, such as plants, algae, and photosynthetic bacteria, use the radiant energy of the sun directly, converting water and carbon dioxide to energy-rich organic compounds, whereas chemotrophs, such as animals, fungi, and many nonphotosynthetic bacteria, obtain energy-rich organic compounds from their environment. Regardless of the nature of their energy and carbon sources, all organisms use oxidation–reduction, or redox, reactions to drive the synthesis of complex biomolecules. Organisms that can use only O_2 as the oxidant (a group that includes most animals) are *aerobic organisms* that cannot survive in the absence of O_2. Many organisms that use other oxidants (such as SO_4^{2-}, NO_3^-, or CO_3^{2-}) or oxidized organic compounds can live only in the absence of O_2, which is a deadly poison for them; such species are called *anaerobic organisms*.

The fundamental reaction by which all green plants and algae obtain energy from sunlight is photosynthesis, the photochemical reduction of CO_2 to a carbon compound such as glucose. Concurrently, oxygen in water is oxidized to O_2 (recall that $h\nu$ is energy from light):

Equation 18.49

$$6CO2 + 6H2O \rightarrow h\nu C6H12O6 photosynthesis + 6O2$$

This reaction is not a spontaneous process as written, so energy from sunlight is used to drive the reaction. Photosynthesis is critical to life on Earth; it produces all the oxygen in our atmosphere.

In many ways, chemotrophs are more diverse than phototrophs because the nature of both the reductant (the nutrient) and the oxidant can vary. The most familiar chemotrophic strategy uses compounds such as glucose as the reductant and molecular oxygen as the oxidant in a process called respiration. (For more

information on respiration, see Chapter 5 "Energy Changes in Chemical Reactions".) The overall reaction of respiration is the reverse of photosynthesis:

Equation 18.50

$$C6H12O6 + 6O2 \rightarrow 6CO2respiration + 6H2O$$

An alternative strategy uses fermentation reactions, in which an organic compound is simultaneously oxidized and reduced. Common examples are alcohol fermentation, used in making wine, beer, and bread, and lactic acid fermentation, used in making yogurt:

Equation 18.51

$$C6H12O6 \rightarrow 2CO2 + 2CH3CH2OHalcohol\ \ fermentation$$

Equation 18.52

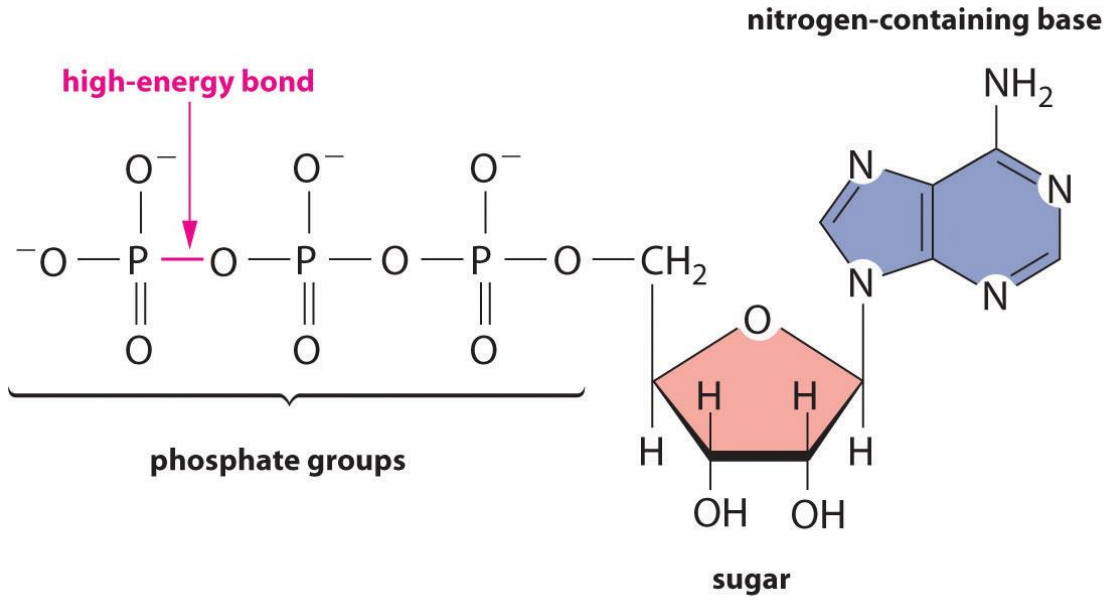
$$C6H12O6 \rightarrow 2CH3CH(OH)CO2Hlactic\ \ acid\ \ fermentation$$

In these reactions, some of the carbon atoms of glucose are oxidized, while others are reduced. Recall that a reaction in which a single species is both oxidized and reduced is called a *disproportionation* reaction.

The Role of NADH and ATP in Metabolism

Regardless of the identity of the substances from which an organism obtains energy, the energy must be released in very small increments if it is to be useful to the cell. Otherwise, the temperature of the cell would rise to lethal levels. Cells store part of the energy that is released as ATP (adenosine triphosphate), a compound that is the universal energy currency of all living organisms (Figure 18.18 "ATP, the Universal Energy Currency of All Cells").

Figure 18.18 *ATP, the Universal Energy Currency of All Cells*



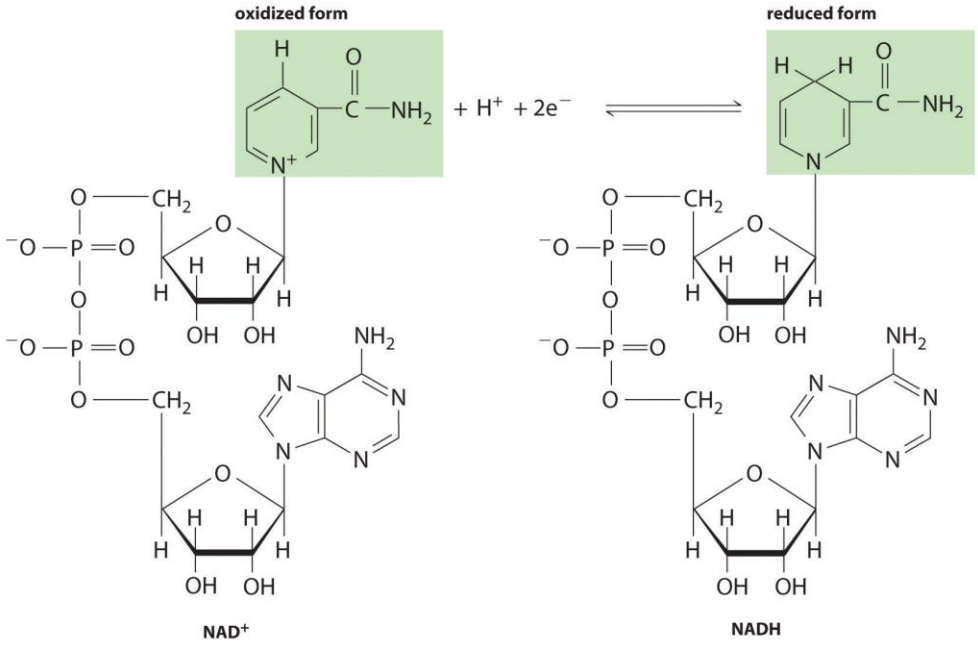
The ATP molecule contains a nitrogen-containing base, a sugar, and three phosphate groups, as well as two high-energy phosphoric acid anhydride bonds.

Most organisms use several intermediate species to shuttle electrons between the terminal reductant (such as glucose) and the terminal oxidant (such as O_2). In virtually all cases, an intermediate species oxidizes the energy-rich reduced compound, and the now-reduced intermediate then migrates to another site where *it* is oxidized. The most important of these electron-carrying intermediates is NAD^+ (nicotinamide adenine dinucleotide; Figure 18.19 "NAD"), whose reduced form, formally containing H^-, is NADH (reduced nicotinamide adenine dinucleotide). The reduction of NAD^+ to NADH can be written as follows:

Equation 18.53

$$NAD^+ + H^+ + 2e^- \rightarrow NADH$$

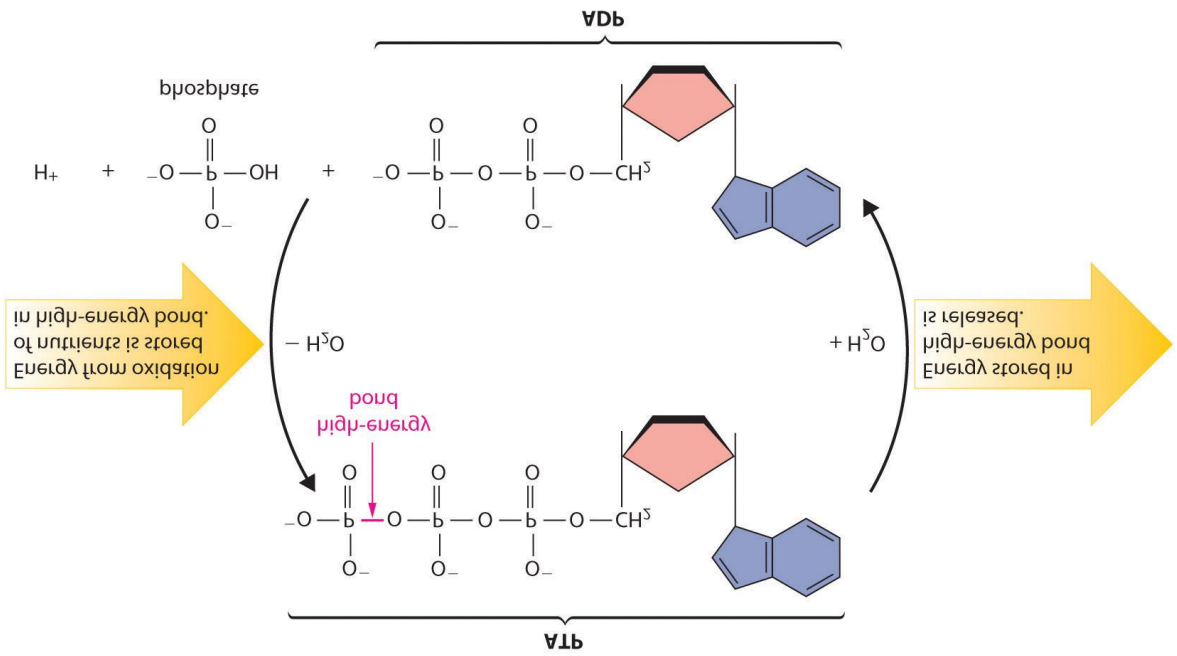
Figure 18.19 *NAD^+ and Its Reduced Form (NADH)*



This electron carrier is used by biological systems to transfer electrons from one species to another. The oxidized form (NAD^+) is reduced to NADH by energy-rich nutrients such as glucose, and the reduced form (NADH), is then oxidized to NAD^+ by O_2 during respiration.

Most organisms use NAD^+ to oxidize energy-rich nutrients such as glucose to CO_2 and water; NADH is then oxidized to NAD^+ using an oxidant such as O_2. During oxidation, a fraction of the energy obtained from the oxidation of the nutrient is stored as ATP. The phosphoric acid anhydride bonds in ATP can then be hydrolyzed by water, releasing energy and forming ADP (adenosine diphosphate). It is through this sequence of reactions that energy from the oxidation of nutrients is made available to cells. Thus ATP has a central role in metabolism: it is synthesized by the oxidation of nutrients, and its energy is then used by cells to drive synthetic reactions and perform work (Figure 18.20 "The ATP Cycle").

Figure 18.20 *The ATP Cycle*



The high-energy phosphoric acid anhydride bond in ATP stores energy released during the oxidation of nutrients. Hydrolysis of the high-energy bond in ATP releases energy, forming adenosine diphosphate (ADP) and phosphate.

Under standard conditions in biochemical reactions, all reactants are present in aqueous concentrations of 1 M at a pressure of 1 atm. For H^+, this corresponds to a pH of zero, but very little biochemistry occurs at pH = 0. For biochemical reactions, chemists have therefore defined a new standard state in which the H^+ concentration is 1×10^{-7} M (pH 7.0), and all other reactants and products are present in their usual standard-state conditions (1 M or 1 atm). The free-energy change and corresponding equilibrium constant for a reaction under these new standard conditions are denoted by the addition of a prime sign (′) to the conventional symbol: $\Delta G^{o\prime}$ and K'. If protons do not participate in a biological reaction, then $\Delta G^{o\prime} = \Delta G^o$. Otherwise, the relationship between $\Delta G^{o\prime}$ and ΔG^o is as follows:

Equation 18.54

$$\Delta G^{\circ\prime} = \Delta G^\circ + RT \ln(10^{-7})n$$

where $\Delta G^{o\prime}$ and ΔG^o are in kilojoules per mole and n is the number of protons produced in the reaction. At 298 K, this simplifies to

Equation 18.55

$$\Delta G^{\circ\prime} = \Delta G^\circ - 39.96n$$

Thus any reaction that involves the release of protons is thermodynamically more favorable at pH 7 than at pH 0.

The chemical equation that corresponds to the hydrolysis of ATP to ADP and phosphate is as follows:

Equation 18.56

$$ATP4- + H2O \rightarrow ADP3- + HPO42- + H+$$

This reaction has a $\Delta G^{\circ\prime}$ of −34.54 kJ/mol, but under typical physiological (or biochemical) conditions, the actual value of $\Delta G'$ for the hydrolysis of ATP is about −50 kJ/mol. Organisms use this energy to drive reactions that are energetically uphill, thereby coupling the reactions to the hydrolysis of ATP. One example is found in the biochemical pathway of *glycolysis*, in which the 6-carbon sugar glucose ($C_6H_{12}O_6$) is split into two 3-carbon fragments that are then used as the fuel for the cell. Initially, a phosphate group is added to glucose to form a phosphate ester, glucose-6-phosphate (abbreviated glucose-6-P), in a reaction analogous to that of an alcohol and phosphoric acid:

Equation 18.57

$$glucose(aq) ROH + HPO42- (aq) + HOPO32- \rightarrow glucose-6-P2-(aq) \rightarrow ROPO32- + H2O(l) + H2O$$

Due to its electrical charge, the phosphate ester is unable to escape from the cell by diffusing back through the membrane surrounding the cell, ensuring that it remains available for further reactions. For the reaction in Equation 18.57, ΔG° is 17.8 kJ/mol and K is 7.6×10^{-4}, indicating that the equilibrium lies far to the left. To force this reaction to occur as written, it is coupled to a thermodynamically favorable reaction, the hydrolysis of ATP to ADP:

$$glucose + HPO42- ATP4- + H2Oglucose + ATP4- \rightarrow glucose-6-P2- + H2O \rightarrow ADP3- + HPO42- + H+ \rightarrow glucose-6-P2- + ADP3- + H+ \Delta G^{\circ\prime} \Delta G^{\circ\prime} \Delta G^{\circ\prime} = 17.8\ kJ/mol = -34.54\ kJ/mol = -16.7\ kJ/molK1K2K3 = 7.6 \times 10- 4 = 2.2 \times 105 = 1.7 \times 102$$

Thus the formation of glucose-6-phosphate is thermodynamically spontaneous if ATP is used as the source of phosphate.

Note the Pattern

Organisms use energy from the hydrolysis of ATP to drive reactions that are thermodynamically nonspontaneous.

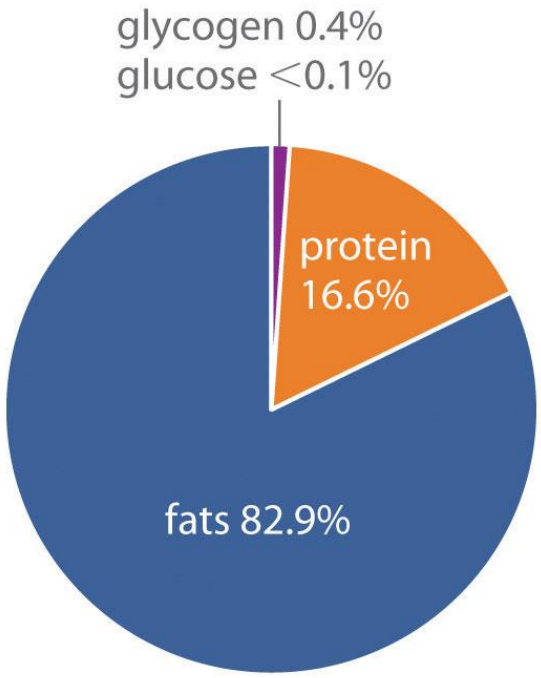
The formation of glucose-6-phosphate is only one of many examples of how cells use ATP to drive an otherwise nonspontaneous biochemical reaction. Under nonstandard physiological conditions, each ATP hydrolyzed actually results in approximately a 10^8increase in the magnitude of the equilibrium constant, compared with the equilibrium constant of the reaction in the absence of ATP. Thus a reaction in which two ATP molecules are converted to ADP increases K by about 10^{16}, three ATP molecules by 10^{24}, and so forth. Virtually any energetically unfavorable reaction or sequence of reactions can be made to occur spontaneously by coupling it to the hydrolysis of a sufficiently large number of ATP molecules.

Energy Storage in Cells

Although all organisms use ATP as the *immediate* free-energy source in biochemical reactions, ATP is not an efficient form in which to store energy on a long-term basis. If the caloric intake of an average resting adult human were stored as ATP, two-thirds of the body weight would have to consist of ATP. Instead, a typical 70 kg adult human has a total of only about 50 g of both ATP and ADP, and, far from being used for long-term storage, each molecule of ATP is turned over about 860 times per day. The entire ATP supply would be exhausted in less than 2 minutes if it were not continuously regenerated.

How does the body store energy for the eventual production of ATP? Three primary means are as sugars, proteins, and fats. The combustion of sugars and proteins yields about 17 kJ of energy per gram, whereas the combustion of fats yields more than twice as much energy per gram, about 39 kJ/g. Moreover, sugars and proteins are hydrophilic and contain about 2 g of water per gram of fuel, even in very concentrated form. In contrast, fats are hydrophobic and can be stored in essentially anhydrous form. As a result, organisms can store about six times more energy per gram as fats than in any other form. A typical 70 kg adult human has about 170 kJ of energy in the form of glucose circulating in the blood, about 2600 kJ of energy stored in the muscles and liver as glycogen (a polymeric form of glucose), about 100,000 kJ stored in the form of protein (primarily muscle tissue), and almost 500,000 kJ in the form of fats (Figure 18.21 "Percentages of Forms of Energy Storage in Adult Humans"). Thus fats constitute by far the greatest energy reserve, while accounting for only about 12 kg of the 70 kg body mass. To store this amount of energy in the form of sugars would require a total body mass of about 144 kg, more than half of which would be sugar.

Figure 18.21 *Percentages of Forms of Energy Storage in Adult Humans*



An average 70 kg adult stores about 6 × 10⁵ kJ of energy in glucose, glycogen, protein, and fats. Fats are the most abundant and most efficient form for storing energy.

EXAMPLE 16

Glucose is one form in which the body stores energy.

a. Calculate Δ*G*°′ for the respiration of glucose to CO_2 and H_2O using these values of ΔG_f°: -910

b. .4 kJ/mol for glucose, −394.4 kJ/mol for CO_2(g), and −237.1 kJ/mol for H_2O(l).

c. Assuming 50% efficiency in the conversion of the released energy to ATP, how many molecules of ATP can be synthesized by the combustion of one molecule of glucose? At 298.15 K, Δ*G*°′ for the hydrolysis of ATP is −34.54 kJ/mol.

Given: balanced chemical equation (Equation 18.50), values of ΔG_f°, *conversion* efficiency, and Δ*G*°′ for hydrolysis of ATP

Asked for: Δ*G*°′ for the combustion reaction and the number of molecules of ATP that can be synthesized

Strategy:

A Using the "products minus reactants" rule, calculate ΔG_{rxn}° for the respiration reaction.

B Multiply the calculated value $of\ \Delta G°rxn$ by the efficiency to obtain the number of kilojoules available for ATP synthesis. Then divide this value by Δ*G*°′ for the hydrolysis of ATP to find the maximum number of ATP molecules that can be synthesized.

Solution:

a. **A** Protons are not released or consumed in the reaction, so Δ*G*°′ = Δ*G*°. We begin by using the balanced chemical equation in Equation 18.50:

$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

From the given values of $\Delta G°f\ is$ remember that $\Delta G°f\ is$ zero for an element such as O_2 itstandard state), we can calculate $\Delta G°rxn$:

b. $$\Delta G°rxn = \sum m\Delta G°f(products) - \sum n\Delta G°f(reactants) = [6(-394.4) + 6(-237.1)] - [(-910.4) + 0] = -2879\ kJ/mol\ of\ glucose$$

c. **B** If we assume that only 50% of the available energy is used, then about 1440 kJ/mol of glucose is available for ATP synthesis. The value of Δ*G*°′ for the hydrolysis of ATP under biochemical conditions is −34.54 kJ/mol, so in principle an organism could synthesize

$$1440\ kJ/mol\ glucose \left| 34.54\ kJ/mol\ ATP \right. = 41.7 \approx 42\ ATP/glucose$$

Most aerobic organisms actually synthesize about 32 molecules of ATP per molecule of glucose, for an efficiency of about 45%.

Exercise

Some bacteria synthesize methane using the following redox reaction:

$CO_2(g) + 4H_2(g) \rightarrow CH_4(g) + 2H_2O(g)$

a. Calculate Δ*G*°′ for this reaction using values of $\Delta G°f\ in$ Chapter 25 "Appendix A: Standard Thermodynamic Quantities for Chemical Substances at 25°C".

b. Calculate how many ATP molecules could be synthesized per mol of CO_2 reduced if the efficiency of the process were 100%.

nswer:

a. −86.6 kJ/mol CO_2

b. 2.5 ATP/mol CO_2

Summary

A living cell is a system that is not in equilibrium with its surroundings; it requires a constant input of energy to maintain its nonequilibrium state. Cells maintain a low-entropy state by increasing the entropy of their surroundings. *Aerobic organisms* cannot survive in the absence of O_2, whereas *anaerobic organisms* can live only in the absence of O_2. Green plants and algae are *phototrophs*, which extract energy from the environment through a process called **photosynthesis**, the photochemical reduction of CO_2 to a reduced carbon compound. Other species, called *chemotrophs*, extract energy from chemical compounds. One of the main processes chemotrophs use to obtain energy is **respiration**, which is the reverse of photosynthesis. Alternatively, some chemotrophs obtain energy by**fermentation**, in which an organic compound is both the oxidant and the reductant. Intermediates used by organisms to shuttle electrons between the reductant and the oxidant include NAD^+ and NADH. Energy from the oxidation of nutrients is made available to cells through the synthesis of ATP, the energy currency of the cell. Its energy is used by cells to synthesize substances through coupled reactions and to perform work. The body stores energy as sugars, protein, or fats before using it to produce ATP.

CONCEPTUAL PROBLEM

1. The tricarboxylic acid (TCA) cycle in aerobic organisms is one of four pathways responsible for the stepwise oxidation of organic intermediates. The final reaction in the TCA cycle has $\Delta G° = 29.7$ kJ/mol, so it should not occur spontaneously. Suggest an explanation for why this reaction proceeds in the forward direction in living cells.

ANSWER

1. It is coupled to another reaction that is spontaneous, which drives this reaction forward (Le Châtelier's principle).

18.9 End-of-Chapter Material

APPLICATION PROBLEMS

Problems marked with a ♦ involve multiple concepts.

1. Electric utilities have been exploring thermal energy storage as a potentially attractive energy-storage solution for peak use. Thermal energy is extracted as steam and stored in rock, oil, or water for later conversion to electricity via heat exchangers. Which steps involve heat transfer? Which involve work done?

2. ♦ During World War II, German scientists developed the first rocket-powered airplane to be flown in combat, the *Messerschmitt 163 Komet*. The *Komet* was powered by the reaction of liquid hydrogen peroxide (H_2O_2) and hydrazine (N_2H_4) as follows:

$$2H_2O_2(l) + N_2H_4(l) \rightarrow N_2(g) + 4H_2O(g)$$

a. Determine the standard molar enthalpy of reaction.

b. What amount of work can be done by the reaction of 1.00 kg of hydrazine with a stoichiometric amount of hydrogen peroxide at 25°C at a constant pressure of 1.00 atm?

c. What is the change in internal energy under these conditions?

3. ♦ During the 1950s, pentaborane-9 was tested as a potential rocket fuel. However, the idea was abandoned when it was discovered that B_2O_3, the product of the reaction of pentaborane-9 with O_2, was an abrasive that destroyed rocket nozzles. The reaction is represented by the equation

$$2B_5H_9(l) + 12O_2(g) \rightarrow 5B_2O_3(s) + 9H_2O(g)$$

a. Determine the standard molar enthalpy of reaction.

b. How much work is done against a pressure of 1.0 atm when 50 lb of fuel are allowed to react with sufficient oxygen to cause the reaction to go to completion at 25°C?

c. What is ΔE for the reaction?

4. ♦ Polar explorers must be particularly careful to keep their clothes from becoming damp because the resulting heat loss could be fatal. If a polar explorer's clothes absorbed 1.0 kg of water and the clothes dried from the polar wind, what would be the heat loss [$\Delta H_{vap}(H_2O)$ = 44 kJ/mol]? How much glucose must be consumed to make up for this heat loss to prevent death [ΔH_{comb}(glucose) = −802 kJ/mol]?

5. Propane gas is generally preferred to kerosene as a fuel for stoves in the boating industry because kerosene stoves require more maintenance. Propane, however, is much more flammable than kerosene and imposes an added risk because it is denser than air and can collect in the bottom of a boat and ignite. The complete combustion of propane produces CO_2 gas and H_2O vapor and has a value of ΔH = −2044 kJ/mol at 25°C. What is ΔE?

6. The propane in Problem 5 can be produced from the hydrogenation of propene according to the following reaction: $C_3H_6(g) + H_2(g) \rightarrow C_3H_8(g)$; ΔH = −124 kJ/mol. Given that the reaction $H2(g)+12O2(g)\rightarrow H2O(g)$

7. has ΔH = −241.8 kJ/mol, what is the

a. standard enthalpy of combustion of propene?

b. value of Δ*E* for the combustion of propene?

8. ♦ The anaerobic conversion of sucrose, a sweetening agent, to lactic acid, which is associated with sour milk, can be described as follows:

$$C12H22O11 + H2Osucrose \rightarrow 4CH3CH(OH)CO2Hlactic\ acid$$

The combustion of sucrose, however, occurs as follows:

$C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l)$

a. Which reaction is thermodynamically more favorable—the anaerobic conversion of sucrose to lactic acid or the aerobic oxidation to CO_2 and H_2O? The values of ΔH_f are as follows: lactic acid, −694.1 kJ/mol; sucrose, −222 kJ/mol; CO_2, −393.5 kJ/mol; and H_2O, −285.8 kJ/mol.

b. What is Δ*E* for the combustion of 12.0 g of sucrose at normal body temperature (37°C)?

9. Phosphorus exists as several allotropes, the most common being red, black, and white phosphorus. White phosphorus consists of tetrahedral P_4 molecules and melts at 44.15°C; it is converted to red phosphorus by heating at 400°C for several hours. The chemical differences between red and white phosphorus are considerable: white phosphorus burns in air, whereas red phosphorus is stable; white phosphorus is soluble in organic compounds, whereas red phosphorus is not; white phosphorus melts at 44.15°C, whereas red phosphorus melts at 597°C. If the enthalpy of fusion of white phosphorus is 0.659 kJ/mol, what is its Δ*S*? Black phosphorus is even less reactive than red. Based on this information, which allotrope would you predict to have the highest entropy? the lowest? Why?

10. ♦ Ruby and sapphire have a common mineral name: corundum (Al_2O_3). Although they are crystalline versions of the same compound, the nature of the imperfections determines the identity of the gem. Outline a method for measuring and comparing the entropy of a ruby with the entropy of a sapphire. How would you expect the entropies to compare with the entropy of a perfect corundum crystal?

11. ♦ Tin has two crystalline forms—α and β—represented in the following equilibrium equation:

$$a\text{-}\ tingray \square\ 18°C b\text{-}\ tinwhite \square\ 232°CSn(l)$$

The earliest known tin artifacts were discovered in Egyptian tombs of the 18th dynasty (1580–1350 BC), although archaeologists are surprised that so few tin objects exist from earlier eras. It has been suggested that many early tin objects were either oxidized to a mixture of stannous and stannic oxides or transformed

to powdery, gray tin. Sketch a thermodynamic cycle similar to part (b) in Figure 18.15 "Two Forms of Elemental Sulfur and a Thermodynamic Cycle Showing the Transition from One to the Other" to show the conversion of liquid tin to gray tin. Then calculate the change in entropy that accompanies the conversion of Sn(l) to α-Sn using the following data: C_p(white) = 26.99,C_p(gray) = 25.77 J/(mol·K), ΔH_{fus} = 7.0 kJ/mol, $\Delta H_{\beta \rightarrow \alpha}$ = −2.2 kJ/mol.

12. The reaction of SO_2 with O_2 to produce SO_3 has great industrial significance because SO_3 is converted to H_2SO_4 by reaction with water. Unfortunately, the reaction is also environmentally important because SO_3 from industrial smokestacks is a primary source of acid rain. Δ*H* for the reaction of SO_2 with O_2 to form SO_3 is −23.49 kJ/mol, and Δ*S* is −22.66 J/(mol·K). Does this reaction occur spontaneously at 25°C? Does it occur spontaneously at 800°C assuming no change in Δ*H* and Δ*S*? Why is this reaction usually carried out at elevated temperatures?
13. Pollutants from industrial societies pose health risks to individuals from exposure to metals such as lead, mercury, and cadmium. The biological effects of a toxic metal may be reduced by removing it from the system using a chelating agent, which binds to the metal and forms a complex that is eliminated from the system without causing more damage. In designing a suitable chelating agent, one must be careful, however, because some chelating agents form metal complexes that are more toxic than the metal itself. Both methylamine (CH_3NH_2) and ethylenediamine ($H_2NCH_2CH_2NH_2$, abbreviated en) could, in principle, be used to treat heavy metal poisoning. In the case of cadmium, the reactions are as follows:

$$D_H D_H Cd2 + +2CH3NH2 \rightarrow Cd(CH3NH2)22 +$$
$$= -7.03\ kcal/mol,\ DS = -1.58\ cal/(mol \cdot K) Cd2 + +en\ DS = 3.15\ cal/(mol \cdot K)$$
$$\rightarrow Cd(en)2+ = -7.02\ kcal/mol,$$

Based strictly on thermodynamic arguments, which would you choose to administer to a patient suffering from cadmium toxicity? Why? Assume a body temperature of 37°C.

14. ♦ Explosive reactions often have a large negative enthalpy change and a large positive entropy change, but the reaction must also be kinetically favorable. For example, the following equation represents the reaction between hydrazine, a rocket propellant, and the oxidizer dinitrogen tetroxide:

$2N_2H_4(l) + N_2O_4(l) \rightarrow 4H_2O(g) + 3N_2(g)$ $\Delta H° = -249$ kJ/mol, $\Delta S° = 218$ J/(mol·K)

a. How much free energy is produced from this reaction at 25°C?
b. Is the reaction thermodynamically favorable?

c. What is *K*?

d. This reaction requires thermal ignition. Why?

15. ♦ Cesium, a silvery-white metal used in the manufacture of vacuum tubes, is produced industrially by the reaction of CsCl with CaC_2:

$2CsCl(l) + CaC_2(s) \rightarrow CaCl_2(l) + 2C(s) + 2Cs(g)$

Compare the free energy produced from this reaction at 25°C and at 1227°C, the temperature at which it is normally run, given these values: $\Delta H^\circ_{298\ K}$ = 32.0 kJ/m, $\Delta S^\circ_{298\ K} = 8.0\ J/(mol \cdot K)$; $\Delta H^\circ_{1500\ K} = -0.6\ kJ/mol$, $\Delta S^\circ_{1500\ K}$ = 3.6 J/(mol·K).

a. If you wanted to minimize energy costs in your production facility by reducing the temperature of the reaction, what is the lowest temperature at which products are favored over reactants (assuming the reaction is kinetically favorable at the lower temperature)? Assume Δ*H*° and Δ*S*° vary linearly with temperature.

b. What is the ratio $K_{1500\ K}/K_{298\ K}$?

16. Dessicants (drying agents) can often be regenerated by heating, although it is generally not economically worthwhile to do so. A dessicant that is commonly regenerated is $CaSO_4 \cdot 2H_2O$:

$CaSO4 \cdot 2H2O(s) \rightarrow CaSO4(s) + 2H2O(g)\ \Delta H^\circ_{298} = 25.1\ kJ/mol,\ \Delta S^\circ_{298} = 69.3\ J/(mol \cdot K)$

Regeneration is carried out at 250°C.

a. What is Δ*G*° for this reaction?

b. What is the equilibrium constant at 25°C?

c. What is the ratio $K_{250°C}/K_{25°C}$?

d. What is the equilibrium constant at 250°C?

e. Is regeneration of $CaSO_4(s) \cdot 2H_2O$ an enthalpy- or entropy-driven process? Explain your answer.

17. The nitrogen triiodide complex with ammonia ($NI_3 \cdot NH_3$) is a simple explosive that can be synthesized from common household products. When detonated, it produces N_2 and I_2. It can be painted on surfaces when wet, but it is shock sensitive when dry (even touching it with a feather can cause an explosion). Do you

expect ΔG for the explosion reaction to be positive or negative? Why doesn't $NI_3 \cdot NH_3$ explode spontaneously?

18. Adenosine triphosphate (ATP) contains high-energy phosphate bonds that are used in energy metabolism, coupling energy-yielding and energy-requiring processes. Cleaving a phosphate link by hydrolysis (ATP hydrolysis) can be described by the reaction $ATP + H2O \square ADP + Pi + H+, where$

19. P_i symbolizes phosphate. Glycerol and ATP react to form glycerol-3-phosphate, ADP, and H^+, with an overall $K = 6.61 \times 10^5$ at 37°C. The reaction of glycerol with phosphate to form glycerol-3-phosphate and water has an equilibrium constant of 2.82×10^{-2}. What is the equilibrium constant for ATP hydrolysis? How much free energy is released from the hydrolysis of ATP?

20. ♦ Consider the biological reduction of molecular nitrogen, for which the following is the minimal reaction stoichiometry under optimal conditions (P_i = phosphate):

$8H^+ + 8e^- + N_2 + 16ATP \rightarrow H_2 + 2NH_3 + 16ADP + 16P_i$

a. What is the approximate ratio of K_{eq} for this reaction and for the same reaction in the absence of ATP?

b. Given the fact that at pH 7 both the reaction of protons and electrons to give H_2 and the reaction of H_2 with N_2 to give ammonia are thermodynamically spontaneous (i.e., $K >> 1$), suggest a reason that nitrogen-fixing bacteria use such a large energy input to drive a reaction that is already spontaneous.

ANSWERS

1.

2.

3.

a. −4315 kJ/mol B_5H_9

b. 1340 kJ

c. -1.55×10^6 kJ per 50 lb of B_5H_9

4.

5. −2046 kJ/mol

6.

7.

a. aerobic conversion

b. −268 kJ

8.

9.

10.

11. Yes, the reaction is spontaneous at 25°C, but its rate is *very* slow. The reaction is not spontaneous at 800°C (ΔG = 0.82 kJ/mol), but the reaction rate is much greater.

12.

13.

a. −314 kJ/mol

b. yes

c. 2.10×10^{45}

d. Ignition is required to overcome the high activation energy to reaction.

14.

15.

a. 4.4 kJ/mol

b. 0.17

c. 78.3

d. 13

e. entropy-driven; $\Delta H° > 0$, so $\Delta S°$ must be positive for the reaction to be spontaneous.

16.

17. 2.34×10^{7}; −43.7 kJ/mol

Chapter 19

Electrochemistry

In oxidation–reduction (redox) reactions, electrons are transferred from one species (the reductant) to another (the oxidant). This transfer of electrons provides a means for converting chemical energy to electrical energy or vice versa.

The study of the relationship between electricity and chemical reactions is called electrochemistry, an area of chemistry we introduced in Chapter 4 "Reactions in Aqueous Solution" andChapter 5 "Energy Changes in Chemical Reactions". In this chapter, we describe electrochemical reactions in more depth and explore some of their applications.

In the first three sections, we review redox reactions; describe how they can be used to generate an electrical potential, or *voltage*; and discuss factors that affect the magnitude of the potential. We then explore the relationships among the electrical potential, the change in free energy, and the equilibrium constant for a redox reaction, which are all measures of the thermodynamic driving force for a reaction. Finally, we examine two kinds of applications of electrochemical principles: (1) those in which a spontaneous reaction is used to provide electricity and (2) those in which electrical energy is used to drive a thermodynamically nonspontaneous reaction. By the end of this chapter, you will understand why different kinds of batteries are used in cars, flashlights, cameras, and portable computers; how rechargeable batteries operate; and why corrosion occurs and how to slow—if not prevent—it. You will also discover how metal objects can be plated with silver or chromium for protection; how silver polish removes tarnish; and how to calculate the amount of electricity needed to produce aluminum, chlorine, copper, and sodium on an industrial scale.

19.1 Describing Electrochemical Cells

LEARNING OBJECTIVE

1. To distinguish between galvanic and electrolytic cells.

In any electrochemical process, electrons flow from one chemical substance to another, driven by an oxidation–reduction (redox) reaction. As we described in Chapter 3 "Chemical Reactions", a redox reaction occurs when electrons are transferred from a substance that is oxidized to one that is being reduced. The reductant is the substance that loses electrons and is oxidized in the process; the oxidant is the species that gains electrons and is reduced in the process. The associated potential energy is determined by the potential difference between the valence electrons in atoms of different elements. (For more information on valence electrons, see Chapter 7 "The Periodic Table and Periodic Trends", Section 7.3 "Energetics of Ion Formation".)

Because it is impossible to have a reduction without an oxidation and vice versa, a redox reaction can be described as two half-reactions, one representing the oxidation process and one the reduction process. For the reaction of zinc with bromine, the overall chemical reaction is as follows:

Equation 19.1

$$Zn(s) + Br_2(aq) \rightarrow Zn^{2+}(aq) + 2Br^-(aq)$$

The half-reactions are as follows:

Equation 19.2

$$\text{reduction half-reaction: } Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$$

Equation 19.3

$$\text{oxidation half-reaction: } Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

Each half-reaction is written to show what is actually occurring in the system; Zn is the reductant in this reaction (it loses electrons), and Br_2 is the oxidant (it gains electrons). Adding the two half-reactions gives the overall chemical reaction (Equation 19.1). A redox reaction is balanced when *the number of electrons lost by the reductant equals the number of electrons gained by the oxidant*. Like any balanced chemical equation, the overall process is electrically neutral; that is, the net charge is the same on both sides of the equation.

Note the Pattern

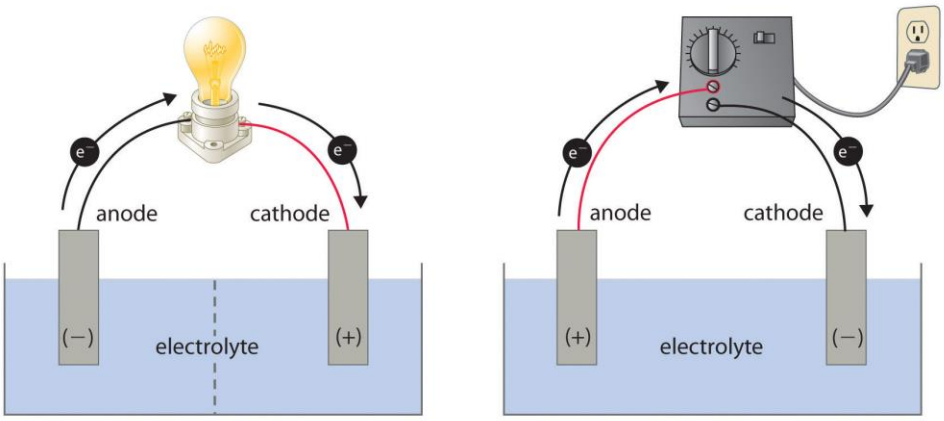
In any redox reaction, the number of electrons lost by the reductant equals the number of electrons gained by the oxidant.

In most of our discussions of chemical reactions, we have assumed that the reactants are in intimate physical contact with one another. Acid–base reactions, for example, are usually carried out with the acid and the base dispersed in a single phase, such as a liquid solution. With redox reactions, however, it is possible to physically separate the oxidation and reduction half-reactions in space, as long as there is a complete circuit, including an external electrical connection, such as a wire, between the two half-reactions. As the reaction progresses, the electrons flow from the reductant to the oxidant over this electrical connection, producing an electric current that can be used to do work. An apparatus that is used to generate electricity from a spontaneous redox reaction or, conversely, that uses electricity to drive a nonspontaneous redox reaction is called an electrochemical cell.

There are two types of electrochemical cells: galvanic cells and electrolytic cells. A galvanic (voltaic) cell [1] uses the energy released during a spontaneous redox reaction ($\Delta G < 0$) to *generate* electricity. This type of electrochemical cell is often called a *voltaic cell* after its inventor, the Italian physicist Alessandro Volta (1745–1827). In contrast, an electrolytic cell *consumes* electrical energy from an external source, using it to cause a nonspontaneous redox reaction to occur ($\Delta G > 0$). Both types contain two electrodes, which are solid metals connected to an external circuit that provides an electrical connection between the two parts of the system (Figure 19.1 "Electrochemical Cells"). The oxidation half-reaction occurs at one electrode (the anode), and the reduction half-reaction occurs at the other

(the cathode). When the circuit is closed, electrons flow from the anode to the cathode. The electrodes are also connected by an *electrolyte*, an ionic substance or solution that allows ions to transfer between the electrode compartments, thereby maintaining the system's electrical neutrality. In this section, we focus on reactions that occur in galvanic cells. We discuss electrolytic cells in Section 19.7 "Electrolysis".

Figure 19.1 *Electrochemical Cells*



A galvanic cell (left) transforms the energy released by a spontaneous redox reaction into electrical energy that can be used to perform work. The oxidative and reductive half-reactions usually occur in separate compartments that are connected by an external electrical circuit; in addition, a second connection that allows ions to flow between the compartments (shown here as a vertical dashed line to represent a porous barrier) is necessary to maintain electrical neutrality. The potential difference between the electrodes (voltage) causes electrons to flow from the reductant to the oxidant through the external circuit, generating an electric current. In an electrolytic cell (right), an external source of electrical energy is used to generate a potential difference between the electrodes that forces electrons to flow, driving a nonspontaneous redox reaction; only a single compartment is employed in most applications. In both kinds of electrochemical cells, the anode is the electrode at which the oxidation half-reaction occurs, and the cathode is the electrode at which the reduction half-reaction occurs.

Galvanic (Voltaic) Cells

To illustrate the basic principles of a galvanic cell, let's consider the reaction of metallic zinc with cupric ion (Cu^{2+}) to give copper metal and Zn^{2+} ion. The balanced chemical equation is as follows:

Equation 19.4

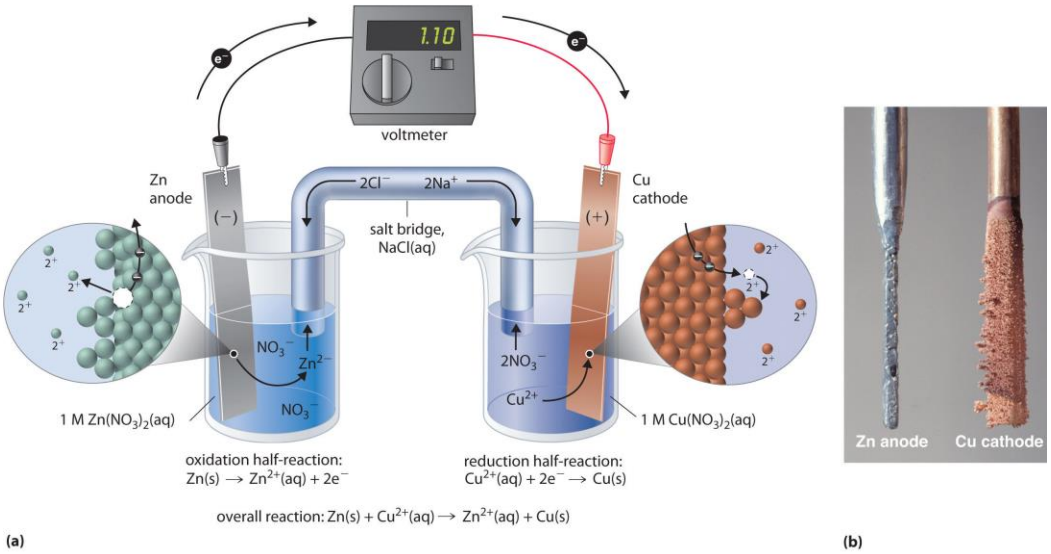
$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

We can cause this reaction to occur by inserting a zinc rod into an aqueous solution of copper(II) sulfate. As the reaction proceeds, the zinc rod dissolves, and a mass of metallic copper forms (Figure 19.2 "The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Single Compartment"). These changes occur spontaneously, but all the energy released is in the form of heat rather than in a form that can be used to do work.

Figure 19.2 The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Single Compartment

This same reaction can be carried out using the galvanic cell illustrated in part (a) inFigure 19.3 "The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Galvanic Cell". To assemble the cell, a copper strip is inserted into a beaker that contains a 1 M solution of Cu^{2+} ions, and a zinc strip is inserted into a different beaker that contains a 1 M solution of Zn^{2+} ions. The two metal strips, which serve as electrodes, are connected by a wire, and the compartments are connected by a salt bridge, a U-shaped tube inserted into both solutions that contains a concentrated liquid or gelled electrolyte. The ions in the salt bridge are selected so that they do not interfere with the electrochemical reaction by being oxidized or reduced themselves or by forming a precipitate or complex; commonly used cations and anions are Na^+ or K^+ and NO_3^- or SO_4^{2-}, respectively. (The ions in the salt bridge do *not* have to be the same as those in the redox couple in either compartment.) When the circuit is closed, a spontaneous reaction occurs: zinc metal is oxidized to Zn^{2+} ions at the zinc electrode (the anode), and Cu^{2+} ions are reduced to Cu metal at the copper electrode (the cathode). As the reaction progresses, the zinc strip dissolves, and the concentration of Zn^{2+} ions in the Zn^{2+} solution increases; simultaneously, the copper strip gains mass, and the concentration of Cu^{2+} ions in the Cu^{2+} solution decreases (part (b) in Figure 19.3 "The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Galvanic Cell"). Thus we have carried out the same reaction as we did using a single beaker, but this time the oxidative and reductive half-reactions are physically separated from each other. The electrons that are released at the anode flow through the wire, producing an electric current. Galvanic cells therefore transform chemical energy into electrical energy that can then be used to do work.

Figure 19.3 *The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Galvanic Cell*



(a) A galvanic cell can be constructed by inserting a copper strip into a beaker that contains an aqueous 1 M solution of Cu^{2+} ions and a zinc strip into a different beaker that contains an aqueous 1 M solution of Zn^{2+} ions. The two metal strips are connected by a wire that allows electricity to flow, and the beakers are connected by a salt bridge. When the switch is closed to complete the circuit, the zinc electrode (the anode) is spontaneously oxidized to Zn^{2+} ions in the left compartment, while Cu^{2+} ions are simultaneously reduced to copper metal at the copper electrode (the cathode). (b) As the reaction progresses, the Zn anode loses mass as it dissolves to give $Zn^{2+}(aq)$ ions, while the Cu cathode gains mass as $Cu^{2+}(aq)$ ions are reduced to copper metal that is deposited on the cathode.

The electrolyte in the salt bridge serves two purposes: it completes the circuit by carrying electrical charge and maintains electrical neutrality in both solutions by allowing ions to migrate between them. The identity of the salt in a salt bridge is unimportant, as long as the component ions do not react or undergo a redox reaction under the operating conditions of the cell. Without such a connection, the total positive charge in the Zn^{2+} solution would increase as the zinc metal dissolves, and the total positive charge in the Cu^{2+} solution would decrease. The salt bridge allows charges to be neutralized by a flow of anions into the Zn^{2+} solution and a flow of cations into the Cu^{2+} solution. In the absence of a salt bridge or some other similar connection, the reaction would rapidly cease because electrical neutrality could not be maintained.

A *voltmeter* can be used to measure the difference in electrical potential between the two compartments. Opening the switch that connects the wires to the anode and the cathode prevents a current from flowing, so no chemical reaction occurs. With the switch closed, however, the external circuit is closed, and an

electric current can flow from the anode to the cathode. The potential (E_{cell}) of the cell, measured in volts, is the difference in electrical potential between the two half-reactions and is related to the energy needed to move a charged particle in an electric field. In the cell we have described, the voltmeter indicates a potential of 1.10 V (part (a) in Figure 19.3 "The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Galvanic Cell"). Because electrons from the oxidation half-reaction are released at the anode, the anode in a galvanic cell is negatively charged. The cathode, which attracts electrons, is positively charged.

Not all electrodes undergo a chemical transformation during a redox reaction. The electrode can be made from an inert, highly conducting metal such as platinum to prevent it from reacting during a redox process, where it does not appear in the overall electrochemical reaction. This phenomenon is illustrated in Example 1.

Note the Pattern

A galvanic (voltaic) cell converts the energy released by a spontaneous chemical reaction to electrical energy. An electrolytic cell consumes electrical energy from an external source to drive a nonspontaneous chemical reaction.

EXAMPLE 1

A chemist has constructed a galvanic cell consisting of two beakers. One beaker contains a strip of tin immersed in aqueous sulfuric acid, and the other contains a platinum electrode immersed in aqueous nitric acid. The two solutions are connected by a salt bridge, and the electrodes are connected by a wire. Current begins to flow, and bubbles of a gas appear at the platinum electrode. The spontaneous redox reaction that occurs is described by the following balanced chemical equation:

$$3Sn(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Sn^{2+}(aq) + 2NO(g) + 4H_2O(l)$$

For this galvanic cell,

a. write the half-reaction that occurs at each electrode.
b. indicate which electrode is the cathode and which is the anode.
c. indicate which electrode is the positive electrode and which is the negative electrode.

Given: galvanic cell and redox reaction

Asked for: half-reactions, identity of anode and cathode, and electrode assignment as positive or negative

Strategy:

A Identify the oxidation half-reaction and the reduction half-reaction. Then identify the anode and cathode from the half-reaction that occurs at each electrode.

B From the direction of electron flow, assign each electrode as either positive or negative.

Solution:

a. **A** In the reduction half-reaction, nitrate is reduced to nitric oxide. (The nitric oxide would then react with oxygen in the air to form NO_2, with its characteristic red-brown color.) In the oxidation half-reaction, metallic tin is oxidized. The half-reactions corresponding to the actual reactions that occur in the system are as follows:

reduction: $NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$oxidation: $Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$

Thus nitrate is reduced to NO, while the tin electrode is oxidized to Sn^{2+}.

b. Because the reduction reaction occurs at the Pt electrode, it is the cathode. Conversely, the oxidation reaction occurs at the tin electrode, so it is the anode.

c. **B** Electrons flow from the tin electrode through the wire to the platinum electrode, where they transfer to nitrate. The electric circuit is completed by the salt bridge, which permits the diffusion of cations toward the cathode and anions toward the anode. Because electrons flow *from* the tin electrode, it must be electrically negative. In contrast, electrons flow *toward* the Pt electrode, so that electrode must be electrically positive.

Exercise

Consider a simple galvanic cell consisting of two beakers connected by a salt bridge. One beaker contains a solution of MnO_4^- in dilute sulfuric acid and has a Pt electrode. The other beaker contains a solution of Sn^{2+} in dilute sulfuric acid, also with a Pt electrode. When the two electrodes are connected by a wire, current flows and a spontaneous reaction occurs that is described by the following balanced chemical equation:

$2MnO_4^-(aq) + 5Sn^{2+}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5Sn^{4+}(aq) + 8H_2O(l)$

For this galvanic cell,

a. write the half-reaction that occurs at each electrode.

b. indicate which electrode is the cathode and which is the anode.

c. indicate which electrode is positive and which is negative.

Answer:

a. $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$; $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$

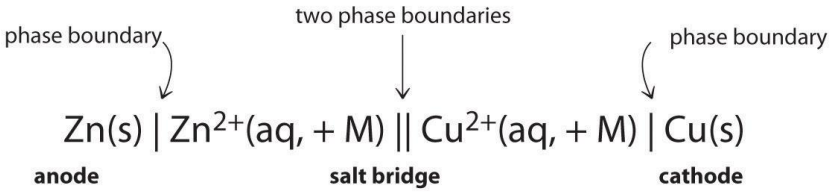
b. The Pt electrode in the permanganate solution is the cathode; the one in the tin solution is the anode.

c. The cathode (electrode in beaker that contains the permanganate solution) is positive, and the anode (electrode in beaker that contains the tin solution) is negative.

Constructing a Cell Diagram

Because it is somewhat cumbersome to describe any given galvanic cell in words, a more convenient notation has been developed. In this line notation, called a *cell diagram*, the identity of the electrodes and the chemical contents of the compartments are indicated by their chemical formulas, with the anode written on the far left and the cathode on the far right. Phase boundaries are shown by single vertical lines, and the salt bridge, which has two phase boundaries, by a double vertical line. Thus the cell diagram for the Zn/Cu cell shown in part (a) in Figure 19.3 "The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Galvanic Cell" is written as follows:

Figure 19.4



A cell diagram includes solution concentrations when they are provided.

Galvanic cells can have arrangements other than the examples we have seen so far. For example, the voltage produced by a redox reaction can be measured more accurately using two electrodes immersed in a single beaker containing an electrolyte that completes the circuit. This arrangement reduces errors caused by resistance to the flow of charge at a boundary, called the *junction potential*. One example of this type of galvanic cell is as follows:

Equation 19.5

$Pt(s)|\ H_2(g)|\ HCl(aq)|\ AgCl(s)|\ Ag(s)$

This cell diagram does not include a double vertical line representing a salt bridge because there is no salt bridge providing a junction between two dissimilar solutions. Moreover, solution concentrations have not

been specified, so they are not included in the cell diagram. The half-reactions and the overall reaction for this cell are as follows:

Equation 19.6
cathode reaction: $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$

Equation 19.7
$$anode\ reaction: 12H2(g) \rightarrow H+(aq)+e-$$

Equation 19.8
$$overall: AgCl(s) + 12H2(g) \rightarrow Ag(s)+Cl-(aq)+H+(aq)$$

A single-compartment galvanic cell will initially exhibit the same voltage as a galvanic cell constructed using separate compartments, but it will discharge rapidly because of the direct reaction of the reactant at the anode with the oxidized member of the cathodic redox couple. Consequently, cells of this type are not particularly useful for producing electricity.

EXAMPLE 2

Draw a cell diagram for the galvanic cell described in Example 1. The balanced chemical reaction is as follows:

$3Sn(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Sn^{2+}(aq) + 2NO(g) + 4H_2O(l)$

Given: galvanic cell and redox reaction

Asked for: cell diagram

Strategy:

Using the symbols described, write the cell diagram beginning with the oxidation half-reaction on the left.

Solution:

The anode is the tin strip, and the cathode is the Pt electrode. Beginning on the left with the anode, we indicate the phase boundary between the electrode and the tin solution by a vertical bar. The anode compartment is thus $Sn(s)|\ Sn^{2+}(aq)$. We could include $H_2SO_4(aq)$ with the contents of the anode compartment, but the sulfate ion (as HSO_4^-) does not participate in the overall reaction, so it does not need to be specifically indicated. The cathode compartment contains aqueous nitric acid, which does participate in the overall reaction, together with the product of the reaction (NO) and the Pt electrode. These are written as $HNO_3(aq)|\ NO(g)|\ Pt(s)$, with single vertical bars indicating the phase boundaries. Combining the two compartments and using a double vertical bar to indicate the salt bridge,

$Sn(s)|\ Sn^{2+}(aq)||\ HNO_3(aq)|\ NO(g)|\ Pt(s)$

The solution concentrations were not specified, so they are not included in this cell diagram.

Exercise

Draw a cell diagram for the following reaction, assuming the concentration of Ag^+ and Mg^{2+} are each 1 M:

$Mg(s) + 2Ag^+(aq) \rightarrow Mg^{2+}(aq) + 2Ag(s)$

Answer: $Mg(s)|\ Mg^{2+}(aq, 1\ M)\|\ Ag^+(aq, 1\ M)|\ Ag(s)$

Summary

Electrochemistry is the study of the relationship between electricity and chemical reactions. The oxidation–reduction reaction that occurs during an electrochemical process consists of two **half-reactions**, one representing the oxidation process and one the reduction process. The sum of the half-reactions gives the overall chemical reaction. The overall redox reaction is balanced when the number of electrons lost by the **reductant** equals the number of electrons gained by the **oxidant**. An electric current is produced from the flow of electrons from the reductant to the oxidant. An **electrochemical cell** can either generate electricity from a spontaneous redox reaction or consume electricity to drive a nonspontaneous reaction. In a **galvanic (voltaic) cell**, the energy from a spontaneous reaction generates electricity, whereas in an **electrolytic cell**, electrical energy is consumed to drive a nonspontaneous redox reaction. Both types of cells use two **electrodes** that provide an electrical connection between systems that are separated in space. The oxidative half-reaction occurs at the **anode**, and the reductive half-reaction occurs at the **cathode**. A **salt bridge** connects the separated solutions, allowing ions to migrate to either solution to ensure the system's electrical neutrality. A voltmeter is a device that measures the flow of electric current between two half-reactions. The **potential** of a cell, measured in volts, is the energy needed to move a charged particle in an electric field. An electrochemical cell can be described using line notation called a cell diagram, in which vertical lines indicate phase boundaries and the location of the salt bridge. Resistance to the flow of charge at a boundary is called the junction potential.

KEY TAKEAWAY

- A galvanic (voltaic) cell uses the energy released during a spontaneous redox reaction to generate electricity, whereas an electrolytic cell consumes electrical energy from an external source to force a reaction to occur.

CONCEPTUAL PROBLEMS

1. Is $2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$ an oxidation–reduction reaction? Why or why not?
2. If two half-reactions are physically separated, how is it possible for a redox reaction to occur? What is the name of the apparatus in which two half-reactions are carried out simultaneously?
3. What is the difference between a galvanic cell and an electrolytic cell? Which would you use to generate electricity?
4. What is the purpose of a salt bridge in a galvanic cell? Is it always necessary to use a salt bridge in a galvanic cell?
5. One criterion for a good salt bridge is that it contains ions that have similar rates of diffusion in aqueous solution, as K^+ and Cl^- ions do. What would happen if the diffusion rates of the anions and cations differed significantly?
6. It is often more accurate to measure the potential of a redox reaction by immersing two electrodes in a single beaker rather than in two beakers. Why?

ANSWER

1.
2.
3.
4.
5. A large difference in cation/anion diffusion rates would increase resistance in the salt bridge and limit electron flow through the circuit.
6.

NUMERICAL PROBLEMS

1. Copper(I) sulfate forms a bright blue solution in water. If a piece of zinc metal is placed in a beaker of aqueous $CuSO_4$ solution, the blue color fades with time, the zinc strip begins to erode, and a black solid forms around the zinc strip. What is happening? Write half-reactions to show the chemical changes that are occurring. What will happen if a piece of copper metal is placed in a colorless aqueous solution of $ZnCl_2$?
2. Consider the following spontaneous redox reaction: $NO_3^-(aq) + H^+(aq) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + HNO_2(aq)$.

a. Write the two half-reactions for this overall reaction.

b. If the reaction is carried out in a galvanic cell using an inert electrode in each compartment, which electrode corresponds to which half-reaction?

c. Which electrode is negatively charged, and which is positively charged?

3. The reaction $Pb(s) + 2VO^{2+}(aq) + 4H^{+}(aq) \rightarrow Pb^{2+}(aq) + 2V^{3+}(aq) + 2H_2O(l)$ occurs spontaneously.

a. Write the two half-reactions for this redox reaction.

b. If the reaction is carried out in a galvanic cell using an inert electrode in each compartment, which reaction occurs at the cathode and which occurs at the anode?

c. Which electrode is positively charged, and which is negatively charged?

4. Phenolphthalein is an indicator that turns pink under basic conditions. When an iron nail is placed in a gel that contains $[Fe(CN)_6]^{3-}$, the gel around the nail begins to turn pink. What is occurring? Write the half-reactions and then write the overall redox reaction.

5. Sulfate is reduced to HS^{-} in the presence of glucose, which is oxidized to bicarbonate. Write the two half-reactions corresponding to this process. What is the equation for the overall reaction?

6. Write the spontaneous half-reactions and the overall reaction for each proposed cell diagram. State which half-reaction occurs at the anode and which occurs at the cathode.

a. $Pb(s)|\ PbSO_4(s)|\ SO_4^{2-}(aq)\|\ Cu^{2+}(aq)|\ Cu(s)$

b. $Hg(l)|\ Hg_2Cl_2(s)|\ Cl^{-}(aq)\ \|\ Cd^{2+}(aq)|\ Cd(s)$

7. For each galvanic cell represented by these cell diagrams, determine the spontaneous half-reactions and the overall reaction. Indicate which reaction occurs at the anode and which occurs at the cathode.

a. $Zn(s)|\ Zn^{2+}(aq)\ \|\ H^{+}(aq)|\ H_2(g), Pt(s)$

b. $Ag(s)|\ AgCl(s)|\ Cl^{-}(aq)\ \|\ H^{+}(aq)|\ H_2(g)|\ Pt(s)$

c. $Pt(s)|\ H_2(g)|\ H^{+}(aq)\ \|\ Fe^{2+}(aq), Fe^{3+}(aq)|\ Pt(s)$

8. For each redox reaction, write the half-reactions and draw the cell diagram for a galvanic cell in which the overall reaction occurs spontaneously. Identify each electrode as either positive or negative.

a. $Ag(s) + Fe^{3+}(aq) \rightarrow Ag^{+}(aq) + Fe^{2+}(aq)$

b. $Fe^{3+}(aq) + 1/2H_2(g) \rightarrow Fe^{2+}(aq) + H^{+}(aq)$

9. Write the half-reactions for each overall reaction, decide whether the reaction will occur spontaneously, and construct a cell diagram for a galvanic cell in which a spontaneous reaction will occur.

a. $2Cl^{-}(aq) + Br_2(l) \rightarrow Cl_2(g) + 2Br^{-}(aq)$

b. $2NO_2(g) + 2OH^{-}(aq) \rightarrow NO_2^{-}(aq) + NO_3^{-}(aq) + H_2O(l)$

c. $2H_2O(l) + 2Cl^{-}(aq) \rightarrow H_2(g) + Cl_2(g) + 2OH^{-}(aq)$

d. $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$

10. Write the half-reactions for each overall reaction, decide whether the reaction will occur spontaneously, and construct a cell diagram for a galvanic cell in which a spontaneous reaction will occur.

a. $Co(s) + Fe^{2+}(aq) \rightarrow Co^{2+}(aq) + Fe(s)$

b. $O_2(g) + 4H^+(aq) + 4Fe^{2+}(aq) \rightarrow 2H_2O(l) + 4Fe^{3+}(aq)$

c. $6Hg^{2+}(aq) + 2NO_3^-(aq) + 8H^+ \rightarrow 3Hg_2^{2+}(aq) + 2NO(g) + 4H_2O(l)$

d. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

ANSWERS

1.

2.

3.

4.

5.

reduction: $SO_4^{2-}(aq) + 9H^+(aq) + 8e^- \rightarrow HS^-(aq) + 4H_2O(l)$oxidation: $C_6H_{12}O_6(aq) + 12H_2O(l) \rightarrow 6HCO_3^-(g) + 30H^+(aq) + 24e^-$overall: $C_6H_{12}O_6(aq) + 3SO_4^{2-}(aq) \rightarrow 6HCO_3^-(g) + 3H^+(aq) + 3HS^-(aq)$

6.

7.

a. reduction: $2H^+(aq) + 2e^- \rightarrow H_2(aq)$; cathode;

oxiation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$; anode;

verall: $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(aq)$

b. reduction: $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$; cathode;

oxidation: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$; anode;

overall: $AgCl(s) + H_2(g) \rightarrow 2H^+(aq) + Ag(s) + Cl^-(aq)$

c. reduction: $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$; cathode;

oxidation: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$; anode;

overall: $2Fe^{3+}(aq) + H_2(g) \rightarrow 2H^+(aq) + 2Fe^{2+}(aq)$

[1] Galvanic cells are named for the Italian physicist and physician Luigi Galvani (1737–1798), who observed that dissected frog leg muscles twitched when a small electric shock was applied, demonstrating the electrical nature of nerve impulses.

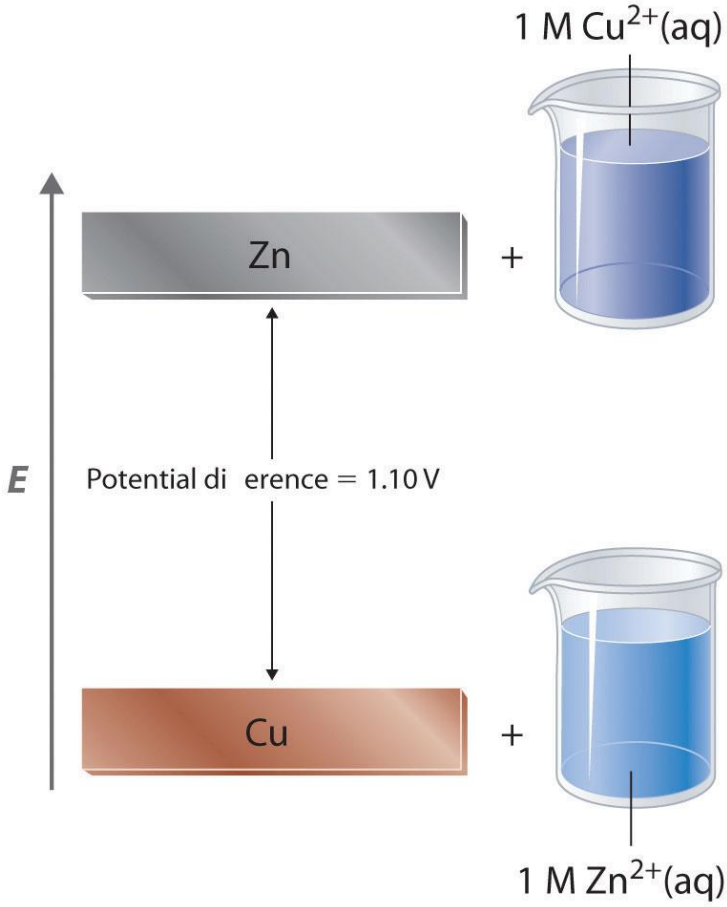
19.2 Standard Potentials

LEARNING OBJECTIVES

1. To use redox potentials to predict whether a reaction is spontaneous.
2. To balance redox reactions using half-reactions.

In a galvanic cell, current is produced when electrons flow externally through the circuit from the anode to the cathode because of a difference in potential energy between the two electrodes in the electrochemical cell. In the Zn/Cu system, the valence electrons in zinc have a substantially higher potential energy than the valence electrons in copper because of shielding of the *s* electrons of zinc by the electrons in filled *d*orbitals. (For more information on atomic orbitals, see Chapter 6 "The Structure of Atoms", Section 6.5 "Atomic Orbitals and Their Energies".) Hence electrons flow spontaneously from zinc to copper(II) ions, forming zinc(II) ions and metallic copper (Figure 19.5 "Potential Energy Difference in the Zn/Cu System"). Just like water flowing spontaneously downhill, which can be made to do work by forcing a waterwheel, the flow of electrons from a higher potential energy to a lower one can also be harnessed to perform work.

Figure 19.5 *Potential Energy Difference in the Zn/Cu System*



The potential energy of a system consisting of metallic Zn and aqueous Cu^{2+} ions is greater than the potential energy of a system consisting of metallic Cu and aqueous Zn^{2+} ions. Much of this potential energy difference is because the valence electrons of metallic Zn are higher in energy than the valence electrons of metallic Cu. Because the Zn(s) + Cu^{2+}(aq) system is higher in energy by 1.10 V than the Cu(s) + Zn^{2+}(aq) system, energy is released when electrons are transferred from Zn to Cu^{2+} to form Cu and Zn^{2+}.

Because the potential energy of valence electrons differs greatly from one substance to another, the voltage of a galvanic cell depends partly on the identity of the reacting substances. If we construct a galvanic cell similar to the one in part (a) in Figure 19.3 "The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Galvanic Cell" but instead of copper use a strip of cobalt metal and 1 M Co^{2+} in the cathode compartment, the measured voltage is not 1.10 V but 0.51 V. Thus we can conclude that the difference in potential energy between the valence electrons of cobalt and zinc is less than the difference between the valence electrons of copper and zinc by 0.59 V.

The measured potential of a cell also depends strongly on the *concentrations* of the reacting species and the *temperature* of the system. To develop a scale of relative potentials that will allow us to predict the direction of

an electrochemical reaction and the magnitude of the driving force for the reaction, the potentials for oxidations and reductions of different substances must be measured under comparable conditions. To do this, chemists use the standard cell potential ($E°_{cell}$), defined as the potential of a cell measured under standard conditions—that is, with all species in their standard states (1 M for solutions, [1] 1 atm for gases, pure solids or pure liquids for other substances) and at a fixed temperature, usually 25°C.

Note the Pattern

Measured redox potentials depend on the potential energy of valence electrons, the concentrations of the species in the reaction, and the temperature of the system.

Measuring Standard Electrode Potentials

It is physically impossible to measure the potential of a single electrode: only the*difference* between the potentials of two electrodes can be measured. (This is analogous to measuring absolute enthalpies or free energies. Recall from Chapter 18 "Chemical Thermodynamics" that only *differences* in enthalpy and free energy can be measured.) We can, however, compare the standard cell potentials for two different galvanic cells that have one kind of electrode in common. This allows us to measure the potential difference between two dissimilar electrodes. For example, the measured standard cell potential ($E°$) for the Zn/Cu system is 1.10 V, whereas $E°$ for the corresponding Zn/Co system is 0.51 V. This implies that the potential difference between the Co and Cu electrodes is 1.10 V − 0.51 V = 0.59 V. In fact, that is exactly the potential measured under standard conditions if a cell is constructed with the following cell diagram:

Equation 19.9

$$Co(s) \mid Co2+(aq, 1\ M) \| Cu2+(aq, 1\ M) \mid Cu\ (s) \quad E° = 0.59\ V$$

This cell diagram corresponds to the oxidation of a cobalt anode and the reduction of Cu^{2+} in solution at the copper cathode.

All tabulated values of *standard electrode potentials* by convention are listed for a reaction written as a reduction, not as an oxidation, to be able to compare standard potentials for different substances. (Standard electrode potentials for various reduction reactions are given in Chapter 29 "Appendix E: Standard Reduction Potentials at 25°C".) The standard cell potential ($E°_{cell}$) is therefore the *difference* between the tabulated reduction potentials of the two half-reactions, not their sum:

Equation 19.10

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

In contrast, recall that half-reactions are written to show the reduction and oxidation reactions that actually occur in the cell, so the overall cell reaction is written as the *sum*of the two half-reactions. According to Equation 19.10, when we know the standard potential for any single half-reaction, we can obtain the value of the standard potential of many other half-reactions by measuring the standard potential of the corresponding cell.

Note the Pattern

The overall cell reaction is the sum of the two half-reactions, but the cell potential is the difference between the reduction potentials: $E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$.

Although it is impossible to measure the potential of any electrode directly, we can choose a reference electrode whose potential is defined as 0 V under standard conditions.

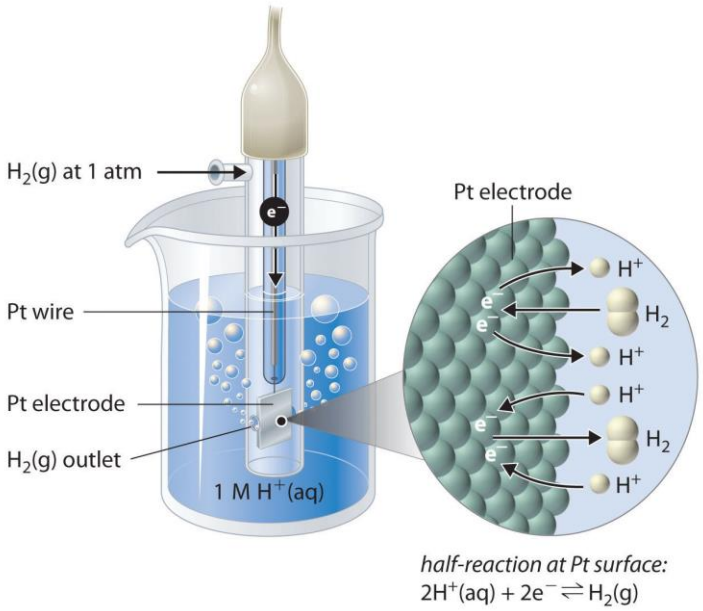
The standard hydrogen electrode (SHE) is universally used for this purpose and is assigned a standard potential of 0 V. It consists of a strip of platinum wire in contact with an aqueous solution containing 1 M H^+. The $[H^+]$ in solution is in equilibrium with H_2 gas at a pressure of 1 atm at the Pt-solution interface (Figure 19.6 "The Standard Hydrogen Electrode"). Protons are reduced or hydrogen molecules are oxidized at the Pt surface according to the following equation:

Equation 19.11

$$2H+(aq)+2e- \square H2(g)$$

One especially attractive feature of the SHE is that the Pt metal electrode is not consumed during the reaction.

Figure 19.6 The Standard Hydrogen Electrode



The SHE consists of platinum wire that is connected to a Pt surface in contact with an aqueous solution containing 1 M H^+ in equilibrium with H_2 gas at a pressure of 1 atm. In the molecular view, the Pt surface catalyzes the oxidation of hydrogen molecules to protons or the reduction of protons to hydrogen gas. (Water is omitted for clarity.) The standard potential of the SHE is arbitrarily assigned a value of 0 V.

Figure 19.7 "Determining a Standard Electrode Potential Using a Standard Hydrogen Electrode" shows a galvanic cell that consists of a SHE in one beaker and a Zn strip in another beaker containing a solution of Zn^{2+} ions. When the circuit is closed, the voltmeter indicates a potential of 0.76 V. The zinc electrode begins to dissolve to form Zn^{2+}, and H^+ ions are reduced to H_2 in the other compartment. Thus the hydrogen electrode is the cathode, and the zinc electrode is the anode. The diagram for this galvanic cell is as follows:

Equation 19.12

$$Zn(s)|\ Zn^{2+}(aq)\|\ H^+(aq,\ 1\ M)|\ H_2(g,\ 1\ atm)|\ Pt(s)$$

The half-reactions that actually occur in the cell and their corresponding electrode potentials are as follows:

Equation 19.13

$$cathode: 2H+(aq)+2e- \rightarrow H2(g) \quad E^\circ cathode = 0\ V$$

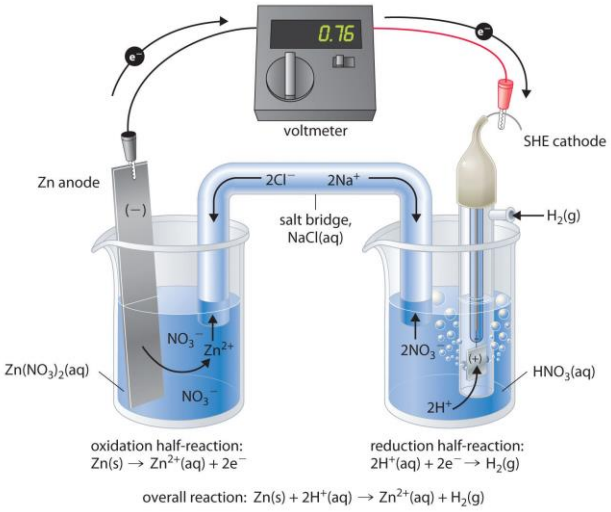
Equation 19.14

$$anode: Zn(s) \rightarrow Zn2+(aq)+2e- \quad E^\circ anode = -0.76\ V$$

Equation 19.15

$$overall: Zn(s) + 2H + (aq) \rightarrow Zn2 + (aq) + H2(g) \qquad E\,\square cell = E\,\square cathode - E\,\square anode = 0.76\ V$$

Figure 19.7 Determining a Standard Electrode Potential Using a Standard Hydrogen Electrode



The voltmeter shows that the standard cell potential of a galvanic cell consisting of a SHE and a Zn/Zn^{2+} couple is $E°_{cell} = 0.76$ V. Because the zinc electrode in this cell dissolves spontaneously to form $Zn^{2+}(aq)$ ions while $H^{+}(aq)$ ions are reduced to H_2 at the platinum surface, the standard electrode potential of the Zn^{2+}/Zn couple is −0.76 V.

Although the reaction at the anode is an oxidation, by convention its tabulated $E°$ value is reported as a *reduction* potential. The potential of a half-reaction measured against the SHE under standard conditions is called the standard electrode potential for that half-reaction.In this example, the standard reduction potential for $Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$ is −0.76 V, which means that the standard electrode potential for the reaction that occurs at the anode, the *oxidation* of Zn to Zn^{2+}, often called the Zn/Zn^{2+} *redox couple*, or the Zn/Zn^{2+} *couple*, is −(−0.76 V) = 0.76 V. We must therefore subtract $E°_{anode}$ from $E°_{cathode}$ to obtain $E°_{cell}$: 0 − (−0.76 V) = 0.76 V.

Because electrical potential is the energy needed to move a charged particle in an electric field, standard electrode potentials for half-reactions are intensive properties and do not depend on the amount of substance involved. Consequently, *$E°$ values are independent of the stoichiometric coefficients for the half-reaction*, and, most important, the coefficients used to produce a balanced overall reaction do not affect the value of the cell potential.

Note the Pattern

$E°$ values do not depend on the stoichiometric coefficients for a half-reaction.

To measure the potential of the Cu/Cu^{2+} couple, we can construct a galvanic cell analogous to the one shown in Figure 19.7 "Determining a Standard Electrode Potential Using a Standard Hydrogen Electrode" but containing a Cu/Cu^{2+} couple in the sample compartment instead of Zn/Zn^{2+}. When we close the circuit this time, the measured potential for the cell is negative (−0.34 V) rather than positive. The negative value of $E°_{cell}$ indicates that the direction of spontaneous electron flow is the opposite of that for the Zn/Zn^{2+} couple. Hence the reactions that occur spontaneously, indicated by a positive $E°_{cell}$, are the reduction of Cu^{2+} to Cu at the copper electrode. The copper electrode gains mass as the reaction proceeds, and H_2 is oxidized to H^+ at the platinum electrode. In this cell, the copper strip is the *cathode*, and the hydrogen electrode is the*anode*. The cell diagram therefore is written with the SHE on the left and the Cu^{2+}/Cu couple on the right:

Equation 19.16

$$Pt(s)|\ H_2(g,\ 1\ atm)|\ H^+(aq,\ 1\ M)\|\ Cu^{2+}(aq,\ 1\ M)|\ Cu(s)$$

The half-cell reactions and potentials of the spontaneous reaction are as follows:

Equation 19.17

$$Cathode: Cu2+(aq)+2e- \rightarrow Cu(g)\ E°cathode = 0.34\ V$$

Equation 19.18

$$Anode: H2(g) \rightarrow 2H+(aq)+2e-\ E°anode = 0\ V$$

Equation 19.19

$$Overall: H2(g)+Cu2+(aq) \rightarrow 2H+(aq)+Cu(s)\ E°cell$$
$$= E°cathode - E°anode = 0.34\ V$$

Thus the standard electrode potential for the Cu^{2+}/Cu couple is 0.34 V.

Balancing Redox Reactions Using the Half-Reaction Method

In Chapter 4 "Reactions in Aqueous Solution", we described a method for balancing redox reactions using oxidation numbers. Oxidation numbers were assigned to each atom in a redox reaction to identify any changes in the oxidation states. Here we present an alternative approach to balancing redox reactions, the half-reaction method, in which the overall redox reaction is divided into an oxidation half-reaction and a reduction half-reaction, each balanced for mass and charge. This method more closely reflects the events that take place in an electrochemical cell, where the two half-reactions may be physically separated from each other.

We can illustrate how to balance a redox reaction using half-reactions with the reaction that occurs when Drano, a commercial solid drain cleaner, is poured into a clogged drain. Drano contains a mixture of sodium hydroxide and powdered aluminum, which in solution reacts to produce hydrogen gas:

Equation 19.20
$Al(s) + OH^-(aq) \rightarrow Al(OH)_4^-(aq) + H_2(g)$

In this reaction, Al(s) is oxidized to Al^{3+}, and H^+ in water is reduced to H_2 gas, which bubbles through the solution, agitating it and breaking up the clogs.

The overall redox reaction is composed of a reduction half-reaction and an oxidation half-reaction. From the standard electrode potentials listed in Chapter 29 "Appendix E: Standard Reduction Potentials at 25°C", we find the corresponding half-reactions that describe the reduction of H^+ ions in water to H_2 and the oxidation of Al to Al^{3+} in basic solution:

Equation 19.21
reduction: $2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$

Equation 19.22
oxidation: $Al(s) + 4OH^-(aq) \rightarrow Al(OH)_4^-(aq) + 3e^-$

The half-reactions chosen must exactly reflect the reaction conditions, such as the basic conditions shown here. Moreover, the physical states of the reactants and the products must be identical to those given in the overall reaction, whether gaseous, liquid, solid, or in solution.

In Equation 19.21, two H^+ ions gain one electron each in the reduction; in Equation 19.22, the aluminum atom loses three electrons in the oxidation. The charges are balanced by multiplying the reduction half-reaction (Equation 19.21) by 3 and the oxidation half-reaction (Equation 19.22) by 2 to give the same number of electrons in both half-reactions:

Equation 19.23
reduction: $6H_2O(l) + 6e^- \rightarrow 6OH^-(aq) + 3H_2(g)$

Equation 19.24
oxidation: $2Al(s) + 8OH^-(aq) \rightarrow 2Al(OH)_4^-(aq) + 6e^-$

Adding the two half-reactions,

Equation 19.25
$6H_2O(l) + 2Al(s) + 8OH^-(aq) \rightarrow 2Al(OH)_4^-(aq) + 3H_2(g) + 6OH^-(aq)$

Simplifying by canceling substances that appear on both sides of the equation,

Equation 19.26

$6H_2O(l) + 2Al(s) + 2OH^-(aq) \rightarrow 2Al(OH)_4^-(aq) + 3H_2(g)$

We have a −2 charge on the left side of the equation and a −2 charge on the right side. Thus the charges are balanced, but we must also check that atoms are balanced:

Equation 19.27
2Al + 8O + 14H = 2Al + 8O + 14H

The atoms also balance, so Equation 19.26 is a balanced chemical equation for the redox reaction depicted in Equation 19.20.

Note the Pattern

The half-reaction method requires that half-reactions exactly reflect reaction conditions, and the physical states of the reactants and the products must be identical to those in the overall reaction.

We can also balance a redox reaction by first balancing the atoms in each half-reaction and then balancing the charges. With this alternative method, we do not need to use the half-reactions listed in Chapter 29 "Appendix E: Standard Reduction Potentials at 25°C" but instead focus on the atoms whose oxidation states change, as illustrated in the following steps:

Step 1: Write the reduction half-reaction and the oxidation half-reaction.

For the reaction shown in Equation 19.20, hydrogen is reduced from H^+ in OH^- to H_2, and aluminum is oxidized from Al^0 to Al^{3+}:

Equation 19.28
reduction: $OH^-(aq) \rightarrow H_2(g)$

Equation 19.29
oxidation: $Al(s) \rightarrow Al(OH)_4^-(aq)$

Step 2: Balance the atoms by balancing elements other than O and H. Then balance O atoms by adding H_2O and balance H atoms by adding H^+.

Elements other than O and H in the previous two equations are balanced as written, so we proceed with balancing the O atoms. We can do this by adding water to the appropriate side of each half-reaction:

Equation 19.30
reduction: $OH^-(aq) \rightarrow H_2(g) + H_2O(l)$

Equation 19.31
oxidation: $Al(s) + 4H_2O(l) \rightarrow Al(OH)_4^-(aq)$

Balancing H atoms by adding H^+, we obtain the following:

Equation 19.32
reduction: $OH^-(aq) + 3H^+(aq) \rightarrow H_2(g) + H_2O(l)$

Equation 19.33

oxidation: $Al(s) + 4H_2O(l) \rightarrow Al(OH)_4^-(aq) + 4H^+(aq)$

We have now balanced the atoms in each half-reaction, but the charges are not balanced.

Step 3: Balance the charges in each half-reaction by adding electrons.

Two electrons are gained in the reduction of H^+ ions to H_2, and three electrons are lost during the oxidation of Al^0 to Al^{3+}:

Equation 19.34

reduction: $OH^-(aq) + 3H^+(aq) + 2e^- \rightarrow H_2(g) + H_2O(l)$

Equation 19.35

oxidation: $Al(s) + 4H_2O(l) \rightarrow Al(OH)_4^-(aq) + 4H^+(aq) + 3e^-$

Step 4: Multiply the reductive and oxidative half-reactions by appropriate integers to obtain the same number of electrons in both half-reactions.

In this case, we multiply Equation 19.34 (the reductive half-reaction) by 3 and Equation 19.35 (the oxidative half-reaction) by 2 to obtain the same number of electrons in both half-reactions:

Equation 19.36

reduction: $3OH^-(aq) + 9H^+(aq) + 6e^- \rightarrow 3H_2(g) + 3H_2O(l)$

Equation 19.37

oxidation: $2Al(s) + 8H_2O(l) \rightarrow 2Al(OH)_4^-(aq) + 8H^+(aq) + 6e^-$

Step 5: Add the two half-reactions and cancel substances that appear on both sides of the equation.

Adding and, in this case, canceling $8H^+$, $3H_2O$, and $6e^-$,

Equation 19.38

$2Al(s) + 5H_2O(l) + 3OH^-(aq) + H^+(aq) \rightarrow 2Al(OH)_4^-(aq) + 3H_2(g)$

We have three OH^- and one H^+ on the left side. Neutralizing the H^+ gives us a total of $5H_2O + H_2O = 6H_2O$ and leaves $2OH^-$ on the left side:

Equation 19.39

$2Al(s) + 6H_2O(l) + 2OH^-(aq) \rightarrow 2Al(OH)_4^-(aq) + 3H_2(g)$

Step 6: Check to make sure that all atoms and charges are balanced.

Equation 19.39 is identical to Equation 19.26, obtained using the first method, so the charges and numbers of atoms on each side of the equation balance.

EXAMPLE 3

In acidic solution, the redox reaction of dichromate ion ($Cr_2O_7^{2-}$) and iodide (I^-) can be monitored visually. The yellow dichromate solution reacts with the colorless iodide solution to produce a solution that is deep amber due to the presence of a green $Cr^{3+}(aq)$ complex and brown $I_2(aq)$ ions (Figure 19.8 "The Reaction of Dichromate with Iodide"):

$$Cr_2O_7^{2-}(aq) + I^-(aq) \rightarrow Cr^{3+}(aq) + I_2(aq)$$

Balance this equation using half-reactions.

Given: redox reaction and Chapter 29 "Appendix E: Standard Reduction Potentials at 25°C"

Asked for: balanced chemical equation using half-reactions

Strategy:

Follow the steps to balance the redox reaction using the half-reaction method.

Solution:

From the standard electrode potentials listed in Chapter 29 "Appendix E: Standard Reduction Potentials at 25°C", we find the half-reactions corresponding to the overall reaction:

reduction: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$oxidation: $2I^-(aq) \rightarrow I_2(aq) + 2e^-$

Balancing the number of electrons by multiplying the oxidation reaction by 3,

oxidation: $6I^-(aq) \rightarrow 3I_2(aq) + 6e^-$

Adding the two half-reactions and canceling electrons,

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6I^-(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3I_2(aq)$$

We must now check to make sure the charges and atoms on each side of the equation balance:

$$(-2) + 14 + (-6) + 62Cr + 7O + 14H + 6I$$
$$= +6 = +6 = 2Cr + 7O + 14H + 6I$$

The charges and atoms balance, so our equation is balanced.

We can also use the alternative procedure, which does not require the half-reactions listed in Chapter 29 "Appendix E: Standard Reduction Potentials at 25°C".

Step 1: Chromium is reduced from Cr^{6+} in $Cr_2O_7^{2-}$to Cr^{3+}, and I^- ions are oxidized to I_2. Dividing the reaction into two half-reactions,

reduction: $Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$oxidation: $I^-(aq) \rightarrow I_2(aq)$

Step 2: Balancing the atoms other than oxygen and hydrogen,

reduction: $Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$oxidation: $2I^-(aq) \rightarrow I_2(aq)$

We now balance the O atoms by adding H_2O—in this case, to the right side of the reduction half-reaction.

Because the oxidation half-reaction does not contain oxygen, it can be ignored in this step.

reduction: $Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

Next we balance the H atoms by adding H^+ to the left side of the reduction half-reaction. Again, we can ignore the oxidation half-reaction.

reduction: $Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow + 2Cr^{3+}(aq) + 7H_2O(l)$

Step 3: We must now add electrons to balance the charges. The reduction half-reaction ($2Cr^{+6}$ to $2Cr^{+3}$) has a +12 charge on the left and a +6 charge on the right, so six electrons are needed to balance the charge. The oxidation half-reaction ($2I^-$ to I_2) has a −2 charge on the left side and a 0 charge on the right, so it needs two electrons to balance the charge:

reduction: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$oxidation: $2I^-(aq) \rightarrow I_2(aq) + 2e^-$

Step 4: To have the same number of electrons in both half-reactions, we must multiply the oxidation half-reaction by 3:

oxidation: $6I^-(aq) \rightarrow 3I_2(s) + 6e^-$

Step 5: Adding the two half-reactions and canceling substances that appear in both reactions,

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6I^-(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3I_2(aq)$

Step 6: This is the same equation we obtained using the first method. Thus the charges and atoms on each side of the equation balance.

Exercise

Copper is commonly found as the mineral covellite (CuS). The first step in extracting the copper is to dissolve the mineral in nitric acid (HNO_3), which oxidizes sulfide to sulfate and reduces nitric acid to NO:

$CuS(s) + HNO_3(aq) \rightarrow NO(g) + CuSO_4(aq)$

Balance this equation using the half-reaction method.

Answer: $3CuS(s) + 8HNO_3(aq) \rightarrow 8NO(g) + 3CuSO_4(aq) + 4H_2O(l)$

Calculating Standard Cell Potentials

The standard cell potential for a redox reaction ($E°_{cell}$) is a measure of the tendency of reactants in their standard states to form products in their standard states; consequently, it is a measure of the driving force for the reaction, which earlier we called *voltage*. We can use the two standard electrode potentials we found earlier to calculate the standard potential for the Zn/Cu cell represented by the following cell diagram:

Equation 19.40

$Zn(s)|\ Zn^{2+}(aq,\ 1\ M)\|\ Cu^{2+}(aq,\ 1\ M)|\ Cu(s)$

We know the values of $E°_{anode}$ for the reduction of Zn^{2+} and $E°_{cathode}$ for the reduction of Cu^{2+}, so we can calculate $E°_{cell}$:

Equation 19.41

$$cathode: Cu2+(aq)+2e- \rightarrow Cu(s) \quad E°cathode = 0.34\ V$$

Equation 19.42

$$anode: Zn(s) \rightarrow Zn2+(aq,\ 1\ M)+2e- \quad E°anode = -0.76\ V$$

Equation 19.43

$$overall: Zn(s)+Cu2+(aq) \rightarrow Zn2+(aq)+Cu(s)$$

$$E°cell = E°cathode - E°anode = 1.10\ V$$

This is the same value that is observed experimentally. If the value of $E°_{cell}$ is positive, the reaction will occur spontaneously as written. If the value of $E°_{cell}$ is negative, then the reaction is not spontaneous, and it will not occur as written under standard conditions; it will, however, proceed spontaneously in the opposite direction.[2] Example 4 and its corresponding exercise illustrate how we can use measured cell potentials to calculate standard potentials for redox couples.

Note the Pattern

A positive $E°_{cell}$ means that the reaction will occur spontaneously as written. A negative $E°_{cell}$ means that the reaction will proceed spontaneously in the opposite direction.

EXAMPLE 4

A galvanic cell with a measured standard cell potential of 0.27 V is constructed using two beakers connected by a salt bridge. One beaker contains a strip of gallium metal immersed in a 1 M solution of $GaCl_3$, and the other contains a piece of nickel immersed in a 1 M solution of $NiCl_2$. The half-reactions that occur when the compartments are connected are as follows:

cathode: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$anode: $Ga(s) \rightarrow Ga^{3+}(aq) + 3e^-$

If the potential for the oxidation of Ga to Ga^{3+} is 0.55 V under standard conditions, what is the potential for the oxidation of Ni to Ni^{2+}?

Given: galvanic cell, half-reactions, standard cell potential, and potential for the oxidation half-reaction under standard conditions

Asked for: standard electrode potential of reaction occurring at the cathode

Strategy:

A Write the equation for the half-reaction that occurs at the anode along with the value of the standard electrode potential for the half-reaction.

B Use Equation 19.10 to calculate the standard electrode potential for the half-reaction that occurs at the cathode. Then reverse the sign to obtain the potential for the corresponding oxidation half-reaction under standard conditions.

Solution:

A We have been given the potential for the oxidation of Ga to Ga^{3+} under standard conditions, but to report the standard electrode potential, we must reverse the sign. For the reduction reaction $Ga^{3+}(aq) + 3e^- \rightarrow Ga(s)$, $E°_{anode} = -0.55$ V.

B Using the value given for $E°_{cell}$ and the calculated value of $E°_{anode}$, we can calculate the standard potential for the reduction of Ni^{2+} to Ni from Equation 19.10:

$$E\square cell 0.27\ VE\square cathode$$
$$= E\square cathode - E\square anode$$
$$= E\square cathode - (-0.55\ V) = -0.28\ V$$

This is the standard electrode potential for the reaction $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$. Because we are asked for the potential for the *oxidation* of Ni to Ni^{2+} under standard conditions, we must reverse the sign of $E°_{cathode}$. Thus $E° = -(-0.28\ V) = 0.28$ V for the oxidation. With three electrons consumed in the reduction and two produced in the oxidation, the overall reaction is not balanced. Recall, however, that standard potentials are *independent* of stoichiometry.

Exercise

A galvanic cell is constructed with one compartment that contains a mercury electrode immersed in a 1 M aqueous solution of mercuric acetate [$Hg(CH_3CO_2)_2$] and one compartment that contains a strip of magnesium immersed in a 1 M aqueous solution of $MgCl_2$. When the compartments are connected, a potential of 3.22 V is measured and the following half-reactions occur:

cathode: $Hg^{2+}(aq) + 2e^- \rightarrow Hg(l)$anode: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

If the potential for the oxidation of Mg to Mg^{2+} is 2.37 V under standard conditions, what is the standard electrode potential for the reaction that occurs at the anode?

Answer: 0.85 V

Reference Electrodes and Measuring Concentrations

When using a galvanic cell to measure the concentration of a substance, we are generally interested in the potential of only one of the electrodes of the cell, the so-called indicator electrode, whose potential is related to the concentration of the substance being measured. To ensure that any change in the measured potential of the cell is due to only the substance being analyzed, the potential of the other electrode, thereference electrode, must be constant. You are already familiar with one example of a reference electrode: the SHE. The potential of a reference electrode must be unaffected by the properties of the solution, and if possible, it should be physically isolated from the solution of interest. To measure the potential of a solution, we select a reference electrode and an appropriate indicator electrode. Whether reduction or oxidation of the substance being analyzed occurs depends on the potential of the half-reaction for the substance of interest (the sample) and the potential of the reference electrode.

Note the Pattern

The potential of any reference electrode should not be affected by the properties of the solution to be analyzed, and it should also be physically isolated.

There are many possible choices of reference electrode other than the SHE. The SHE requires a constant flow of highly flammable hydrogen gas, which makes it inconvenient to use. Consequently, two other electrodes are commonly chosen as reference electrodes. One is the silver–silver chloride electrode, which consists of a silver wire coated with a very thin layer of AgCl that is dipped into a chloride ion solution with a fixed concentration. The cell diagram and reduction half-reaction are as follows:

Equation 19.44

$$Cl-(aq)\,|\,AgCl(s)\,|\,Ag(s)\;AgCl(s)+e-\rightarrow Ag(s)+Cl-(aq)$$

If a saturated solution of KCl is used as the chloride solution, the potential of the silver–silver chloride electrode is 0.197 V versus the SHE. That is, 0.197 V must be subtracted from the measured value to obtain the standard electrode potential measured against the SHE.

A second common reference electrode is the saturated calomel electrode (SCE), which has the same general form as the silver–silver chloride electrode. The SCE consists of a platinum wire inserted into a moist paste of liquid mercury (Hg_2Cl_2; called*calomel* in the old chemical literature) and KCl. This interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution (part (a) in Figure 19.9 "Three Common Types of Electrodes"). Although it sounds and

looks complex, this cell is actually easy to prepare and maintain, and its potential is highly reproducible.

The SCE cell diagram and corresponding half-reaction are as follows:

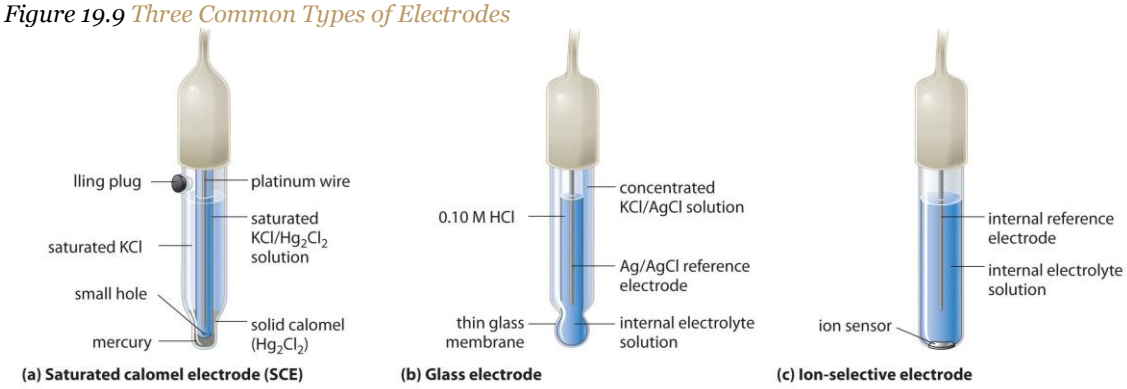
Equation 19.45

$Pt(s)|\ Hg_2Cl_2(s)|\ KCl(aq, sat)$

Equation 19.46

$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq)$

Figure 19.9 *Three Common Types of Electrodes*



(a) The SCE is a reference electrode that consists of a platinum wire inserted into a moist paste of liquid mercury (calomel; Hg_2Cl_2) and KCl. The interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution. (b) In a glass electrode, an internal Ag/AgCl electrode is immersed in a 1 M HCl solution that is separated from the sample solution by a very thin glass membrane. The potential of the electrode depends on the H^+ ion concentration of the sample. (c) The potential of an ion-selective electrode depends on the concentration of only a single ionic species in solution.

At 25°C, the potential of the SCE is 0.2415 V versus the SHE, which means that 0.2415 V must be subtracted from the potential versus an SCE to obtain the standard electrode potential.

One of the most common uses of electrochemistry is to measure the H^+ ion concentration of a solution. A glass electrode is generally used for this purpose, in which an internal Ag/AgCl electrode is immersed in a 0.10 M HCl solution that is separated from the solution by a very thin glass membrane (part (b) in Figure 19.9 "Three Common Types of Electrodes"). The glass membrane absorbs protons, which affects the measured potential. The extent of the adsorption on the inner side is fixed because $[H^+]$ is fixed inside the electrode, but the adsorption of protons on the outer surface depends on the pH of the solution. The potential of the glass electrode depends on $[H^+]$ as follows (recall that $pH = -\log[H^+]$:

Equation 19.47

$E_{glass} = E' + (0.0591\ V \times \log[H^+]) = E' - 0.0591\ V \times pH$

The voltage E' is a constant that depends on the exact construction of the electrode. Although it can be measured, in practice, a glass electrode is *calibrated*; that is, it is inserted into a solution of known pH, and the display on the pH meter is adjusted to the known value. Once the electrode is properly calibrated, it can be placed in a solution and used to determine an unknown pH.

Ion-selective electrodes are used to measure the concentration of a particular species in solution; they are designed so that their potential depends on only the concentration of the desired species (part (c) in Figure 19.9 "Three Common Types of Electrodes"). These electrodes usually contain an internal reference electrode that is connected by a solution of an electrolyte to a crystalline inorganic material or a membrane, which acts as the sensor. For example, one type of ion-selective electrode uses a single crystal of Eu-doped LaF_3 as the inorganic material. When fluoride ions in solution diffuse to the surface of the solid, the potential of the electrode changes, resulting in a so-called *fluoride electrode*. Similar electrodes are used to measure the concentrations of other species in solution. Some of the species whose concentrations can be determined in aqueous solution using ion-selective electrodes and similar devices are listed in Table 19.1 "Some Species Whose Aqueous Concentrations Can Be Measured Using Electrochemical Methods".

Table 19.1 Some Species Whose Aqueous Concentrations Can Be Measured Using Electrochemical Methods

Species	Type of Sample
H^+	laboratory samples, blood, soil, and ground and surface water
NH_3/NH_4^+	wastewater and runoff water
K^+	blood, wine, and soil
CO_2/HCO_3^-	blood and groundwater
F^-	groundwater, drinking water, and soil
Br^-	grains and plant extracts
I^-	milk and pharmaceuticals
NO_3^-	groundwater, drinking water, soil, and fertilizer

Summary

The flow of electrons in an electrochemical cell depends on the identity of the reacting substances, the difference in the potential energy of their valence electrons, and their concentrations. The potential of the cell under standard conditions (1 M for solutions, 1 atm for gases, pure solids or liquids for other

substances) and at a fixed temperature (25°C) is called the **standard cell potential ($E°_{cell}$)**. Only the *difference* between the potentials of two electrodes can be measured. By convention, all tabulated values of *standard electrode potentials* are listed as standard reduction potentials. The overall cell potential is the reduction potential of the reductive half-reaction minus the reduction potential of the oxidative half-reaction ($E°_{cell} = E°_{cathode} - E°_{anode}$). The potential of the**standard hydrogen electrode (SHE)** is defined as 0 V under standard conditions. The potential of a half-reaction measured against the SHE under standard conditions is called its **standard electrode potential**. The standard cell potential is a measure of the driving force for a given redox reaction. All $E°$ values are independent of the stoichiometric coefficients for the half-reaction. Redox reactions can be balanced using the half-reaction method, in which the overall redox reaction is divided into an oxidation half-reaction and a reduction half-reaction, each balanced for mass and charge. The half-reactions selected from tabulated lists must exactly reflect reaction conditions. In an alternative method, the atoms in each half-reaction are balanced, and then the charges are balanced. Whenever a half-reaction is reversed, the sign of $E°$ corresponding to that reaction must also be reversed. If $E°_{cell}$ is positive, the reaction will occur spontaneously under standard conditions. If $E°_{cell}$ is negative, then the reaction is not spontaneous under standard conditions, although it will proceed spontaneously in the opposite direction. The potential of an **indicator electrode**is related to the concentration of the substance being measured, whereas the potential of the **reference electrode** is held constant. Whether reduction or oxidation occurs depends on the potential of the sample versus the potential of the reference electrode. In addition to the SHE, other reference electrodes are the**silver–silver chloride electrode**; the **saturated calomel electrode (SCE)**; the **glass electrode**, which is commonly used to measure pH; and **ion-selective electrodes**, which depend on the concentration of a single ionic species in solution. Differences in potential between the SHE and other reference electrodes must be included when calculating values for $E°$.

KEY TAKEAWAYS

- Redox reactions can be balanced using the half-reaction method.
- The standard cell potential is a measure of the driving force for the reaction.

KEY EQUATION

Standard cell potential

Equation 19.10: $E°_{cell} = E°_{cathode} - E°_{anode}$

CONCEPTUAL PROBLEMS

1. Is a hydrogen electrode chemically inert? What is the major disadvantage to using a hydrogen electrode?
2. List two factors that affect the measured potential of an electrochemical cell and explain their impact on the measurements.
3. What is the relationship between electron flow and the potential energy of valence electrons? If the valence electrons of substance A have a higher potential energy than those of substance B, what is the direction of electron flow between them in a galvanic cell?
4. If the components of a galvanic cell include aluminum and bromine, what is the predicted direction of electron flow? Why?
5. Write a cell diagram representing a cell that contains the Ni/Ni^{2+} couple in one compartment and the SHE in the other compartment. What are the values of $E°_{cathode}$, $E°_{anode}$, and $E°_{cell}$?
6. Explain why $E°$ values are independent of the stoichiometric coefficients in the corresponding half-reaction.
7. Identify the oxidants and the reductants in each redox reaction.

a. $Cr(s) + Ni^{2+}(aq) \rightarrow Cr^{2+}(aq) + Ni(s)$

b. $Cl_2(g) + Sn^{2+}(aq) \rightarrow 2Cl^-(aq) + Sn^{4+}(aq)$

c. $H_3AsO_4(aq) + 8H^+(aq) + 4Zn(s) \rightarrow AsH_3(g) + 4H_2O(l) + 4Zn^{2+}(aq)$

d. $2NO_2(g) + 2OH^-(aq) \rightarrow NO_2^-(aq) + NO_3^-(aq) + H_2O(l)$

8. Identify the oxidants and the reductants in each redox reaction.

a. $Br_2(l) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(s)$

b. $Cu^{2+}(aq) + 2Ag(s) \rightarrow Cu(s) + 2Ag^+(aq)$

c. $H^+(aq) + 2MnO_4^-(aq) + 5H_2SO_3(aq) \rightarrow 2Mn^{2+}(aq) + 3H_2O(l) + 5HSO_4^-(aq)$

d. $IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \rightarrow 3I_2(s) + 3H_2O(l)$

9. All reference electrodes must conform to certain requirements. List the requirements and explain their significance.
10. For each application, describe the reference electrode you would use and explain why. In each case, how would the measured potential compare with the corresponding $E°$?

a. measuring the potential of a Cl^-/Cl_2 couple

b. measuring the pH of a solution

c. measuring the potential of a MnO_{4-}/Mn^{2+} couple

ANSWERS

1.

2.

3.

4.

5.

$Ni(s)|\ Ni^{2+}(aq)\|\ H^{+}(aq,\ 1\ M)|\ H_2(g,\ 1\ atm)|\ Pt(s)$

$$E\ \square anode E\ \square cathode E\ \square cell Ni2+\left(aq\right)+2e\text{-}$$
$$\rightarrow Ni\left(s\right);\ \text{-}0.257\ V2H+\left(aq\right)+2e\text{-}\rightarrow H2\left(g\right);$$
$$0.000\ V2H+\left(aq\right)+Ni\left(s\right)\rightarrow H2\left(g\right)+Ni2+\left(aq\right);\ 0.257$$
$$V$$

6.

7.

a. oxidant: $Ni^{2+}(aq)$; reductant: Cr(s)

b. oxidant: $Cl_2(g)$; reductant: $Sn^{2+}(aq)$

c. oxidant: $H_3AsO_4(aq)$; reductant: Zn(s)

d. oxidant: $NO_2(g)$; reductant: $NO_2(g)$

8.

9.

10.

NUMERICAL PROBLEMS

1. Draw the cell diagram for a galvanic cell with an SHE and a copper electrode that carries out this overall reaction: $H_2(g) + Cu^{2+}(aq) \rightarrow 2H^{+}(aq) + Cu(s)$.
2. Draw the cell diagram for a galvanic cell with an SHE and a zinc electrode that carries out this overall reaction: $Zn(s) + 2H^{+}(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$.
3. Balance each reaction and calculate the standard electrode potential for each. Be sure to include the physical state of each product and reactant.

a. $Cl_2(g) + H_2(g) \rightarrow 2Cl^{-}(aq) + 2H^{+}(aq)$

b. $Br_2(aq) + Fe^{2+}(aq) \rightarrow 2Br^{-}(aq) + Fe^{3+}(aq)$

c. $Fe^{3+}(aq) + Cd(s) \rightarrow Fe^{2+}(aq) + Cd^{2+}(aq)$

4. Balance each reaction and calculate the standard reduction potential for each. Be sure to include the physical state of each product and reactant.

a. $Cu^{+}(aq) + Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + Ag(s)$

b. $Sn(s) + Fe^{3+}(aq) \rightarrow Sn^{2+}(aq) + Fe^{2+}(aq)$

c. $Mg(s) + Br_2(l) \rightarrow 2Br^{-}(aq) + Mg^{2+}(aq)$

5. Write a balanced chemical equation for each redox reaction.

a. $H_2PO_2^{-}(aq) + SbO_2^{-}(aq) \rightarrow HPO_3^{2-}(aq) + Sb(s)$ in basic solution

b. $HNO_2(aq) + I^{-}(aq) \rightarrow NO(g) + I_2(s)$ in acidic solution

c. $N_2O(g) + ClO^{-}(aq) \rightarrow Cl^{-}(aq) + NO_2^{-}(aq)$ in basic solution

d. $Br_2(l) \rightarrow Br^{-}(aq) + BrO_3^{-}(aq)$ in basic solution

e. $Cl(CH_2)_2OH(aq) + K_2Cr_2O_7(aq) \rightarrow ClCH_2CO_2H(aq) + Cr^{3+}(aq)$ in acidic solution

6. Write a balanced chemical equation for each redox reaction.

a. $I^{-}(aq) + HClO_2(aq) \rightarrow IO_3^{-}(aq) + Cl_2(g)$ in acidic solution

b. $Cr^{2+}(aq) + O_2(g) \rightarrow Cr^{3+}(aq) + H_2O(l)$ in acidic solution

c. $CrO_2^{-}(aq) + ClO^{-}(aq) \rightarrow CrO_4^{2-}(aq) + Cl^{-}(aq)$ in basic solution

d. $S(s) + HNO_2(aq) \rightarrow H_2SO_3(aq) + N_2O(g)$ in acidic solution

e. $F(CH_2)_2OH(aq) + K_2Cr_2O_7(aq) \rightarrow FCH_2CO_2H(aq) + Cr^{3+}(aq)$ in acidic solution

7. The standard cell potential for the oxidation of Pb to Pb^{2+} with the concomitant reduction of Cu^{+} to Cu is 0.39 V. You know that $E°$ for the Pb^{2+}/Pb couple is −0.13 V. What is $E°$ for the Cu^{+}/Cu couple?

8. You have built a galvanic cell similar to the one in Figure 19.7 "Determining a Standard Electrode Potential Using a Standard Hydrogen Electrode" using an iron nail, a solution of $FeCl_2$, and an SHE. When the cell is connected, you notice that the iron nail begins to corrode. What else do you observe? Under standard conditions, what is E_{cell}?

9. Carbon is used to reduce iron ore to metallic iron. The overall reaction is as follows:

$$2Fe_2O_3 \cdot xH_2O(s) + 3C(s) \rightarrow 4Fe(l) + 3CO_2(g) + 2xH_2O(g)$$

Write the two half-reactions for this overall reaction.

10. Will each reaction occur spontaneously under standard conditions?

a. $Cu(s) + 2H^{+}(aq) \rightarrow Cu^{2+}(aq) + H_2(g)$

b. $Zn^{2+}(aq) + Pb(s) \rightarrow Zn(s) + Pb^{2+}(aq)$

11. Each reaction takes place in acidic solution. Balance each reaction and then determine whether it occurs spontaneously as written under standard conditions.

a. $Se(s) + Br_2(l) \rightarrow H_2SeO_3(aq) + Br^-(aq)$

b. $NO_3^-(aq) + S(s) \rightarrow HNO_2(aq) + H_2SO_3(aq)$

c. $Fe^{3+}(aq) + Cr^{3+}(aq) \rightarrow Fe^{2+}(aq) + Cr_2O_7^{2-}(aq)$

12. Calculate $E°_{cell}$ and $\Delta G°$ for the redox reaction represented by the cell diagram $Pt(s)|\ Cl_2(g, 1\ atm)\|\ ZnCl_2(aq, 1\ M)|\ Zn(s)$. Will this reaction occur spontaneously?

13. If you place Zn-coated (galvanized) tacks in a glass and add an aqueous solution of iodine, the brown color of the iodine solution fades to a pale yellow. What has happened? Write the two half-reactions and the overall balanced chemical equation for this reaction. What is $E°_{cell}$?

14. Your lab partner wants to recover solid silver from silver chloride by using a 1.0 M solution of HCl and 1 atm H_2 under standard conditions. Will this plan work?

ANSWERS

1. $Pt(s)|\ H_2(g, 1\ atm)\ |\ H^+(aq, 1M)\|\ Cu^{2+}(aq)|\ Cu(s)$

2.

3.

a. $Cl_2(g) + H_2(g) \rightarrow 2Cl^-(aq) + 2H^+(aq)$; $E° = 1.358$ V

b. $Br_2(l) + 2Fe^{2+}(aq) \rightarrow 2Br^-(aq) + 2Fe^{3+}(aq)$; $E° = 0.316$ V

c. $2Fe^{3+}(aq) + Cd(s) \rightarrow 2Fe^{2+}(aq) + Cd^{2+}(aq)$; $E° = 1.174$ V

[1] Concentrated solutions of salts (about 1 M) generally do not exhibit ideal behavior, and the actual standard state corresponds to an *activity* of 1 rather than a concentration of 1 M. Corrections for nonideal behavior are important for precise quantitative work but not for the more qualitative approach that we are taking here.

[2] As we shall see in Section 19.7 "Electrolysis", this does not mean that the reaction cannot be made to occur at all under standard conditions. With a sufficient input of electrical energy, virtually any reaction can be forced to occur.

19.3 Comparing Strengths of Oxidants and Reductants

LEARNING OBJECTIVE

1. To know how to predict the relative strengths of various oxidants and reductants.

We can use the procedure described in Section 19.2 "Standard Potentials" to measure the standard potentials for a wide variety of chemical substances, some of which are listed in Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C". (Chapter 29 "Appendix E: Standard Reduction Potentials at 25°C" contains a more extensive listing.) These data allow us to compare the oxidative and reductive strengths of a variety of substances. The half-reaction for the standard hydrogen electrode (SHE) lies more than halfway down the list in Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C". All reactants that lie *above* the SHE in the table are stronger oxidants than H^+, and all those that lie below the SHE are weaker. The strongest oxidant in the table is F_2, with a standard electrode potential of 2.87 V. This high value is consistent with the high electronegativity of fluorine and tells us that fluorine has a stronger tendency to accept electrons (it is a stronger oxidant) than any other element.

Table 19.2 Standard Potentials for Selected Reduction Half-Reactions at 25°C

Half-Reaction	$E°$ (V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O(l)$	1.78
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	1.72
$PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$	1.69
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$	1.23
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O(l)$	1.22
$Br_2(aq) + 2e^- \longrightarrow 2Br^-(aq)$	1.09
$NO_3^-(aq) + 3H^+(aq) + 2e^- \longrightarrow HNO_2(aq) + H_2O(l)$	0.93
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	0.77
$H_2SeO_3(aq) + 4H^+ + 4e^- \longrightarrow Se(s) + 3H_2O(l)$	0.74
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	0.70
$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	0.60
$MnO_4^{2-}(aq) + 2H_2O(l) + 2e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	0.60

Half-Reaction	$E°$ (V)
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	0.54
$H_2SO_3(aq) + 4H^+(aq) + 4e^- \rightarrow S(s) + 3H_2O(l)$	0.45
$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	0.34
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	0.22
$Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$	0.15
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	−0.14
$2SO_4^{2-}(aq) + 4H+(aq) + 2e^- \rightarrow S_2O_6^{2-}(aq) + 2H_2O(l)$	−0.22
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	−0.26
$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$	−0.36
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	−0.40
$Cr^{3+}(aq) + e^- \rightarrow Cr^{2+}(aq)$	−0.41
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	−0.45
$Ag_2S(s) + 2e^- \rightarrow 2Ag(s) + S^{2-}(aq)$	−0.69
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	−0.76
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	−1.662
$Be^{2+}(aq) + 2e^- \rightarrow Be(s)$	−1.85
$Li^+(aq) + e^- \rightarrow Li(s)$	−3.04

Similarly, all species in Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C" that lie *below* H_2 are stronger reductants than H_2, and those that lie above H_2 are weaker. The strongest reductant in the table is thus metallic lithium, with a standard electrode potential of −3.04 V. This fact might be surprising because cesium, not lithium, is the least electronegative element. The apparent anomaly can be explained by the fact that electrode potentials are measured in aqueous solution, where intermolecular interactions are important, whereas ionization potentials and electron affinities are measured in the gas phase. Due to its small size, the Li^+ ion is stabilized in aqueous solution by strong electrostatic interactions with the negative dipole end of water molecules. These interactions result in a

significantly greater $\Delta H_{\text{hydration}}$ for Li^+compared with Cs^+. Lithium metal is therefore the strongest reductant (most easily oxidized) of the alkali metals in aqueous solution.

Note the Pattern

Species in Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C" that lie below H_2 are stronger reductants (more easily oxidized) than H_2. Species that lie above H_2 are stronger oxidants. Because the half-reactions shown in Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C" are arranged in order of their $E°$ values, we can use the table to quickly predict the relative strengths of various oxidants and reductants. Any species on the left side of a half-reaction will spontaneously oxidize any species on the right side of another half-reaction that lies *below* it in the table. Conversely, any species on the right side of a half-reaction will spontaneously reduce any species on the left side of another half-reaction that lies *above* it in the table. We can use these generalizations to predict the spontaneity of a wide variety of redox reactions ($E°_{\text{cell}} > 0$), as illustrated in Example 5.

EXAMPLE 5

The black tarnish that forms on silver objects is primarily Ag_2S. The half-reaction for reversing the tarnishing process is as follows:

a. $$Ag2S(s) + 2e- \rightarrow 2Ag(s) + S2-(aq) \quad E° = -0.69\ V$$

b. Referring to Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C", predict which species—$H_2O_2(aq)$, $Zn(s)$, $I^-(aq)$, $Sn^{2+}(aq)$—can reduce Ag_2S to Ag under standard conditions.

c. Of these species—$H_2O_2(aq)$, $Zn(s)$, $I^-(aq)$, $Sn^{2+}(aq)$, identify which is the strongest reducing agent in aqueous solution and thus the best candidate for a commercial product.

d. From the data in Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C", suggest an alternative reducing agent that is readily available, inexpensive, and possibly more effective at removing tarnish.

Given: reduction half-reaction, standard electrode potential, and list of possible reductants

Asked for: reductants for Ag_2S, strongest reductant, and potential reducing agent for removing tarnish

Strategy:

A From their positions in Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C", decide which species can reduce Ag_2S. Determine which species is the strongest reductant.

B Use Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C"to identify a reductant for Ag_2S that is a common household product.

Solution:

We can solve the problem in one of two ways: (1) compare the relative positions of the four possible reductants with that of the Ag_2S/Ag couple in Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C" or (2) compare $E°$ for each species with $E°$ for the Ag_2S/Ag couple (−0.69 V).

a. **A** The species in Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C" are arranged from top to bottom in order of increasing reducing strength. Of the four species given in the problem, $I^-(aq)$, $Sn^{2+}(aq)$, and $H_2O_2(aq)$ lie above Ag_2S, and one [Zn(s)] lies below it. We can therefore conclude that Zn(s) can reduce $Ag_2S(s)$ under standard conditions, whereas $I^-(aq)$, $Sn^{2+}(aq)$, and $H_2O_2(aq)$ cannot. $Sn^{2+}(aq)$ and $H_2O_2(aq)$ appear twice in the table: on the left side (oxidant) in one half-reaction and on the right side (reductant) in another.

b. The strongest reductant is Zn(s), the species on the right side of the half-reaction that lies closer to the bottom of Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C" than the half-reactions involving $I^-(aq)$, $Sn^{2+}(aq)$, and $H_2O_2(aq)$. (Commercial products that use a piece of zinc are often marketed as a “miracle product” for removing tarnish from silver. All that is required is to add warm water and salt for electrical conductivity.)

c. **B** Of the reductants that lie below Zn(s) in Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C", and therefore are stronger reductants, only one is commonly available in household products: Al(s), which is sold as aluminum foil for wrapping foods.

Exercise

Refer to Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C" to predict

a. which species—$Sn^{4+}(aq)$, $Cl^-(aq)$, $Ag^+(aq)$, $Cr^{3+}(aq)$, and/or $H_2O_2(aq)$—can oxidize $MnO_2(s)$ to MNO_4^- under standard conditions.

b. which species—$Sn^{4+}(aq)$, $Cl^-(aq)$, $Ag^+(aq)$, $Cr^{3+}(aq)$, and/or $H_2O_2(aq)$—is the strongest oxidizing agent in aqueous solution.

Answer:

a. $Ag^{+}(aq)$; $H_2O_2(aq)$

b. $H_2O_2(aq)$

EXAMPLE 6

Use the data in Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C" to determine whether each reaction is likely to occur spontaneously under standard conditions:

a. $Sn(s) + Be^{2+}(aq) \rightarrow Sn^{2+}(aq) + Be(s)$

a. $MnO_2(s) + H_2O_2(aq) + 2H^{+}(aq) \rightarrow O_2(g) + Mn^{2+}(aq) + 2H_2O(l)$

Given: redox reaction and list of standard electrode potentials (Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C")

Asked for: reaction spontaneity

Strategy:

A Identify the half-reactions in each equation. Using Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C", determine the standard potentials for the half-reactions in the appropriate direction.

B Use Equation 19.10 to calculate the standard cell potential for the overall reaction. From this value, determine whether the overall reaction is spontaneous.

Solution:

a. **A** Metallic tin is oxidized to $Sn^{2+}(aq)$, and $Be^{2+}(aq)$ is reduced to elemental beryllium. We can find the standard electrode potentials for the latter (reduction) half-reaction (−1.85 V) and for the former (oxidation) half-reaction (−0.14 V) directly from Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C".

B Adding the two half-reactions gives the overall reaction:

$$cathode : anode : overall : MnO2(s) + 4H + (aq) + 2e -$$
$$\rightarrow Mn2 + (aq) + 2H2O(l) H2O2(aq) \rightarrow O2(g) + 2H + (aq)$$
$$+2e - MnO2(s) + H2O2(aq) + 2H + (aq) \rightarrow \quad O2(g) + Mn2$$
$$+(aq) + 2H2O(l) E°cathode = 1.22 \ VE°anode = 0.70 \ VE°cell$$
$$= E°cathode - E°anode \quad = -0.53 \ V$$

The standard cell potential is quite negative, so the reaction will *not* occur spontaneously as written. That is, metallic tin cannot be used to reduce Be^{2+} to beryllium metal under standard conditions. Instead, the

reverse process, the reduction of stannous ions (Sn^{2+}) by metallic beryllium, which has a positive value of $E°_{cell}$, will occur spontaneously.

b. **A** MnO_2 is the oxidant (Mn^{4+} is reduced to Mn^{2+}), while H_2O_2 is the reductant (O^{2-} is oxidized to O_2). We can obtain the standard electrode potentials for the reduction and oxidation half-reactions directly fromTable 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C".

B The two half-reactions and their corresponding potentials are as follows:

$$cathode : anode : overall : MnO2(s) + 4H + (aq) + 2e -$$
$$\rightarrow Mn2 + (aq) + 2H2O(l) H2O2(aq) \rightarrow O2(g) + 2H +$$
$$(aq) + 2e - MnO2(s) + H2O2(a$$
$$q) + 2H + (aq) \rightarrow \quad O2(g) + Mn2 + (aq)$$
$$+2H2O(l) E°cathode = 1.22 \; VE°anode$$
$$= 0.70 \; VE°cell = E°cathode - E°anode \quad = -0.53 \; V$$

The standard potential for the reaction is positive, indicating that under standard conditions, it will occur spontaneously as written. Hydrogen peroxide will reduce MnO_2, and oxygen gas will evolve from the solution.

Exercise

Use the data in Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C" to determine whether each reaction is likely to occur spontaneously under standard conditions:

a. $2Ce^{4+}(aq) + 2Cl^{-}(aq) \rightarrow 2Ce^{3+}(aq) + Cl_2(g)$

b. $4MnO_2(s) + 3O_2(g) + 4OH^{-}(aq) \rightarrow 4MnO_4^{-}(aq) + 2H_2O$

Answer:

a. spontaneous ($E°_{cell}$ = 0.36 V)

b. nonspontaneous ($E°_{cell}$ = −0.20 V)

Although the sign of $E°_{cell}$ tells us whether a particular redox reaction will occur spontaneously under standard conditions, it does not tell us to what *extent* the reaction proceeds, and it does not tell us what will happen under nonstandard conditions. To answer these questions requires a more quantitative understanding of the relationship between electrochemical cell potential and chemical thermodynamics, as described inSection 19.4 "Electrochemical Cells and Thermodynamics".

Summary

The oxidative and reductive strengths of a variety of substances can be compared using standard electrode potentials. Apparent anomalies can be explained by the fact that electrode potentials are measured in aqueous solution, which allows for strong intermolecular electrostatic interactions, and not in the gas phase.

KEY TAKEAWAY

- The relative strengths of various oxidants and reductants can be predicted using $E°$ values.

CONCEPTUAL PROBLEMS

1. The order of electrode potentials cannot always be predicted by ionization potentials and electron affinities. Why? Do you expect sodium metal to have a higher or a lower electrode potential than predicted from its ionization potential? What is its approximate electrode potential?
2. Without referring to tabulated data, of Br_2/Br^-, Ca^{2+}/Ca, O_2/OH^-, and Al^{3+}/Al, which would you expect to have the *least* negative electrode potential and which the *most* negative? Why?
3. Because of the sulfur-containing amino acids present in egg whites, eating eggs with a silver fork will tarnish the fork. As a chemist, you have all kinds of interesting cleaning products in your cabinet, including a 1 M solution of oxalic acid ($H_2C_2O_4$). Would you choose this solution to clean the fork that you have tarnished from eating scrambled eggs?
4. The electrode potential for the reaction $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ is 0.34 V under standard conditions. Is the potential for the oxidation of 0.5 mol of Cu equal to −0.34/2 V? Explain your answer.

ANSWER

1.
2.
3. No; $E° = -0.691$ V for $Ag_2S(s) + 2e^- \rightarrow Ag(s) + S^{2-}(aq)$, which is too negative for Ag_2S to be spontaneously reduced by oxalic acid [$E° = 0.49$ V for $2CO_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2C_2O_4(aq)$]
4.

19.4 Electrochemical Cells and Thermodynamics

LEARNING OBJECTIVES

1. To understand the relationship between cell potential and the equilibrium constant.

2. To use cell potentials to calculate solution concentrations.

Changes in reaction conditions can have a tremendous effect on the course of a redox reaction. For example, under standard conditions, the reaction of Co(s) with Ni^{2+}(aq) to form Ni(s) and Co^{2+}(aq) occurs spontaneously, but if we reduce the concentration of Ni^{2+} by a factor of 100, so that [Ni^{2+}] is 0.01 M, then the reverse reaction occurs spontaneously instead. The relationship between voltage and concentration is one of the factors that must be understood to predict whether a reaction will be spontaneous.

The Relationship between Cell Potential and Free Energy

Electrochemical cells convert chemical energy to electrical energy and vice versa. The total amount of energy produced by an electrochemical cell, and thus the amount of energy available to do electrical work, depends on both the cell potential and the total number of electrons that are transferred from the reductant to the oxidant during the course of a reaction. The resulting electric current is measured in coulombs (C), an SI unit that measures the number of electrons passing a given point in 1 s. A coulomb relates energy (in joules) to electrical potential (in volts). Electric current is measured inamperes (A); 1 A is defined as the flow of 1 C/s past a given point (1 C = 1 A·s):

Equation 19.48

$$1\ J 1\ V = 1\ C = A \times s$$

In chemical reactions, however, we need to relate the coulomb to the charge on a *mole*of electrons. Multiplying the charge on the electron by Avogadro's number gives us the charge on 1 mol of electrons, which is called the faraday (*F*), named after the English physicist and chemist Michael Faraday (1791–1867):

Equation 19.49

$$F = (1.60218 \times 10 - 19\ C)(6.02214 \times 10231\ mol\ e-)$$
$$= 9.64855 \times 104\ C / mol\ e- \approx 96,486 / (V \times mol\ e-)$$

The total charge transferred from the reductant to the oxidant is therefore *nF*, where *n*is the number of moles of electrons.

Michael Faraday (1791–1867)

Faraday was a British physicist and chemist who was arguably one of the greatest experimental scientists in history. The son of a blacksmith, Faraday was self-educated and became an apprentice bookbinder at age 14 before turning to science. His experiments in electricity and magnetism made electricity a routine tool in science and led to both the electric motor and the electric generator. He discovered the

phenomenon of electrolysis and laid the foundations of electrochemistry. In fact, most of the specialized terms introduced in this chapter (electrode, anode, cathode, and so forth) are due to Faraday. In addition, he discovered benzene and invented the system of oxidation state numbers that we use today. Faraday is probably best known for "The Chemical History of a Candle," a series of public lectures on the chemistry and physics of flames.

The maximum amount of work that can be produced by an electrochemical cell (w_{max}) is equal to the product of the cell potential (E_{cell}) and the total charge transferred during the reaction (nF):

Equation 19.50

$$w_{max} = nFE_{cell}$$

Work is expressed as a negative number because work is being done *by* a system (an electrochemical cell with a positive potential) *on* its surroundings.

As you learned in Chapter 18 "Chemical Thermodynamics", the change in free energy (ΔG) is also a measure of the maximum amount of work that can be performed during a chemical process ($\Delta G = w_{max}$). Consequently, there must be a relationship between the potential of an electrochemical cell and ΔG, the most important thermodynamic quantity discussed in Chapter 18 "Chemical Thermodynamics". This relationship is as follows:

Equation 19.51

$$\Delta G = -nFE_{cell}$$

A spontaneous redox reaction is therefore characterized by a *negative* value of ΔG and a*positive* value of E_{cell}, consistent with our earlier discussions. When both reactants and products are in their standard states, the relationship between ΔG° and E°_{cell} is as follows:

Equation 19.52

$$\Delta G^\circ = -nFE^\circ_{cell}$$

Note the Pattern

A spontaneous redox reaction is characterized by a negative value of ΔG°, which corresponds to a positive value of E°_{cell}.

EXAMPLE 7

Suppose you want to prepare elemental bromine from bromide using the dichromate ion as an oxidant. Using the data in Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C", calculate

the free-energy change (Δ*G*°) for this redox reaction under standard conditions. Is the reaction spontaneous?

Given: redox reaction

Asked for: Δ*G*° for the reaction and spontaneity

Strategy:

A From the relevant half-reactions and the corresponding values of *E*°, write the overall reaction and calculate $E°_{cell}$ using Equation 19.10.

B Determine the number of electrons transferred in the overall reaction. Then use Equation 19.52 to calculate Δ*G*°. If Δ*G*° is negative, then the reaction is spontaneous.

Solution:

A As always, the first step is to write the relevant half-reactions and use them to obtain the overall reaction and the magnitude of *E*°. From Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C", we can find the reduction and oxidation half-reactions and corresponding *E*° values:

$$cathode: anode: Cr2O72\text{-}(aq) + 14H + (aq) + 6e$$
$$\text{-} \rightarrow 2Cr3 + (aq) + 7H2O(l) 2Br\text{-}(aq) \rightarrow Br2(aq)$$
$$+2e\text{-} \quad E\square cathode = 1.23 \; VE\square anode = 1.09 \; V$$

To obtain the overall balanced chemical equation, we must multiply both sides of the oxidation half-reaction by 3 to obtain the same number of electrons as in the reduction half-reaction, remembering that the magnitude of *E*° is not affected:

$$cathode: anode: overall: Cr2O72\text{-}(aq)$$
$$+14H + (aq) + 6e\text{-} \rightarrow 2Cr3 + (aq) + 7H2O(l)$$
$$6Br\text{-}(aq) \rightarrow 3Br2(aq) + 6e\text{-} \quad Cr2O72\text{-}(aq) + 6Br\text{-}(aq)$$
$$+14H + (aq) \rightarrow \quad 2Cr3 + (aq) + 3Br2(aq)$$
$$+7H2O(l) \quad E°cathode = 1.23 \; VE°anode = 1.09 \; VE°cell = 0.14 \; V$$

B We can now calculate Δ*G*° using Equation 19.52. Because six electrons are transferred in the overall reaction, the value of *n* is 6:

$$DG° = \text{-}(n)(F)(E\square cell) = \text{-}(6 \; mole)[96,468 \; J$$
$$/(V \cdot mol)(0.14 \; V)] = \text{-}8.1 \times 104 \; J = \text{-}81 \; kJ/mol \; Cr2O72\text{-}$$

Thus Δ*G*° is −81 kJ for the reaction as written, and the reaction is spontaneous.

Exercise

Use the data in Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C" to calculate $\Delta G°$ for the reduction of ferric ion by iodide:

$$2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(s)$$

Is the reaction spontaneous?

Answer: −44 kJ/mol I_2; yes

Potentials for the Sums of Half-Reactions

Although Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C" and Chapter 29 "Appendix E: Standard Reduction Potentials at 25°C" list several half-reactions, many more are known. When the standard potential for a half-reaction is not available, we can use relationships between standard potentials and free energy to obtain the potential of any other half-reaction that can be written as the sum of two or more half-reactions whose standard potentials are available. For example, the potential for the reduction of $Fe^{3+}(aq)$ to Fe(s) is not listed in the table, but two related reductions are given:

Equation 19.53

$$Fe3+(aq)+e- \rightarrow Fe2+(aq) E° = 0.77\ V$$

Equation 19.54

$$Fe2+(aq)+2e- \rightarrow Fe(aq) E° = -0.45\ V$$

Although the sum of these two half-reactions gives the desired half-reaction, we cannot simply add the potentials of two reductive half-reactions to obtain the potential of a third reductive half-reaction *because* $E°$ *is not a state function*. However, because $\Delta G°$ is a state function, the sum of the $\Delta G°$ values for the individual reactions gives us $\Delta G°$ for the overall reaction, which is proportional to *both* the potential *and* the number of electrons (n) transferred. To obtain the value of $E°$ for the overall half-reaction, we first must add the values of $\Delta G°$ ($= -nFE°$) for each individual half-reaction to obtain $\Delta G°$ for the overall half-reaction:

Equation 19.55

$$Fe3+(aq)+e- \; Fe2+(aq)+2e- \; Fe3+(aq)+3e- \rightarrow Fe2+(aq) \; - \rightarrow - - - - - - - - \; Fe(s) \; - \rightarrow - - - - - - - - - \; Fe(s) \; \Delta G° \; \Delta G° \; \Delta G° = -(1)(F)(0.77\ V) = -(2)(F)(-.045\ V) = [-(1)(F)(0.77\ V)] + [-(2)(F)(-0.45\ V)]$$

Solving the last expression for ΔG° for the overall half-reaction,

Equation 19.56
$\Delta G^\circ = F[(-0.77\ \text{V}) + (-2)(-0.45\ \text{V})] = F(0.13\ \text{V})$

Three electrons ($n = 3$) are transferred in the overall reaction (Equation 19.55), so substituting into Equation 19.52 and solving for E° gives the following:

$$\Delta G^\circ F(0.13\ V) E^\circ = -nFE_{cell} =$$
$$-(3)(F)(E_{cell}) = -0.13\ V\,3 = -0.043\ V$$

This value of E° is *very* different from the value that is obtained by simply adding the potentials for the two half-reactions (0.32 V) and even has the opposite sign.

Note the Pattern

Values of E° for half-reactions cannot be added to give E° for the sum of the half-reactions; only values of $\Delta G^\circ = -nFE^\circ_{cell}$ for half-reactions can be added.

The Relationship between Cell Potential and the Equilibrium Constant

We can use the relationship between ΔG° and the equilibrium constant K, defined in Chapter 18 "Chemical Thermodynamics", to obtain a relationship between E°_{cell} and K. Recall that for a general reaction of the type $a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$, the standard free-energy change and the equilibrium constant are related by the following equation:

Equation 19.57
$\Delta G^\circ = -RT \ln K$

Given the relationship between the standard free-energy change and the standard cell potential (Equation 19.52), we can write

Equation 19.58
$-nFE^\circ_{cell} = -RT \ln K$

Rearranging this equation,

Equation 19.59
$$E_{cell} = (RTnF) \ln K$$

For $T = 298$ K, Equation 19.59 can be simplified as follows:

Equation 19.60
$$E_{cell} = (RTnF) \ln K = [8.314\ J/(mol \times K)$$
$$(298K)]n[96,486\ J/(V \times mol)]2.303\ log\ K = (0.0591\ Vn) log\ K$$

Thus $E°_{cell}$ is directly proportional to the logarithm of the equilibrium constant. This means that large equilibrium constants correspond to large positive values of $E°_{cell}$ and vice versa.

EXAMPLE 8

Use the data in Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C" to calculate the equilibrium constant for the reaction of metallic lead with PbO_2 in the presence of sulfate ions to give $PbSO_4$ under standard conditions. (This reaction occurs when a car battery is discharged.) Report your answer to two significant figures.

Given: redox reaction

Asked for: *K*

Strategy:

A Write the relevant half-reactions and potentials. From these, obtain the overall reaction and $E°_{cell}$.

B Determine the number of electrons transferred in the overall reaction. Use Equation 19.60 to solve for log *K* and then *K*.

Solution:

A The relevant half-reactions and potentials from Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C" are as follows:

$$cathode: anode: overall: PbO2(s) + SO42\text{-}(aq) + 4H + (aq) + 2e\text{-}$$
$$\rightarrow PbSO4(s) + 2H2O(l) Pb(s) + SO42\text{-}(aq) \rightarrow PbSO4(s) + 2e\text{-} Pb(s) +$$
$$PbO2(s) + 2SO42\text{-}(aq) + 4H + (aq) \rightarrow 2PbSO4(s) + 2H2O(l) E \square cathode$$
$$= 1.69\ VE \square anode = \text{-}0.36\ VE \square cell = 2.05\ V$$

B Two electrons are transferred in the overall reaction, so *n* = 2. Solving Equation 19.60 for log *K* and inserting the values of *n* and *E*°,

$$log\ KK = nE°0.0591\ V = 2(2.05\ V)0.0591\ V = 69.37 = 2.3´\ 1069$$

Thus the equilibrium lies far to the right, favoring a discharged battery (as anyone who has ever tried unsuccessfully to start a car after letting it sit for a long time will know).

Exercise

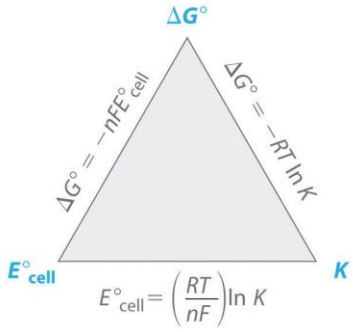
Use the data in Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C" to calculate the equilibrium constant for the reaction of $Sn^{2+}(aq)$ with oxygen to produce $Sn^{4+}(aq)$ and water under standard conditions. Report your answer to two significant figures. The reaction is as follows:

$$2Sn2+(aq)+O2(g)+4H+(aq) \square \quad 2Sn4+(aq)+2H2O(l)$$

Answer: 1.2×10^{73}

Figure 19.10 "The Relationships among Criteria for Thermodynamic Spontaneity"summarizes the relationships that we have developed based on properties of the*system*—that is, based on the equilibrium constant, standard free-energy change, and standard cell potential—and the criteria for spontaneity ($\Delta G^\circ < 0$). Unfortunately, these criteria apply only to systems in which all reactants and products are present in their standard states, a situation that is seldom encountered in the real world. A more generally useful relationship between cell potential and reactant and product concentrations, as we are about to see, uses the relationship between ΔG and the reaction quotient Q developed in Chapter 18 "Chemical Thermodynamics".

Figure 19.10 The Relationships among Criteria for Thermodynamic Spontaneity



ΔG°	E°_{cell}	K	Direction of Reaction
< 0	> 0	> 1	spontaneous in forward direction
> 0	< 0	< 1	spontaneous in reverse direction
0	0	1	no net reaction: system at equilibrium

The three properties of a system that can be used to predict the spontaneity of a redox reaction under standard conditions are K, ΔG°, and E°_{cell}. If we know the value of one of these quantities, then these relationships enable us to calculate the value of the other two. The signs of ΔG° and E°_{cell} and the magnitude of K determine the direction of spontaneous reaction under standard conditions.

The Effect of Concentration on Cell Potential: The Nernst Equation

Recall from Chapter 18 "Chemical Thermodynamics" that the *actual* free-energy change for a reaction under nonstandard conditions, ΔG, is given as follows:

Equation 19.61

$\Delta G = \Delta G^\circ + RT \ln Q$

We also know that $\Delta G = -nFE_{cell}$ and $\Delta G^\circ = -nFE^\circ_{cell}$. Substituting these expressions into Equation 19.61, we obtain

Equation 19.62

$-nFE_{cell} = -nFE^\circ_{cell} + RT \ln Q$

Dividing both sides of this equation by $-nF$,

Equation 19.63

$$Ecell = E\square cell - (RTnF) ln\ Q$$

Equation 19.44 is called the Nernst equation, after the German physicist and chemist Walter Nernst (1864–1941), who first derived it. The Nernst equation is arguably the most important relationship in electrochemistry. When a redox reaction is at equilibrium ($\Delta G = 0$), Equation 19.44 reduces to Equation 19.59 because $Q = K$, and there is no net transfer of electrons (i.e., $E_{cell} = 0$).

Substituting the values of the constants into Equation 19.44 with $T = 298$ K and converting to base-10 logarithms give the relationship of the actual cell potential (E_{cell}), the standard cell potential (E°_{cell}), and the reactant and product concentrations at room temperature (contained in Q):

Equation 19.64

$$Ecell = E\square cell - (0.0591\ Vn) log\ Q$$

Note the Pattern

The Nernst equation can be used to determine the value of E_{cell}, and thus the direction of spontaneous reaction, for any redox reaction under any conditions.

Equation 19.64 allows us to calculate the potential associated with any electrochemical cell at 298 K for any combination of reactant and product concentrations under any conditions. We can therefore determine the spontaneous direction of any redox reaction under any conditions, as long as we have tabulated values for the relevant standard electrode potentials. Notice in Equation 19.64 that the cell potential changes by $0.0591/n$ V for each 10-fold change in the value of Q because $\log 10 = 1$.

EXAMPLE 9

In the exercise in Example 6, you determined that the following reaction proceeds spontaneously under standard conditions because $E^\circ_{cell} > 0$ (which you now know means that $\Delta G^\circ < 0$):

$$2Ce4+(aq) + 2Cl-(aq) \rightarrow 2Ce3+(aq) + Cl2(g) \quad E\square cell = 0.25\ V$$

Calculate E for this reaction under the following nonstandard conditions and determine whether it will occur spontaneously: $[Ce^{4+}] = 0.013$ M, $[Ce^{3+}] = 0.60$ M, $[Cl^-] = 0.0030$ M, $PCl2 =$ 1.0 atm, and $T = 25°C$.

Given: balanced redox reaction, standard cell potential, and nonstandard conditions

Asked for: cell potential

Strategy:

Determine the number of electrons transferred during the redox process. Then use the Nernst equation to find the cell potential under the nonstandard conditions.

Solution:

We can use the information given and the Nernst equation to calculate E_{cell}. Moreover, because the temperature is 25°C (298 K), we can use Equation 19.64instead of 19.46. The overall reaction involves the net transfer of two electrons:

$$2Ce^{4+}(aq) + 2e^- \rightarrow 2Ce^{3+}(aq)2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$$

so $n = 2$. Substituting the concentrations given in the problem, the partial pressure of Cl_2, and the value of $E°_{cell}$ into Equation 19.64,

$$Ecell = E\square cell - (0.0591\ Vn)log\ Q = 0.25\ V - (0.0591\ V2)log$$
$$[Ce3+]2PCl2[Ce4+]2[Cl-\ ]2 = 0.25\ V - [(0.0296\ V)(8.37)] = 0.00$$
$$V$$

Thus the reaction will *not* occur spontaneously under these conditions (because $E = 0$ V and $\Delta G = 0$). The composition specified is that of an equilibrium mixture.

Exercise

In the exercise in Example 6, you determined that molecular oxygen will not oxidize MnO_2 to permanganate via the reaction

$$4MnO2(s) + 3O2(g) + 4OH\ -(aq)$$
$$\rightarrow 4MnO4\ -(aq) + 2H2O(l)E\square cell = -0.20\ V$$

Calculate E_{cell} for the reaction under the following nonstandard conditions and decide whether the reaction will occur spontaneously: pH 10, $PO2 = 0.20$ atm, $[MNO_4^-] = 1.0 \times 10^{-4}$ M, and $T = 25°C$.

Answer: $E_{cell} = -0.22$ V; the reaction will not occur spontaneously.

Applying the Nernst equation to a simple electrochemical cell such as the Zn/Cu cell discussed in Section 19.2 "Standard Potentials" allows us to see how the cell voltage varies as the reaction progresses and the concentrations of the dissolved ions change. Recall that the overall reaction for this cell is as follows:

Equation 19.65

$$Zn(s) + Cu2 + (aq) \rightarrow Zn2 + (aq) + Cu(s) E \square cell = 1.10\ V$$

The reaction quotient is therefore $Q = [Zn^{2+}]/[Cu^{2+}]$. Suppose that the cell initially contains 1.0 M Cu^{2+} and 1.0×10^{-6} M Zn^{2+}. The initial voltage measured when the cell is connected can then be calculated from Equation 19.64:

Equation 19.66

$$Ecell = E \square cell - (0.0591\ Vn) log[Zn2+][Cu2+]$$
$$= 1.10\ V - (0.0591\ V2) log(1.0 \acute{} 10 - 61.0) = 1.28\ V$$

Thus the initial voltage is *greater* than $E°$ because $Q < 1$. As the reaction proceeds, $[Zn^{2+}]$ in the anode compartment increases as the zinc electrode dissolves, while $[Cu^{2+}]$ in the cathode compartment decreases as metallic copper is deposited on the electrode. During this process, the ratio $Q = [Zn^{2+}]/[Cu^{2+}]$ steadily increases, and the cell voltage therefore steadily decreases. Eventually, $[Zn^{2+}] = [Cu^{2+}]$, so $Q = 1$ and $E_{cell} = E°_{cell}$. Beyond this point, $[Zn^{2+}]$ will continue to increase in the anode compartment, and $[Cu^{2+}]$ will continue to decrease in the cathode compartment. Thus the value of Qwill increase further, leading to a further decrease in E_{cell}. When the concentrations in the two compartments are the opposite of the initial concentrations (i.e., 1.0 M $Zn^{2+}$and 1.0×10^{-6} M Cu^{2+}), $Q = 1.0 \times 10^{6}$, and the cell potential will be reduced to 0.92 V.

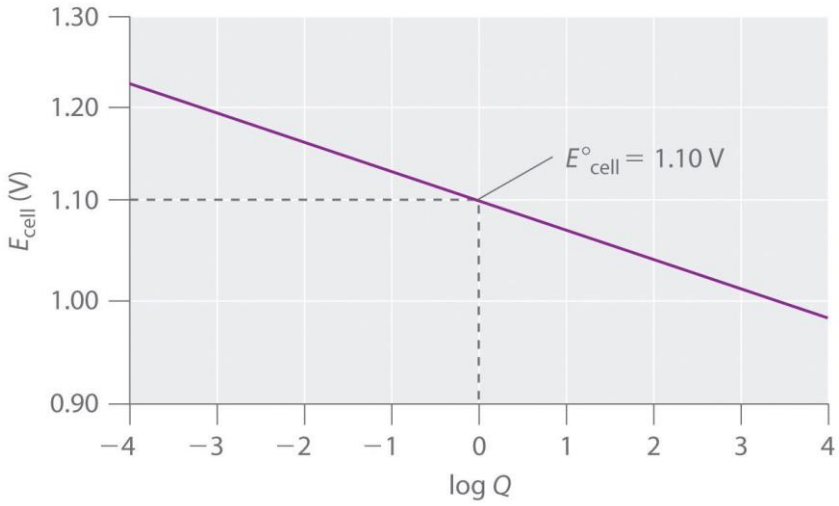
The variation of E_{cell} with log Q over this range is linear with a slope of $-0.0591/n$, as illustrated in Figure 19.11 "The Variation of ". As the reaction proceeds still further, Qcontinues to increase, and E_{cell} continues to decrease. If neither of the electrodes dissolves completely, thereby breaking the electrical circuit, the cell voltage will eventually reach zero. This is the situation that occurs when a battery is "dead." The value of Q when $E_{cell} = 0$ is calculated as follows:

Equation 19.67

$$EcellE°log\ QQ = E \square cell - (0.0591\ Vn) logQ = 0 = (0.0591\ Vn) log\ Q = E°n0.0591\ V$$
$$= (1.10\ V)(2)0.0591\ V = 37.23 = 1037.23 = 1.7 \acute{}$$

1037

Figure 19.11 *The Variation of E_{cell} with Log Q for a Zn/Cu Cell*



Initially, log Q < 0, and the voltage of the cell is greater than $E°_{cell}$. As the reaction progresses, log Q increases, and E_{cell} decreases. When $[Zn^{2+}] = [Cu^{2+}]$, log Q = 0 and $E_{cell} = E°_{cell}$ = 1.10 V. As long as the electrical circuit remains intact, the reaction will continue, and log Q will increase until Q = K and the cell voltage reaches zero. At this point, the system will have reached equilibrium.

Recall that at equilibrium, $Q = K$. Thus the equilibrium constant for the reaction of Zn metal with Cu^{2+} to give Cu metal and Zn^{2+} is 1.7×10^{37} at 25°C.

Concentration Cells

A voltage can also be generated by constructing an electrochemical cell in which each compartment contains the same redox active solution but at different concentrations. The voltage is produced as the concentrations equilibrate. Suppose, for example, we have a cell with 0.010 M $AgNO_3$ in one compartment and 1.0 M $AgNO_3$ in the other. The cell diagram and corresponding half-reactions are as follows:

Equation 19.68

$Ag(s)|\ Ag^+(aq, 0.010\ M)||\ Ag^+(aq, 1.0\ M)|\ Ag(s)$

Equation 19.69

cathode: $Ag^+(aq, 1.0\ M) + e^- \rightarrow Ag(s)$

Equation 19.70

anode: $Ag(s) \rightarrow Ag^+(aq, 0.010\ M) + e^-$

Equation 19.71

$$overall: Ag+(aq, 1.0\ M) \rightarrow Ag+(aq, 0.010\ M)$$

As the reaction progresses, the concentration of Ag^+ will increase in the left (oxidation) compartment as the silver electrode dissolves, while the Ag^+ concentration in the right (reduction) compartment decreases as the electrode in that compartment gains mass. The *total* mass of Ag(s) in the cell will remain constant, however. We can calculate the potential of the cell using the Nernst equation, inserting 0 for $E°_{cell}$ because $E°_{cathode} = -E°_{anode}$:

$$Ecell = E\,\square cell - (0.0591\ Vn) log\ Q$$
$$= 0 - (0.0591\ V1) log(0.0101.0) = 0.12\ V$$

An electrochemical cell of this type, in which the anode and cathode compartments are identical except for the concentration of a reactant, is called a concentration cell. As the reaction proceeds, the difference between the concentrations of Ag^+ in the two compartments will decrease, as will E_{cell}. Finally, when the concentration of Ag^+ is the same in both compartments, equilibrium will have been reached, and the measured potential difference between the two compartments will be zero ($E_{cell} = 0$).

EXAMPLE 10

Calculate the voltage in a galvanic cell that contains a manganese electrode immersed in a 2.0 M solution of $MnCl_2$ as the cathode, and a manganese electrode immersed in a 5.2×10^{-2} M solution of $MnSO_4$ as the anode (T = 25°C).

Given: galvanic cell, identities of the electrodes, and solution concentrations

Asked for: voltage

Strategy:

A Write the overall reaction that occurs in the cell.

B Determine the number of electrons transferred. Substitute this value into the Nernst equation to calculate the voltage.

Solution:

A This is a concentration cell, in which the electrode compartments contain the same redox active substance but at different concentrations. The anions (Cl^- and SO_4^{2-}) do not participate in the reaction, so their identity is not important. The overall reaction is as follows:

$$Mn^{2+}(aq, 2.0\ M) \rightarrow Mn^{2+}(aq, 5.2 \times 10^{-2}\ M)$$

B For the reduction of $Mn^{2+}(aq)$ to Mn(s), n = 2. We substitute this value and the given Mn^{2+} concentrations into Equation 19.64:

$$Ecell = E\,\square cell - (0.0591\ V n) log\ Q$$
$$= 0\ V - (0.0591\ V 2) log(5.2 \acute{} 10 - 22.0) = 0.047\ V$$

Thus manganese will dissolve from the electrode in the compartment that contains the more dilute solution and will be deposited on the electrode in the compartment that contains the more concentrated solution.

Exercise

Suppose we construct a galvanic cell by placing two identical platinum electrodes in two beakers that are connected by a salt bridge. One beaker contains 1.0 M HCl, and the other a 0.010 M solution of Na_2SO_4 at pH 7.00. Both cells are in contact with the atmosphere, wit $h\ PO2 = 0.20$ atm. If the relevant electrochemical reaction in both compartments is the four-electron reduction of oxygen to water, $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$, what will be the potential when the circuit is closed?

Answer: 0.41 V

Using Cell Potentials to Measure Solubility Products

Because voltages are relatively easy to measure accurately using a voltmeter, electrochemical methods provide a convenient way to determine the concentrations of very dilute solutions and the solubility products (K_{sp}) of sparingly soluble substances. As you learned in Chapter 17 "Solubility and Complexation Equilibriums", solubility products can be very small, with values of less than or equal to 10^{-30}. Equilibrium constants of this magnitude are virtually impossible to measure accurately by direct methods, so we must use alternative methods that are more sensitive, such as electrochemical methods.

To understand how an electrochemical cell is used to measure a solubility product, consider the cell shown in Figure 19.12 "A Galvanic Cell for Measuring the Solubility Product of AgCl", which is designed to measure the solubility product of silver chloride: $K_{sp} = [Ag^+][Cl^-]$. In one compartment, the cell contains a silver wire inserted into a 1.0 M solution of Ag^+; the other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl. In this system, the Ag^+ ion concentration in the first compartment equals K_{sp}. We can see this by dividing both sides of the equation for K_{sp} by $[Cl^-]$ and substituting: $[Ag^+] = K_{sp}/[Cl^-] = K_{sp}/1.0 = K_{sp}$. The overall cell reaction is as follows:

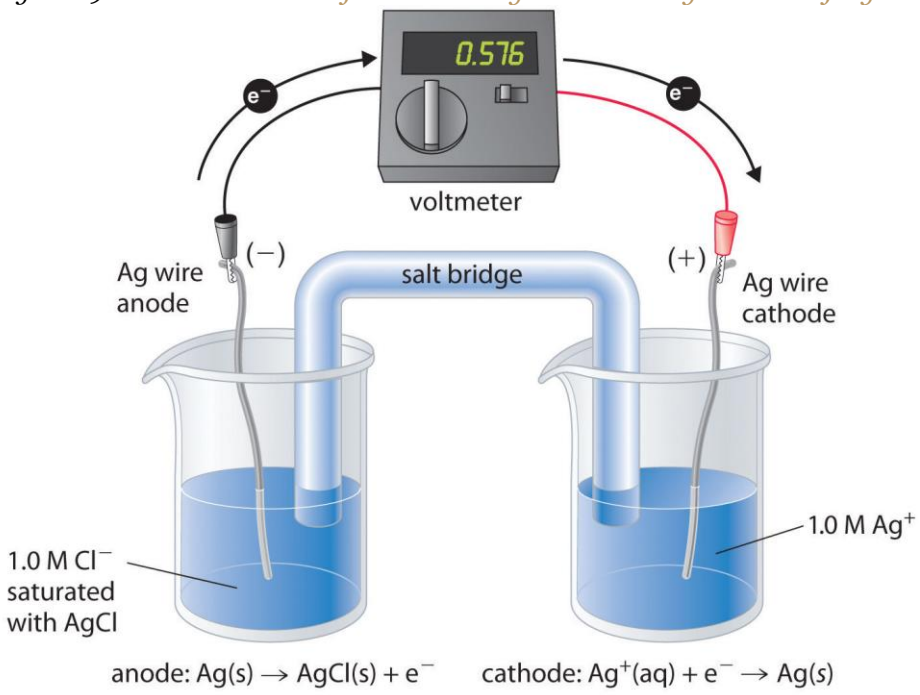
$Ag^+(aq, concentrated) \rightarrow Ag^+(aq, dilute)$

Thus the voltage of the concentration cell due to the difference in $[Ag^+]$ between the two cells is as follows:

Equation 19.72

$$Ecell = 0\ V - (0.0591\ V1)log([Ag+]dilute[Ag+]concentrated)$$
$$= - 0.0591\ V\ log(Ksp1.0) = - 0.0591\ V\ log\ Ksp$$

Figure 19.12 A Galvanic Cell for Measuring the Solubility Product of AgCl



One compartment contains a silver wire inserted into a 1.0 M solution of Ag^+, and the other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl. The potential due to the difference in $[Ag^+]$ between the two cells can be used to determine K_{sp}.

By closing the circuit, we can measure the potential caused by the difference in $[Ag^+]$ in the two cells. In this case, the experimentally measured voltage of the concentration cell at 25°C is 0.580 V.

Solving Equation 19.72 for K_{sp},

Equation 19.73

$$log\ KspKsp = - Ecell0.0591\ V = - 0.580\ V0.0591\ V = - 9.81 = 1.5\ ´\ 10 - 10$$

Thus a single potential measurement can provide the information we need to determine the value of the solubility product of a sparingly soluble salt.

EXAMPLE 11

To measure the solubility product of lead(II) sulfate ($PbSO_4$) at 25°C, you construct a galvanic cell like the one shown in Figure 19.12 "A Galvanic Cell for Measuring the Solubility Product of AgCl", which contains a 1.0 M solution of a very soluble Pb^{2+} salt [lead(II) acetate trihydrate] in one compartment that is connected

by a salt bridge to a 1.0 M solution of Na_2SO_4 saturated with $PbSO_4$ in the other. You then insert a Pb electrode into each compartment and close the circuit. Your voltmeter shows a voltage of 230 mV. What is K_{sp} for $PbSO_4$? Report your answer to two significant figures.

Given: galvanic cell, solution concentrations, electrodes, and voltage

Asked for: K_{sp}

Strategy:

A From the information given, write the equation for K_{sp}. Express this equation in terms of the concentration of Pb^{2+}.

B Determine the number of electrons transferred in the electrochemical reaction. Substitute the appropriate values into Equation 19.72 and solve for K_{sp}.

Solution:

A You have constructed a concentration cell, with one compartment containing a 1.0 M solution of Pb^{2+} and the other containing a dilute solution of Pb^{2+} in 1.0 M Na_2SO_4. As for any concentration cell, the voltage between the two compartments can be calculated using the Nernst equation. The first step is to relate the concentration of Pb^{2+} in the dilute solution to K_{sp}:

$$[Pb2+][SO42-][Pb2+] = Ksp = Ksp[SO42-] = Ksp1.0\ M = Ksp$$

B The reduction of Pb^{2+} to Pb is a two-electron process and proceeds according to the following reaction:

$Pb^{2+}(aq, concentrated) \rightarrow Pb^{2+}(aq, dilute)$

so

$$Ecell0.230\ V - 7.771.7\acute{}\ 10 - 8 = E\square cell - (0.0591n)log\ Q = 0\ V$$

$$- (0.0591\ V2)log([Pb2+]dilute[Pb2+]concentrated) = - 0.0296\ V\ log(Ksp1.0) = log\ Ksp = Ksp$$

Exercise

A concentration cell similar to the one described in Example 11 contains a 1.0 M solution of lanthanum nitrate [$La(NO_3)_3$] in one compartment and a 1.0 M solution of sodium fluoride saturated with LaF_3 in the other. A metallic La strip is inserted into each compartment, and the circuit is closed. The measured potential is 0.32 V. What is the K_{sp} for LaF_3? Report your answer to two significant figures.

Answer: 5.7×10^{-17}

Using Cell Potentials to Measure Concentrations

Another use for the Nernst equation is to calculate the concentration of a species given a measured potential and the concentrations of all the other species. We saw an example of this in Example 11, in which the experimental conditions were defined in such a way that the concentration of the metal ion was equal to K_{sp}. Potential measurements can be used to obtain the concentrations of dissolved species under other conditions as well, which explains the widespread use of electrochemical cells in many analytical devices. Perhaps the most common application is in the determination of $[H^+]$ using a pH meter, as illustrated in Example 12.

EXAMPLE 12

Suppose a galvanic cell is constructed with a standard Zn/Zn^{2+} couple in one compartment and a modified hydrogen electrode in the second compartment (Figure 19.7 "Determining a Standard Electrode Potential Using a Standard Hydrogen Electrode"). The pressure of hydrogen gas is 1.0 atm, but $[H^+]$ in the second compartment is unknown. The cell diagram is as follows:

$$Zn(s)|\ Zn^{2+}(aq,\ 1.0\ M)\ ||\ H^+(aq,\ ?\ M)|\ H_2(g,\ 1.0\ atm)|\ Pt(s)$$

What is the pH of the solution in the second compartment if the measured potential in the cell is 0.26 V at 25°C?

Given: galvanic cell, cell diagram, and cell potential

Asked for: pH of the solution

Strategy:

A Write the overall cell reaction.

B Substitute appropriate values into the Nernst equation and solve for $-\log[H^+]$ to obtain the pH.

Solution:

A Under standard conditions, the overall reaction that occurs is the reduction of protons by zinc to give H_2 (note that Zn lies below H_2 in Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C"):

$$Zn(s) + 2H2 + (aq) \rightarrow Zn2 + (aq) + H2(g) \quad E° = 0.76\ V$$

B By substituting the given values into the simplified Nernst equation (Equation 19.64), we can calculate $[H^+]$ under nonstandard conditions:

$$Ecell 0.26\ V 16.98.468.5 = E\ \square cell -$$
$$(0.0591\ Vn) log[Zn2+] PH2 [H+]2$$
$$= 0.76\ V - (0.0591\ V2) log(1.0)(1.0)[H+]2 = log$$

$$1[H+]2) = log[H+] - 2 = (-2)log[H+] = -log[H+] = pH$$

Thus the potential of a galvanic cell can be used to measure the pH of a solution.

Exercise

Suppose you work for an environmental laboratory and you want to use an electrochemical method to measure the concentration of Pb^{2+} in groundwater. You construct a galvanic cell using a standard oxygen electrode in one compartment ($E°_{cathode}$ = 1.23 V). The other compartment contains a strip of lead in a sample of groundwater to which you have added sufficient acetic acid, a weak organic acid, to ensure electrical conductivity. The cell diagram is as follows"

$$Pb(s) \mid Pb^{2+}(aq, ? M) \| H^{+}(aq), 1.0 M \mid O_2(g, 1.0 atm) \mid Pt(s)$$

When the circuit is closed, the cell has a measured potential of 1.62 V. Use Table 19.3 "Comparison of Galvanic and Electrolytic Cells" and Chapter 29 "Appendix E: Standard Reduction Potentials at 25°C" to determine the concentration of Pb^{2+} in the groundwater.

Answer: 1.2×10^{-9} M

Summary

A **coulomb (C)** relates electrical potential, expressed in volts, and energy, expressed in joules. The current generated from a redox reaction is measured in **amperes (A)**, where 1 A is defined as the flow of 1 C/s past a given point. The **faraday (*F*)** is Avogadro's number multiplied by the charge on an electron and corresponds to the charge on 1 mol of electrons. The product of the cell potential and the total charge is the maximum amount of energy available to do work, which is related to the change in free energy that occurs during the chemical process. Adding together the ΔG values for the half-reactions gives ΔG for the overall reaction, which is proportional to *both* the potential *and* the number of electrons (n) transferred. Spontaneous redox reactions have a negative ΔG and therefore a positive E_{cell}. Because the equilibrium constant K is related to ΔG, $E°_{cell}$ and K are also related. Large equilibrium constants correspond to large positive values of $E°$. The **Nernst equation** allows us to determine the spontaneous direction of any redox reaction under any reaction conditions from values of the relevant standard electrode potentials. **Concentration cells** consist of anode and cathode compartments that are identical except for the concentrations of the reactant. Because $\Delta G = 0$ at equilibrium, the measured potential of a concentration cell is zero at equilibrium (the concentrations are equal). A galvanic cell can also be used to

measure the solubility product of a sparingly soluble substance and calculate the concentration of a species given a measured potential and the concentrations of all the other species.

KEY TAKEAWAY

- The Nernst equation can be used to determine the direction of spontaneous reaction for any redox reaction in aqueous solution.

KEY EQUATIONS

Charge on a mole of electrons (faraday)

Equation 19.49: $F \approx 96{,}486\ \text{J/(V·mol)}$

Maximum work from an electrochemical cell

Equation 19.50: $w_{max} = -nFE_{cell}$

Relationship between Δ *G* ° and Δ *E* °

Equation 19.52: $\Delta G^\circ = -nFE^\circ_{cell}$

Relationship between Δ *G* ° and *K* for a redox reaction

Equation 19.57: $\Delta G^\circ = -RT \ln K$

Relationship between Δ *E* ° and *K* for a redox reaction at 25°C

Equation 19.59: $E^\circ_{cell} = (RTnF) \ln K$

$$Equation\ 19.60: E^\circ_{cell} = (0.0591\ Vn) \log K$$

Relationship between Δ *G* ° and *Q*

Equation 19.61: $\Delta G = \Delta G^\circ + RT \ln Q$

Relationship between E_{cell} and *Q* at 25°C

$$Equation\ 19.64: E_{cell} = E^\circ_{cell} - (0.0591\ Vn) \log Q$$

CONCEPTUAL PROBLEMS

1. State whether you agree or disagree with this reasoning and explain your answer: Standard electrode potentials arise from the number of electrons transferred. The greater the number of electrons transferred, the greater the measured potential difference. If 1 mol of a substance produces 0.76 V when 2 mol of electrons are transferred—as in $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$—then 0.5 mol of the substance will produce 0.76/2 V because only 1 mol of electrons is transferred.

2. What is the relationship between the *measured cell potential* and the *total charge* that passes through a cell? Which of these is dependent on concentration? Which is dependent on the identity of the oxidant or the reductant? Which is dependent on the number of electrons transferred?
3. In the equation $w_{max} = -nFE°_{cell}$, which quantities are extensive properties and which are intensive properties?
4. For any spontaneous redox reaction, E is positive. Use thermodynamic arguments to explain why this is true.
5. State whether you agree or disagree with this statement and explain your answer: Electrochemical methods are especially useful in determining the reversibility or irreversibility of reactions that take place in a cell.
6. Although the sum of two half-reactions gives another half-reaction, the sum of the potentials of the two half-reactions cannot be used to obtain the potential of the net half-reaction. Why? When does the sum of two half-reactions correspond to the overall reaction? Why?
7. Occasionally, you will find high-quality electronic equipment that has its electronic components plated in gold. What is the advantage of this?
8. *Blood analyzers, which measure pH, PCO2,*
9. *and PO2, are frequently used in clinical emergencies. For example, blood PCO2 is measured with a pH electrode covered with a plastic*
10. membrane that is permeable to CO_2. Based on your knowledge of how electrodes function, explain how such an electrode might work. Hint: $CO_2(g) + H_2O(l) \rightarrow HCO_3^-(aq) + H^+(aq)$.
11. Concentration cells contain the same species in solution in two different compartments. Explain what produces a voltage in a concentration cell. When does V = 0 in such a cell?
12. Describe how an electrochemical cell can be used to measure the solubility of a sparingly soluble salt.

ANSWERS

1.
2.
3. extensive: w_{max} and n; intensive: $E°_{cell}$
4.
5.
6.
7. Gold is highly resistant to corrosion because of its very positive reduction potential.
8.

9.

10.

NUMERICAL PROBLEMS

1. The chemical equation for the combustion of butane is as follows:

$$C4H10(g)+132O2(g)\rightarrow 4CO2(g)+5H2O(g)$$

This reaction has $\Delta H° = -2877$ kJ/mol. Calculate $E°_{cell}$ and then determine $\Delta G°$. Is this a spontaneous process? What is the change in entropy that accompanies this process at 298 K?

2. How many electrons are transferred during the reaction $Pb(s) + Hg_2Cl_2(s) \rightarrow PbCl_2(aq) + 2Hg(l)$? What is the standard cell potential? Is the oxidation of Pb by Hg_2Cl_2spontaneous? Calculate $\Delta G°$ for this reaction.
3. For the cell represented as $Al(s)|\ Al^{3+}(aq)||\ Sn^{2+}(aq), Sn^{4+}(aq)|\ Pt(s)$, how many electrons are transferred in the redox reaction? What is the standard cell potential? Is this a spontaneous process? What is $\Delta G°$?
4. Explain why the sum of the potentials for the half-reactions $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ and $Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$ does not equal the potential for the reaction $Sn^{4+}(aq) + 4e^- \rightarrow Sn(s)$. What is the net cell potential? Compare the values of $\Delta G°$ for the sum of the potentials and the actual net cell potential.
5. Based on Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C"and Chapter 29 "Appendix E: Standard Reduction Potentials at 25°C", do you agree with the proposed potentials for the following half-reactions? Why or why not?

a. $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$, $E° = 0.68$ V

b. $Ce^{4+}(aq) + 4e^- \rightarrow Ce(s)$, $E° = -0.62$ V

6. For each reaction, calculate $E°_{cell}$ and then determine $\Delta G°$. Indicate whether each reaction is spontaneous.

a. $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$

b. $K_2S_2O_6(aq) + I_2(s) \rightarrow 2KI(aq) + 2K_2SO_4(aq)$

c. $Sn(s) + CuSO_4(aq) \rightarrow Cu(s) + SnSO_4(aq)$

7. What is the standard change in free energy for the reaction between Ca^{2+} and Na(s) to give Ca(s) and Na^+? Do the sign and magnitude of $\Delta G°$ agree with what you would expect based on the positions of these elements in the periodic table? Why or why not?
8. In acidic solution, permanganate (MnO_4^-) oxidizes Cl^- to chlorine gas, and MnO_4^- is reduced to $Mn^{2+}(aq)$.

a. Write the balanced chemical equation for this reaction.

b. Determine $E°_{cell}$.

c. Calculate the equilibrium constant.

9. Potentiometric titrations are an efficient method for determining the endpoint of a redox titration. In such a titration, the potential of the solution is monitored as measured volumes of an oxidant or a reductant are added. Data for a typical titration, the potentiometric titration of Fe(II) with a 0.1 M solution of Ce(IV), are given in the following table. The starting potential has been arbitrarily set equal to zero because it is the *change* in potential with the addition of the oxidant that is important.

Titrant (mL)	*E* (mV)
2.00	50
6.00	100
9.00	255
10.00	960
11.00	1325
12.00	1625
14.00	1875

a. Write the balanced chemical equation for the oxidation of Fe^{2+} by Ce^{4+}.

b. Plot the data and then locate the endpoint.

c. How many millimoles of Fe^{2+} did the solution being titrated originally contain?

10. The standard electrode potential ($E°$) for the half-reaction $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ is −0.257 V. What pH is needed for this reaction to take place in the presence of 1.00 atm $H_2(g)$ as the reductant if $[Ni^{2+}]$ is 1.00 M?

11. The reduction of Mn(VII) to Mn(s) by $H_2(g)$ proceeds in five steps that can be readily followed by changes in the color of the solution. Here is the redox chemistry:

a. $MnO_4^-(aq) + e^- \rightarrow MnO_4^{2-}(aq)$; $E° = +0.56$ V (purple → dark green)

b. $MnO_4^{2-}(aq) + 2e^- + 4H^+(aq) \rightarrow MnO_2(s)$; $E° = +2.26$ V (dark green → dark brown solid)

c. $MnO_2(s) + e^- + 4H^+(aq) \rightarrow Mn^{3+}(aq)$; $E° = +0.95$ V (dark brown solid → red-violet)

d. $Mn^{3+}(aq) + e^- \rightarrow Mn^{2+}(aq)$; $E° = +1.51$ V (red-violet → pale pink)

e. $Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$; $E° = -1.18$ V (pale pink → colorless)

f. Is the reduction of MnO_4^- to $Mn^{3+}(aq)$ by $H_2(g)$ spontaneous under standard conditions? What is $E°_{cell}$?

g. Is the reduction of $Mn^{3+}(aq)$ to Mn(s) by $H_2(g)$ spontaneous under standard conditions? What is $E°_{cell}$?

12. Mn(III) can disproportionate (both oxidize and reduce itself) by means of the following half-reactions:

a. $Mn3+(aq)+e- \rightarrow Mn2+(aq) E° = 1.51\ V$

b. $Mn3+(aq)+2H2O(l) \rightarrow MnO2(s)+4H+(aq)+e- E° = 0.95\ V$

c. What is $E°$ for the disproportionation reaction?

d. Is disproportionation more or less thermodynamically favored at low pH than at pH 7.0? Explain your answer.

e. How could you prevent the disproportionation reaction from occurring?

13. For the reduction of oxygen to water, $E°$ = 1.23 V. What is the potential for this half-reaction at pH 7.00? What is the potential in a 0.85 M solution of NaOH?

14. The biological molecule abbreviated as NADH (reduced nicotinamide adenine dinucleotide) can be formed by reduction of NAD^+ (nicotinamide adenine dinucleotide) via the half-reaction $NAD^+ + H^+ + 2e^- \rightarrow$ NADH; $E°$ = −0.32 V.

a. Would NADH be able to reduce acetate to pyruvate?

b. Would NADH be able to reduce pyruvate to lactate?

c. What potential is needed to convert acetate to lactate?

15. $pyruvate + 2H++2e- \rightarrow lactate\ E° = -0.185\ V$

16. $pyruvate + 2H++2e- \rightarrow lactate\ E° = -0.185\ V$

17. Given the following biologically relevant half-reactions, will FAD (flavin adenine dinucleotide), a molecule used to transfer electrons whose reduced form is $FADH_2$, be an effective oxidant for the conversion of acetaldehyde to acetate at pH 4.00?

18. $acetate + 2H++2e- \rightarrow acetaldehyde+H2O E° = -0.58\ V$

19. $FAD + 2H++2e- \rightarrow FADH2 E° = -0.18\ V$

20. Ideally, any half-reaction with $E°$ > 1.23 V will oxidize water as a result of the half-reaction $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$.

a. Will FeO_4^{2-} oxidize water if the half-reaction for the reduction of Fe(VI) → Fe(III) is $FeO_4^{2-}(aq) + 8H^+(aq) + 3e^- \rightarrow Fe^{3+}(aq) + 4H_2O$; $E°$ = 1.9 V?

b. What is the highest pH at which this reaction will proceed spontaneously if [Fe^{3+}] = [FeO_4^{2-}] = 1.0 M and $d\ PO2 =$

c. 1.0 atm?

21. Under acidic conditions, ideally any half-reaction with $E°$ > 1.23 V will oxidize water via the reaction $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$.

a. Will aqueous acidic $KMnO_4$ evolve oxygen with the formation of MnO_2?

b. At pH 14.00, what is $E°$ for the oxidation of water by aqueous $KMnO_4$ (1 M) with the formation of MnO_2?

c. At pH 14.00, will water be oxidized if you are trying to form MnO_2 from MnO_4^{2-} via the reaction $2MnO_4^{2-}(aq) + 2H_2O(l) \rightarrow 2MnO_2(s) + O_2(g) + 4OH^-(aq)$?

22. Complexing agents can bind to metals and result in the net stabilization of the complexed species. What is the net thermodynamic stabilization energy that results from using CN^- as a complexing agent for Mn^{3+}/Mn^{2+}?

23. $Mn3+(aq)+e- \rightarrow Mn2+(aq)\ E° = 1.51\ V$

24. $Mn(CN)63-(aq)+e- \rightarrow Mn(CN)64-\ E° = -0.24\ V$

25. You have constructed a cell with zinc and lead amalgam electrodes described by the cell diagram $Zn(Hg)(s)|\ Zn(NO_3)_2(aq)\|\ Pb(NO_3)_2(aq)|\ Pb(Hg)(s)$. If you vary the concentration of $Zn(NO_3)_2$ and measure the potential at different concentrations, you obtain the following data:

$Zn(NO_3)_2$ (M)	E_{cell} (V)
0.0005	0.7398
0.002	0.7221
0.01	0.7014

a. Write the half-reactions that occur in this cell.

b. What is the overall redox reaction?

c. What is $E°_{cell}$? What is $\Delta G°$ for the overall reaction?

d. What is the equilibrium constant for this redox reaction?

26. Hydrogen gas reduces Ni^{2+} according to the following reaction: $Ni^{2+}(aq) + H_2(g) \rightarrow Ni(s) + 2H^+(aq)$; $E°_{cell}$ = −0.25 V; ΔH = 54 kJ/mol.

a. What is K for this redox reaction?

b. Is this reaction likely to occur?

c. What conditions can be changed to increase the likelihood that the reaction will occur as written?

d. Is the reaction more likely to occur at higher or lower pH?

27. The silver–silver bromide electrode has a standard potential of 0.07133 V. What is K_{sp} of AgBr?

ANSWERS

1.

2.

3. $6e^-$; $E°_{cell}$ = 1.813 V; the reaction is spontaneous; $\Delta G°$ = −525 kJ/mol Al.

4.

5.

6.

7.

8.

9.

10.

11.

12.

13.

14.

15. yes; $E°$ = 0.40 V

16.

17.

a. yes; $E°$ = 0.45 V

b. 0.194 V

c. yes; $E°$ = 0.20 V

19.5 Commercial Galvanic Cells

LEARNING OBJECTIVE

1. To learn how commercial galvanic cells work.

Because galvanic cells can be self-contained and portable, they can be used as batteries and fuel cells.

A battery (storage cell) is a galvanic cell (or a series of galvanic cells) that contains all the reactants needed to produce electricity. In contrast, a fuel cell is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. In this section, we describe the chemistry behind some of the more common types of batteries and fuel cells.

Batteries

There are two basic kinds of batteries: *disposable*, or *primary*, batteries, in which the electrode reactions are effectively irreversible and which cannot be recharged; and*rechargeable*, or *secondary*, batteries, which form an insoluble product that adheres to the electrodes. These batteries can be recharged by applying an electrical potential in the reverse direction. The recharging process temporarily converts a rechargeable battery from a galvanic cell to an electrolytic cell.

Batteries are cleverly engineered devices that are based on the same fundamental laws as galvanic cells. The major difference between batteries and the galvanic cells we have previously described is that commercial batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass. The use of highly concentrated or solid reactants has another beneficial effect: the concentrations of the reactants and the products do not change greatly as the battery is discharged; consequently, the output voltage remains remarkably constant during the discharge process. This behavior is in contrast to that of the Zn/Cu cell, whose output decreases logarithmically as the reaction proceeds (Figure 19.11 "The Variation of "). When a battery consists of more than one galvanic cell, the cells are usually connected in series—that is, with the positive (+) terminal of one cell connected to the negative (–) terminal of the next, and so forth. The overall voltage of the battery is therefore the sum of the voltages of the individual cells.

Leclanché Dry Cell

The dry cell, by far the most common type of battery, is used in flashlights, electronic devices such as the Walkman and Game Boy, and many other devices. Although the dry cell was patented in 1866 by the French chemist Georges Leclanché and more than 5 billion such cells are sold every year, the details of its electrode chemistry are still not completely understood. In spite of its name, the Leclanché dry cell is actually a “wet cell”: the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$,

graphite, and starch (part (a) in Figure 19.13 "Three Kinds of Primary (Nonrechargeable) Batteries"). The half-reactions at the anode and the cathode can be summarized as follows:

Equation 19.74
cathode: $2MnO_2(s) + 2NH_4^+(aq) + 2e^- \rightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$

Equation 19.75
anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

The Zn^{2+} ions formed by the oxidation of Zn(s) at the anode react with NH_3 formed at the cathode and Cl^- ions present in solution, so the overall cell reaction is as follows:

Equation 19.76
overall: $2MnO_2(s) + 2NH_4Cl(aq) + Zn(s) \rightarrow Mn_2O_3(s) + Zn(NH_3)_2Cl_2(s) + H_2O(l)$

The dry cell produces about 1.55 V and is inexpensive to manufacture. It is not, however, very efficient in producing electrical energy because only the relatively small fraction of the MnO_2 that is near the cathode is actually reduced and only a small fraction of the zinc cathode is actually consumed as the cell discharges. In addition, dry cells have a limited shelf life because the Zn anode reacts spontaneously with NH_4Cl in the electrolyte, causing the case to corrode and allowing the contents to leak out.

The alkaline battery is essentially a Leclanché cell adapted to operate under alkaline, or basic, conditions. The half-reactions that occur in an alkaline battery are as follows:

Equation 19.77
cathode: $2MnO_2(s) + H_2O(l) + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq)$

Equation 19.78
anode: $Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$

Equation 19.79
$$overall: Zn(s) + 2MnO2(s) \rightarrow ZnO(s) + Mn2O3(s)$$

This battery also produces about 1.5 V, but it has a longer shelf life and more constant output voltage as the cell is discharged than the Leclanché dry cell. Although the alkaline battery is more expensive to produce than the Leclanché dry cell, the improved performance makes this battery more cost-effective.

Button Batteries

Although some of the small *button* batteries used to power watches, calculators, and cameras are miniature alkaline cells, most are based on a completely different chemistry. In these batteries, the anode is a zinc–mercury amalgam rather than pure zinc, and the cathode uses either HgO or Ag_2O as the oxidant

rather than MnO_2 (part (b) in Figure 19.13 "Three Kinds of Primary (Nonrechargeable) Batteries"). The cathode and overall reactions and cell output for these two types of button batteries are as follows:

Equation 19.80
cathode (Hg): $HgO(s) + H_2O(l) + 2e^- \rightarrow Hg(l) + 2OH^-(aq)$

Equation 19.81
$$overall\ (Hg): Zn(s) + 2HgO(s) \rightarrow Hg(l) + ZnO(s) \quad Ecell = 1.35\ V$$

Equation 19.82
cathode (Ag): $Ag_2O(s) + H_2O(l) + 2e^- \rightarrow 2Ag(s) + 2OH^-(aq)$

Equation 19.83
$$overall\ (Ag): Zn(s) + 2Ag2O(s)$$
$$\rightarrow 2Ag(s) + ZnO(s) \quad Ecell = 1.6\ V$$

The major advantages of the mercury and silver cells are their reliability and their high output-to-mass ratio. These factors make them ideal for applications where small size is crucial, as in cameras and hearing aids. The disadvantages are the expense and the environmental problems caused by the disposal of heavy metals, such as Hg and Ag.

Lithium–Iodine Battery

None of the batteries described above is actually “dry.” They all contain small amounts of liquid water, which adds significant mass and causes potential corrosion problems. Consequently, substantial effort has been expended to develop water-free batteries.

One of the few commercially successful water-free batteries is the lithium–iodine battery. The anode is lithium metal, and the cathode is a solid complex of I_2. Separating them is a layer of solid LiI, which acts as the electrolyte by allowing the diffusion of Li^+ ions. The electrode reactions are as follows:

Equation 19.84
cathode: $I_2(s) + 2e^- \rightarrow 2I^-(LiI)$

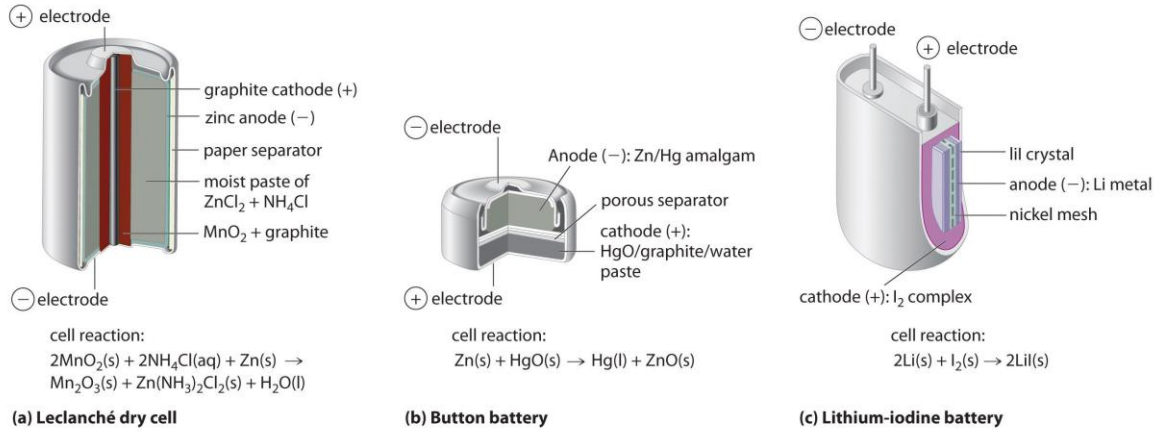
Equation 19.85
anode: $2Li(s) \rightarrow 2Li^+(LiI) + 2e^-$

Equation 19.86
$$overall: 2Li(s) + I2(s) \rightarrow 2LiI(s)$$
$$Ecell = 3.5\ VAs\ shown\ in\ part$$

(c) in Figure 19.13 "Three Kinds of Primary (Nonrechargeable) Batteries", a typical lithium–iodine battery consists of two cells separated by a nickel metal mesh that collects charge from the anode. Because of the high internal resistance

caused by the solid electrolyte, only a low current can be drawn. Nonetheless, such batteries have proven to be long-lived (up to 10 yr) and reliable. They are therefore used in applications where frequent replacement is difficult or undesirable, such as in cardiac pacemakers and other medical implants and in computers for memory protection. These batteries are also used in security transmitters and smoke alarms. Other batteries based on lithium anodes and solid electrolytes are under development, using TiS_2, for example, for the cathode.

Figure 19.13 *Three Kinds of Primary (Nonrechargeable) Batteries*



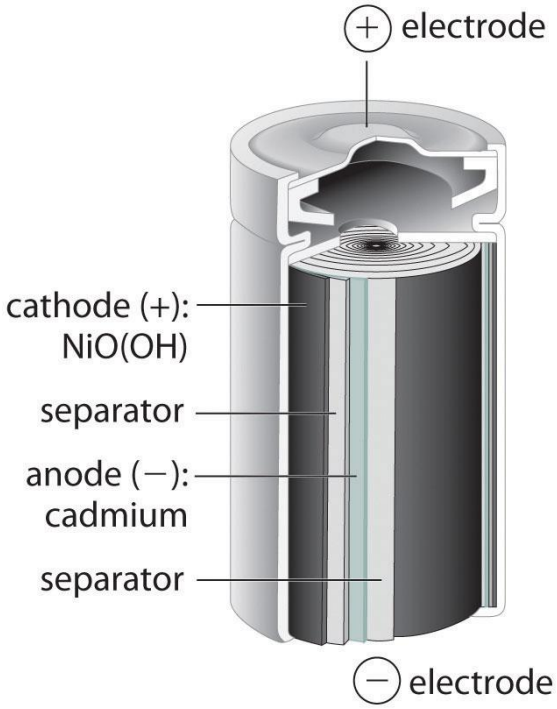
(a) A Leclanché dry cell is actually a "wet cell," in which the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch. Though inexpensive to manufacture, the cell is not very efficient in producing electrical energy and has a limited shelf life. (b) In a button battery, the anode is a zinc–mercury amalgam, and the cathode can be either HgO (shown here) or Ag_2O as the oxidant. Button batteries are reliable and have a high output-to-mass ratio, which allows them to be used in applications such as calculators and watches, where their small size is crucial. (c) A lithium–iodine battery consists of two cells separated by a metallic nickel mesh that collects charge from the anodes. The anode is lithium metal, and the cathode is a solid complex of I_2. The electrolyte is a layer of solid LiI that allows Li^+ ions to diffuse from the cathode to the anode. Although this type of battery produces only a relatively small current, it is highly reliable and long-lived.

Dry cells, button batteries, and lithium–iodine batteries are disposable and cannot be recharged once they are discharged. Rechargeable batteries, in contrast, offer significant economic and environmental advantages because they can be recharged and discharged numerous times. As a result, manufacturing and disposal costs drop dramatically for a given number of hours of battery usage. Two common rechargeable batteries are the nickel–cadmium battery and the lead–acid battery, which we describe next.

Nickel–Cadmium (NiCad) Battery

The nickel–cadmium, or *NiCad*, battery is used in small electrical appliances and devices like drills, portable vacuum cleaners, and AM/FM digital tuners. It is a water-based cell with a cadmium anode and a highly oxidized nickel cathode that is usually described as the nickel(III) oxo-hydroxide, NiO(OH). As shown in Figure 19.14 "The Nickel–Cadmium (NiCad) Battery, a Rechargeable Battery", the design maximizes the surface area of the electrodes and minimizes the distance between them, which decreases internal resistance and makes a rather high discharge current possible.

Figure 19.14 *The Nickel–Cadmium (NiCad) Battery, a Rechargeable Battery*



cell reaction:

$$Cd(s) + 2NiO(OH)(s) + 2H_2O(l) \rightarrow Cd(OH)_2(s) + 2Ni(OH)_2(s)$$

NiCad batteries contain a cadmium anode and a highly oxidized nickel cathode. This design maximizes the surface area of the electrodes and minimizes the distance between them, which gives the battery both a high discharge current and a high capacity.

The electrode reactions during the discharge of a NiCad battery are as follows:

Equation 19.87

cathode: $2NiO(OH)(s) + 2H_2O(l) + 2e^- \rightarrow 2Ni(OH)_2(s) + 2OH^-(aq)$

Equation 19.88

anode: $Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$

Equation 19.89

$$overall: Cd(s) + 2NiO(OH)(s) + 2H2O(l) \rightarrow Cd(OH)2(s) + 2Ni(OH)2(s) \quad Ecell = 1.4\ V$$

Because the products of the discharge half-reactions are solids that adhere to the electrodes [$Cd(OH)_2$ and $2Ni(OH)_2$], the overall reaction is readily reversed when the cell is recharged. Although NiCad cells are lightweight, rechargeable, and high capacity, they have certain disadvantages. For example, they tend to lose capacity quickly if not allowed to discharge fully before recharging, they do not store well for long periods when fully charged, and they present significant environmental and disposal problems because of the toxicity of cadmium.

A variation on the NiCad battery is the nickel–metal hydride battery (NiMH) used in hybrid automobiles, wireless communication devices, and mobile computing. The overall chemical equation for this type of battery is as follows:

$NiO(OH)(s) + MH \rightarrow Ni(OH)_2(s) + M(s)$

The NiMH battery has a 30%–40% improvement in capacity over the NiCad battery; it is more environmentally friendly so storage, transportation, and disposal are not subject to environmental control; and it is not as sensitive to recharging memory. It is, however, subject to a 50% greater self-discharge rate, a limited service life, and higher maintenance, and it is more expensive than the NiCad battery.

Lead–Acid (Lead Storage) Battery

The lead–acid battery is used to provide the starting power in virtually every automobile and marine engine on the market. Marine and car batteries typically consist of multiple cells connected in series. The total voltage generated by the battery is the potential per cell (E°_{cell}) times the number of cells. As shown in Figure 19.15 "One Cell of a Lead–Acid Battery", the anode of each cell in a lead storage battery is a plate or grid of spongy lead metal, and the cathode is a similar grid containing powdered lead dioxide (PbO_2). The electrolyte is usually an approximately 37% solution (by mass) of sulfuric acid in water, with a density of 1.28 g/mL (about 4.5 M H_2SO_4). Because the redox active species are solids, there is no need to separate the electrodes. The electrode reactions in each cell during discharge are as follows:

Equation 19.90

$$cathode: PbO2(s) + HSO4^-(aq) + 3H^+(aq) + 2e^- \rightarrow PbSO4(s) + 2H2O(l) \quad E^\circ cathode = 1.685\ V$$

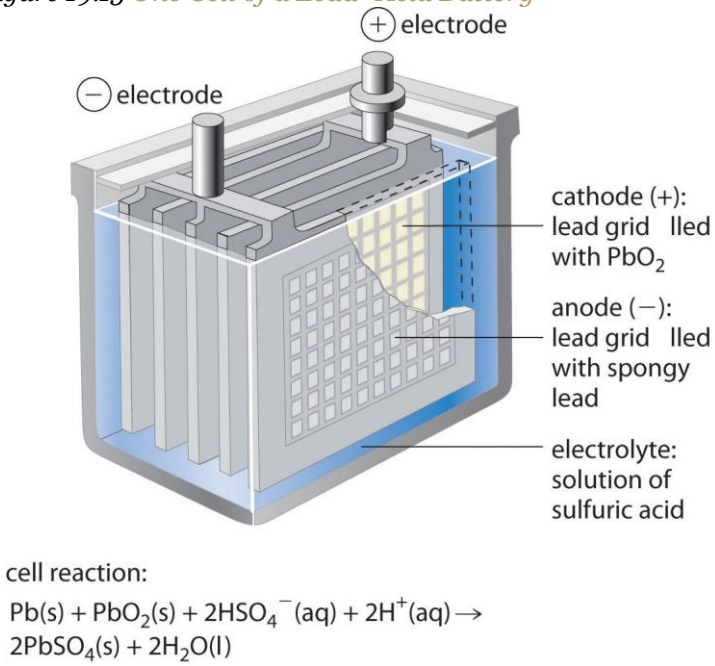
Equation 19.91

$$anode: Pb(s) + HSO4^-(aq) \rightarrow PbSO4(s) + H^+(aq) + 2e^- \quad E^\circ anode = -0.356\ V$$

Equation 19.92

$$overall: Pb(s) + PbO2(s) + 2HSO4^-(aq) + 2H^+(aq) \rightarrow 2PbSO4(s) + 2H2O(l) \quad E^\circ cell = 2.041\ V$$

Figure 19.15 One Cell of a Lead–Acid Battery



The anodes in each cell of a rechargeable battery are plates or grids of lead containing spongy lead metal, while the cathodes are similar grids containing powdered lead dioxide (PbO_2). The electrolyte is an aqueous solution of sulfuric acid. The value of E° for such a cell is about 2 V. Connecting three such cells in series produces a 6 V battery, whereas a typical 12 V car battery contains six cells in series. When treated properly, this type of high-capacity battery can be discharged and recharged many times over.

As the cell is discharged, a powder of $PbSO_4$ forms on the electrodes. Moreover, sulfuric acid is consumed and water is produced, decreasing the density of the electrolyte and providing a convenient way of monitoring the status of a battery by simply measuring the density of the electrolyte.

When an external voltage in excess of 2.04 V per cell is applied to a lead–acid battery, the electrode reactions reverse, and $PbSO_4$ is converted back to metallic lead and PbO_2. If the battery is recharged too vigorously, however, electrolysis of water can occur, resulting in the evolution of potentially explosive hydrogen gas. (For more information on electrolysis, see Section 19.7 "Electrolysis".) The gas bubbles formed in this way can dislodge some of the $PbSO_4$ or PbO_2 particles from the grids, allowing them to fall to the bottom of the cell, where they can build up and cause an internal short circuit. Thus the recharging process must be carefully monitored to optimize the life of the battery. With proper care, however, a lead–acid battery can be discharged and recharged thousands of times. In automobiles, the alternator supplies the electric current that causes the discharge reaction to reverse.

Fuel Cells

A fuel cell is a galvanic cell that requires a constant external supply of reactants because the products of the reaction are continuously removed. Unlike a battery, it does not store chemical or electrical energy; a fuel cell allows electrical energy to be extracted directly from a chemical reaction. In principle, this should be a more efficient process than, for example, burning the fuel to drive an internal combustion engine that turns a generator, which is typically less than 40% efficient, and in fact, the efficiency of a fuel cell is generally between 40% and 60%. Unfortunately, significant cost and reliability problems have hindered the wide-scale adoption of fuel cells. In practice, their use has been restricted to applications in which mass may be a significant cost factor, such as US manned space vehicles.

These space vehicles use a hydrogen/oxygen fuel cell that requires a continuous input of $H_2(g)$ and $O_2(g)$, as illustrated in Figure 19.16 "A Hydrogen Fuel Cell Produces Electrical Energy Directly from a Chemical Reaction". The electrode reactions are as follows:

Equation 19.93

cathode: $O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(g)$

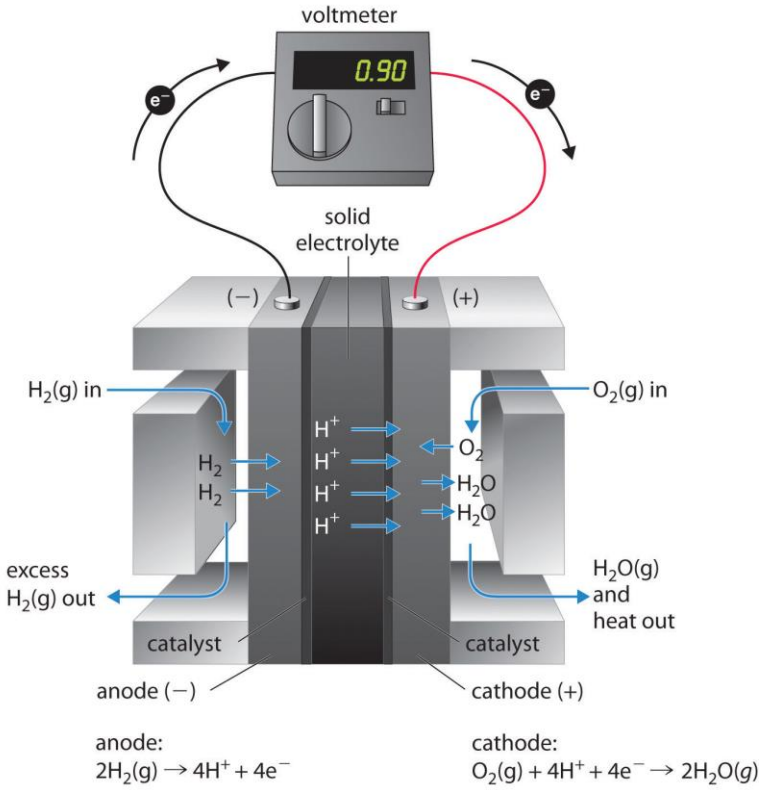
Equation 19.94

anode: $2H_2(g) \rightarrow 4H^+ + 4e^-$

Equation 19.95

$$overall: 2H2(g)+O2(g)\rightarrow 2H2O(g)$$

Figure 19.16 *A Hydrogen Fuel Cell Produces Electrical Energy Directly from a Chemical Reaction*



Hydrogen is oxidized to protons at the anode, and the electrons are transferred through an external circuit to the cathode, where oxygen is reduced and combines with H^+ to form water. A solid electrolyte allows the protons to diffuse from the anode to the cathode. Although fuel cells are an essentially pollution-free means of obtaining electrical energy, their expense and technological complexity have thus far limited their applications.

The overall reaction represents an essentially pollution-free conversion of hydrogen and oxygen to water, which in space vehicles is then collected and used. Although this type of fuel cell should produce 1.23 V under standard conditions, in practice the device achieves only about 0.9 V. One of the major barriers to achieving greater efficiency is the fact that the four-electron reduction of $O_2(g)$ at the cathode is intrinsically rather slow, which limits current that can be achieved. All major automobile manufacturers have major research programs involving fuel cells: one of the most important goals is the development of a better catalyst for the reduction of O_2.

Summary

A **battery** is a contained unit that produces electricity, whereas a **fuel cell** is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. One type of battery is the **Leclanché dry cell**, which contains an electrolyte in an acidic water-based paste. This battery is

called an **alkaline battery** when adapted to operate under alkaline conditions. Button batteries have a high output-to-mass ratio; **lithium–iodine batteries** consist of a solid electrolyte; the **nickel–cadmium** (NiCad) battery is rechargeable; and the **lead–acid battery**, which is also rechargeable, does not require the electrodes to be in separate compartments. A fuel cell requires an external supply of reactants as the products of the reaction are continuously removed. In a fuel cell, energy is not stored; electrical energy is provided by a chemical reaction.

KEY TAKEAWAY

- Commercial batteries are galvanic cells that use solids or pastes as reactants to maximize the electrical output per unit mass.

CONCEPTUAL PROBLEMS

1. What advantage is there to using an alkaline battery rather than a Leclanché dry cell?
2. Why does the density of the fluid in lead–acid batteries drop when the battery is discharged?
3. What type of battery would you use for each application and why?

a. powering an electric motor scooter

b. a backup battery for a smartphone

c. powering an iPod

4. Why are galvanic cells used as batteries and fuel cells? What is the difference between a battery and a fuel cell? What is the advantage to using highly concentrated or solid reactants in a battery?

ANSWER

1.

2.

3.

a. lead storage battery

b. lithium–iodine battery

c. NiCad, NiMH, or lithium ion battery (rechargeable)

4.

NUMERICAL PROBLEM

1. This reaction is characteristic of a lead storage battery:

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

If you have a battery with an electrolyte that has a density of 1.15 g/cm^3 and contains 30.0% sulfuric acid by mass, is the potential greater than or less than that of the standard cell?

ANSWER

1. $[H_2SO_4]$ = 3.52 M; $E > E°$

19.6 Corrosion

LEARNING OBJECTIVE

1. To understand the process of corrosion.

Corrosion is a galvanic process by which metals deteriorate through oxidation—usually but not always to their oxides. For example, when exposed to air, iron rusts, silver tarnishes, and copper and brass acquire a bluish-green surface called a *patina*. Of the various metals subject to corrosion, iron is by far the most important commercially. An estimated $100 billion per year is spent in the United States alone to replace iron-containing objects destroyed by corrosion. Consequently, the development of methods for protecting metal surfaces from corrosion constitutes a very active area of industrial research. In this section, we describe some of the chemical and electrochemical processes responsible for corrosion. We also examine the chemical basis for some common methods for preventing corrosion and treating corroded metals.

Note the Pattern

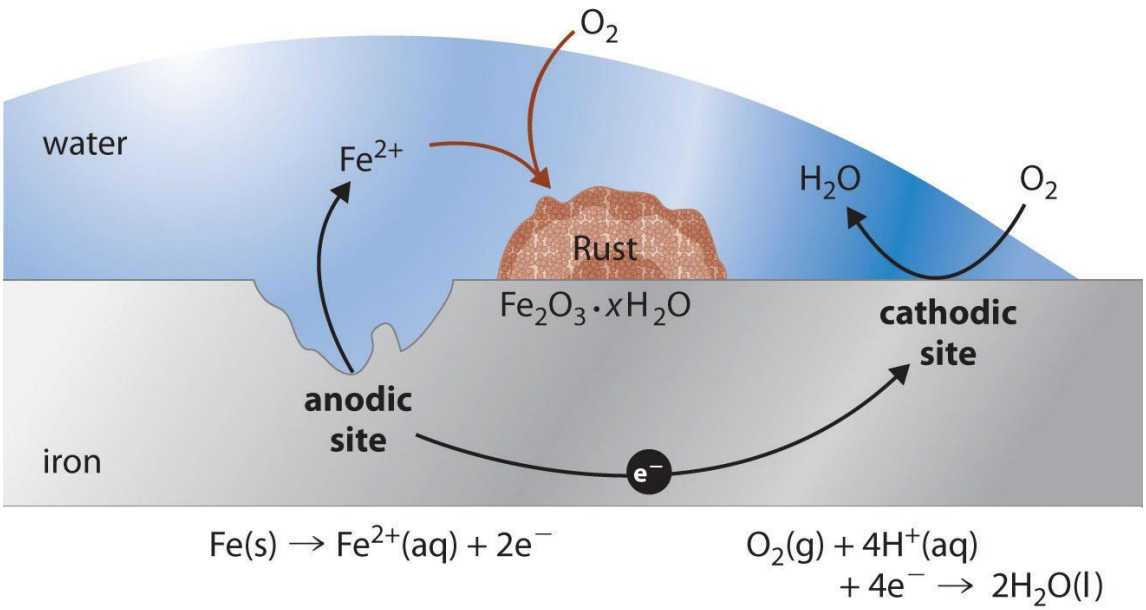
Corrosion is a galvanic process.

Under ambient conditions, the oxidation of most metals is thermodynamically spontaneous, with the notable exception of gold and platinum. Hence it is actually somewhat surprising that any metals are useful at all in Earth's moist, oxygen-rich atmosphere. Some metals, however, are resistant to corrosion for kinetic reasons. For example, aluminum in soft-drink cans and airplanes is protected by a thin coating of metal oxide that forms on the surface of the metal and acts as an impenetrable barrier that prevents further destruction. Aluminum cans also have a thin plastic layer to prevent reaction of the oxide with acid in the soft drink. Chromium, magnesium, and nickel also form protective oxide films. Stainless steels are remarkably resistant to corrosion because they usually contain a significant proportion of chromium, nickel, or both.

In contrast to these metals, when iron corrodes, it forms a red-brown hydrated metal oxide ($Fe_2O_3 \cdot xH_2O$), commonly known as *rust*, that does not provide a tight protective film (Figure 19.17 "Rust, the Result of Corrosion of Metallic Iron"). Instead, the rust continually flakes off to expose a fresh metal surface vulnerable to reaction with oxygen and water. Because both oxygen and water are required for rust to form, an iron nail immersed in

deoxygenated water will not rust—even over a period of several weeks. Similarly, a nail immersed in an organic solvent such as kerosene or mineral oil saturated with oxygen will not rust because of the absence of water.

Figure 19.17 *Rust, the Result of Corrosion of Metallic Iron*



Iron is oxidized to $Fe^{2+}(aq)$ at an anodic site on the surface of the iron, which is often an impurity or a lattice defect. Oxygen is reduced to water at a different site on the surface of the iron, which acts as the cathode. Electrons are transferred from the anode to the cathode through the electrically conductive metal. Water is a solvent for the Fe^{2+} that is produced initially and acts as a salt bridge. Rust ($Fe_2O_3 \cdot xH_2O$) is formed by the subsequent oxidation of Fe^{2+} by atmospheric oxygen.

In the corrosion process, iron metal acts as the anode in a galvanic cell and is oxidized to Fe^{2+}; oxygen is reduced to water at the cathode. The relevant reactions are as follows:

Equation 19.96

$$cathode: O2(g) + 4H + (aq) + 4e - \rightarrow 2H2O(l) \quad E° = 1.23\ V$$

Equation 19.97

$$anode: Fe(s) \rightarrow Fe2 + (aq) + 2e - \quad E° = -0.45\ V$$

$$overall: 2Fe(s) + O2(g) + 4H + (aq) \rightarrow 2Fe2 + (aq) + 2H2O(l) \quad E° = 1.68\ V$$

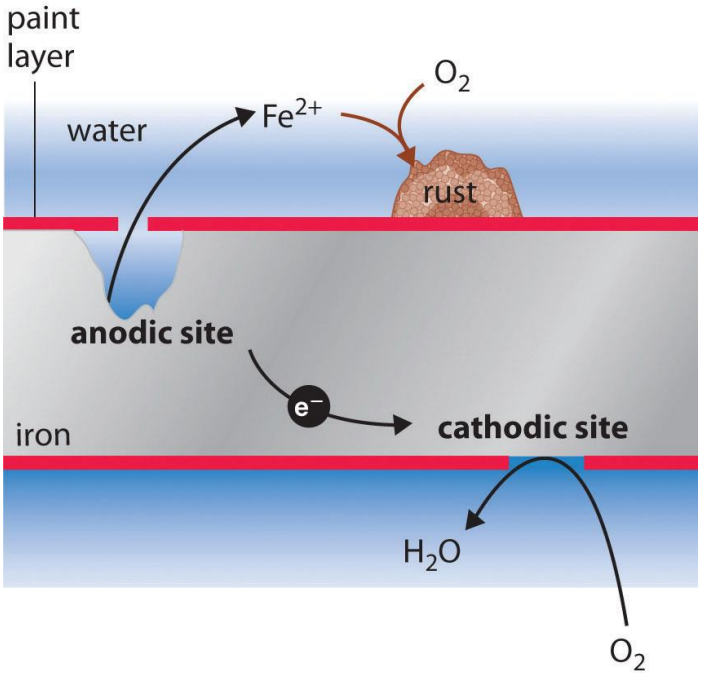
The Fe^{2+} ions produced in the initial reaction are then oxidized by atmospheric oxygen to produce the insoluble hydrated oxide containing Fe^{3+}, as represented in the following equation:

Equation 19.99

$$4Fe^{2+}(aq) + O_2(g) + (2 + 4x)H_2O \rightarrow 2Fe_2O_3{\cdot}xH_2O + 4H^+(aq)$$

The sign and magnitude of $E°$ for the corrosion process (Equation 19.98) indicate that there is a strong driving force for the oxidation of iron by O_2 under standard conditions (1 M H^+). Under neutral conditions, the driving force is somewhat less but still appreciable (E = 1.25 V at pH 7.0). Normally, the reaction of atmospheric CO_2 with water to form H^+ and HCO_3^- provides a low enough pH to enhance the reaction rate, as does acid rain. (For more information on acid rain, see Chapter 4 "Reactions in Aqueous Solution", Section 4.7 "The Chemistry of Acid Rain".) Automobile manufacturers spend a great deal of time and money developing paints that adhere tightly to the car's metal surface to prevent oxygenated water, acid, and salt from coming into contact with the underlying metal. Unfortunately, even the best paint is subject to scratching or denting, and the electrochemical nature of the corrosion process means that two scratches relatively remote from each other can operate together as anode and cathode, leading to sudden mechanical failure (Figure 19.18 "Small Scratches in a Protective Paint Coating Can Lead to the Rapid Corrosion of Iron").

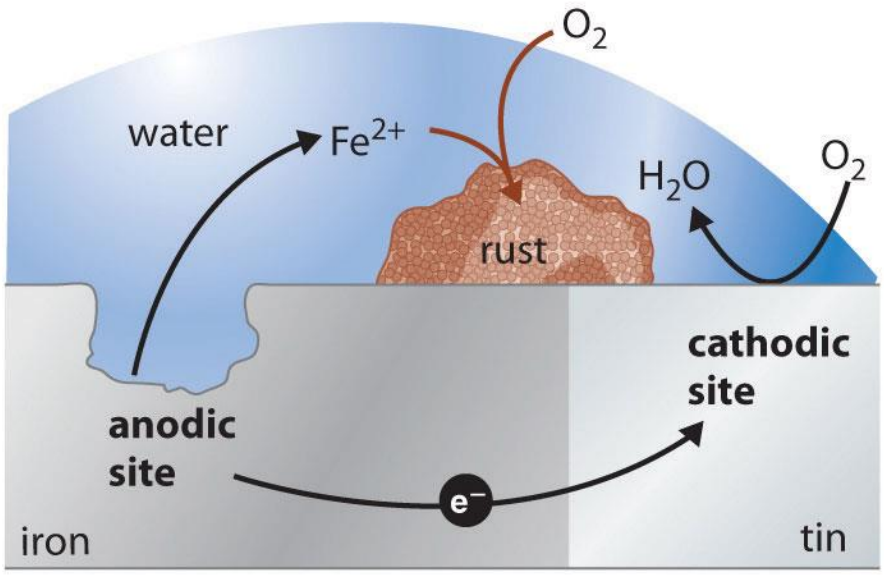
Figure 19.18 *Small Scratches in a Protective Paint Coating Can Lead to the Rapid Corrosion of Iron*



Holes in a protective coating allow oxygen to be reduced at the surface with the greater exposure to air (the cathode), while metallic iron is oxidized to $Fe^{2+}(aq)$ at the less exposed site (the anode). Rust is formed when $Fe^{2+}(aq)$ diffuses to a location where it can react with atmospheric oxygen, which is often remote from the anode. The electrochemical interaction between cathodic and anodic sites can cause a large pit to form under a painted surface, eventually resulting in sudden failure with little visible warning that corrosion has occurred.

One of the most common techniques used to prevent the corrosion of iron is applying a protective coating of another metal that is more difficult to oxidize. Faucets and some external parts of automobiles, for example, are often coated with a thin layer of chromium using an electrolytic process that will be discussed in Section 19.7 "Electrolysis". With the increased use of polymeric materials in cars, however, the use of chrome-plated steel has diminished in recent years. Similarly, the "tin cans" that hold soups and other foods are actually made of steel coated with a thin layer of tin. Neither chromium nor tin is intrinsically resistant to corrosion, but both form protective oxide coatings. As with a protective paint, scratching a protective metal coating will allow corrosion to occur. In this case, however, the presence of the second metal can actually increase the rate of corrosion. The values of the standard electrode potentials for Sn^{2+} ($E^\circ = -0.14$ V) and Fe^{2+} ($E^\circ = -0.45$ V) in Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C" show that Fe is more easily oxidized than Sn. As a result, the more corrosion-resistant metal (in this case, tin) accelerates the corrosion of iron by acting as the cathode and providing a large surface area for the reduction of oxygen (Figure 19.19 "Galvanic Corrosion"). This process is seen in some older homes where copper and iron pipes have been directly connected to each other. The less easily oxidized copper acts as the cathode, causing iron to dissolve rapidly near the connection and occasionally resulting in a catastrophic plumbing failure.

Figure 19.19 *Galvanic Corrosion*



If iron is in contact with a more corrosion-resistant metal such as tin, copper, or lead, the other metal can act as a large cathode that greatly increases the rate of reduction of oxygen. Because the reduction of oxygen is coupled to the oxidation of iron, this can result in a dramatic increase in the rate at which iron is oxidized at the anode. Galvanic corrosion is likely to occur whenever two dissimilar metals are connected directly, allowing electrons to be transferred from one to the other.

One way to avoid these problems is to use a more easily oxidized metal to protect iron from corrosion. In this approach, called *cathodic protection*, a more reactive metal such as Zn ($E^\circ = -0.76$ V for $Zn^{2+} + 2e^- \rightarrow Zn$) becomes the anode, and iron becomes the cathode. This prevents oxidation of the iron and protects the iron object from corrosion. The reactions that occur under these conditions are as follows:

Equation 19.100
cathode: $O_2(g) + 4e^- + 4H^+(aq) \rightarrow 2H_2O(l)$

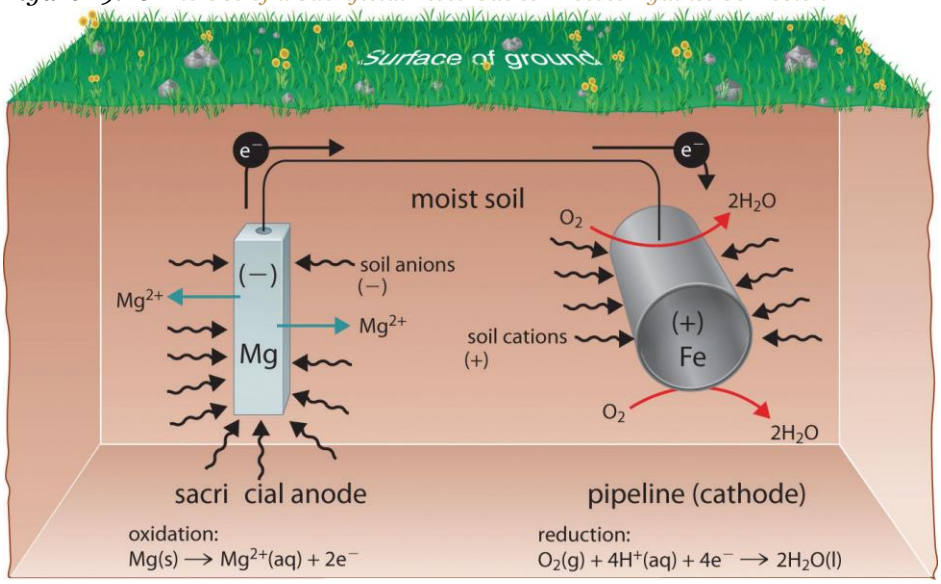
Equation 19.101
anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Equation 19.102
$$overall: 2Zn(s) + O2(g) + 4H + (aq) \rightarrow 2Zn2 + (aq) + 2H2O(l)$$

The more reactive metal reacts with oxygen and will eventually dissolve, "sacrificing" itself to protect the iron object. Cathodic protection is the principle underlying*galvanized steel*, which is steel protected by a thin layer of zinc. Galvanized steel is used in objects ranging from nails to garbage cans. In a similar strategy,sacrificial electrodes using magnesium, for example, are used to protect underground tanks or pipes

(Figure 19.20 "The Use of a Sacrificial Electrode to Protect Against Corrosion"). Replacing the sacrificial electrodes is more cost-effective than replacing the iron objects they are protecting.

Figure 19.20 *The Use of a Sacrificial Electrode to Protect Against Corrosion*



Connecting a magnesium rod to an underground steel pipeline protects the pipeline from corrosion. Because magnesium ($E° = -2.37$ V) is much more easily oxidized than iron ($E° = -0.45$ V), the Mg rod acts as the anode in a galvanic cell. The pipeline is therefore forced to act as the cathode at which oxygen is reduced. The soil between the anode and the cathode acts as a salt bridge that completes the electrical circuit and maintains electrical neutrality. As Mg(s) is oxidized to Mg^{2+} at the anode, anions in the soil, such as nitrate, diffuse toward the anode to neutralize the positive charge. Simultaneously, cations in the soil, such as H^+ or NH_4^+, diffuse toward the cathode, where they replenish the protons that are consumed as oxygen is reduced. A similar strategy uses many miles of somewhat less reactive zinc wire to protect the Alaska oil pipeline.

EXAMPLE 13

Suppose an old wooden sailboat, held together with iron screws, has a bronze propeller (recall that bronze is an alloy of copper containing about 7%–10% tin).

a. If the boat is immersed in seawater, what corrosion reaction will occur? What is $E°_{cell}$?

b. How could you prevent this corrosion from occurring?

Given: identity of metals

Asked for: corrosion reaction, $E°_{cell}$, and preventive measures

Strategy:

A Write the reactions that occur at the anode and the cathode. From these, write the overall cell reaction and calculate $E°_{cell}$.

B Based on the relative redox activity of various substances, suggest possible preventive measures.

Solution:

a. **A** According to Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C", both copper and tin are less active metals than iron (i.e., they have higher positive values of $E°$ than iron). Thus if tin or copper is brought into electrical contact by seawater with iron in the presence of oxygen, corrosion will occur. We therefore anticipate that the bronze propeller will act as the cathode at which O_2 is reduced, and the iron screws will act as anodes at which iron dissolves:

$$cathode: anode: overall: O2(s) + 4H + (aq) + 4e - \rightarrow 2H2O(l) Fe(s) \rightarrow Fe2 + +2e - 2Fe(s) + O2(g) + 4H + (aq) \rightarrow 2Fe2 + (aq) + 2H2O(l) E$$

$$\square cathode = 1.23\ VE\ \square anode = - 0.45\ VE\ \square cell = 1.68\ V$$

Over time, the iron screws will dissolve, and the boat will fall apart.

b. **B** Possible ways to prevent corrosion, in order of decreasing cost and inconvenience, are as follows: disassembling the boat and rebuilding it with bronze screws; removing the boat from the water and storing it in a dry place; or attaching an inexpensive piece of zinc metal to the propeller shaft to act as a sacrificial electrode and replacing it once or twice a year. Because zinc is a more active metal than iron, it will act as the sacrificial anode in the electrochemical cell and dissolve (Equation 19.102).

Exercise

Suppose the water pipes leading into your house are made of lead, while the rest of the plumbing in your house is iron. To eliminate the possibility of lead poisoning, you call a plumber to replace the lead pipes. He quotes you a very low price if he can use up his existing supply of copper pipe to do the job.

a. Do you accept his proposal?

b. What else should you have the plumber do while at your home?

Answer:

a. Not unless you plan to sell the house very soon because the Cu/Fe pipe joints will lead to rapid corrosion.

b. Any existing Pb/Fe joints should be examined carefully for corrosion of the iron pipes due to the Pb–Fe junction; the less active Pb will have served as the cathode for the reduction of O_2, promoting oxidation of the more active Fe nearby.

Summary

The deterioration of metals through oxidation is a galvanic process called **corrosion**. Protective coatings consist of a second metal that is more difficult to oxidize than the metal being protected. Alternatively, a more easily oxidized metal can be applied to a metal surface, thus providing cathodic protection of the surface. A thin layer of zinc protects galvanized steel. **Sacrificial electrodes** can also be attached to an object to protect it.

KEY TAKEAWAY

- Corrosion is a galvanic process that can be prevented using cathodic protection.

CONCEPTUAL PROBLEMS

1. Do you expect a bent nail to corrode more or less rapidly than a straight nail? Why?
2. What does it mean when a metal is described as being coated with a sacrificial layer? Is this different from galvanic protection?
3. Why is it important for automobile manufacturers to apply paint to the metal surface of a car? Why is this process particularly important for vehicles in northern climates, where salt is used on icy roads?

ANSWER

1.
2.
3. Paint keeps oxygen and water from coming into direct contact with the metal, which prevents corrosion. Paint is more necessary because salt is an electrolyte that increases the conductivity of water and facilitates the flow of electric current between anodic and cathodic sites.

19.7 Electrolysis

LEARNING OBJECTIVE

1. To understand electrolysis and describe it quantitatively.

In this chapter, we have described various galvanic cells in which a spontaneous chemical reaction is used to generate electrical energy. In an electrolytic cell, however, the opposite process, called electrolysis, occurs: an external voltage is applied to drive a nonspontaneous reaction (Figure 19.1 "Electrochemical Cells"). In this section, we look at how electrolytic cells are constructed and explore some of their many commercial applications.

Note the Pattern

In an electrolytic cell, an external voltage is applied to drive a nonspontaneous reaction.

Electrolytic Cells

If we construct an electrochemical cell in which one electrode is copper metal immersed in a 1 M Cu^{2+} solution and the other electrode is cadmium metal immersed in a 1 M Cd^{2+} solution and then close the circuit, the potential difference between the two compartments will be 0.74 V. The cadmium electrode will begin to dissolve (Cd is oxidized to Cd^{2+}) and is the anode, while metallic copper will be deposited on the copper electrode (Cu^{2+} is reduced to Cu), which is the cathode (part (a) in Figure 19.21 "An Applied Voltage Can Reverse the Flow of Electrons in a Galvanic Cd/Cu Cell"). The overall reaction is as follows:

Equation 19.103

$$Cd(s) + Cu2 + (aq) \rightarrow Cd2 + (aq) + Cu(s) E \square cell = 0.74\ V$$

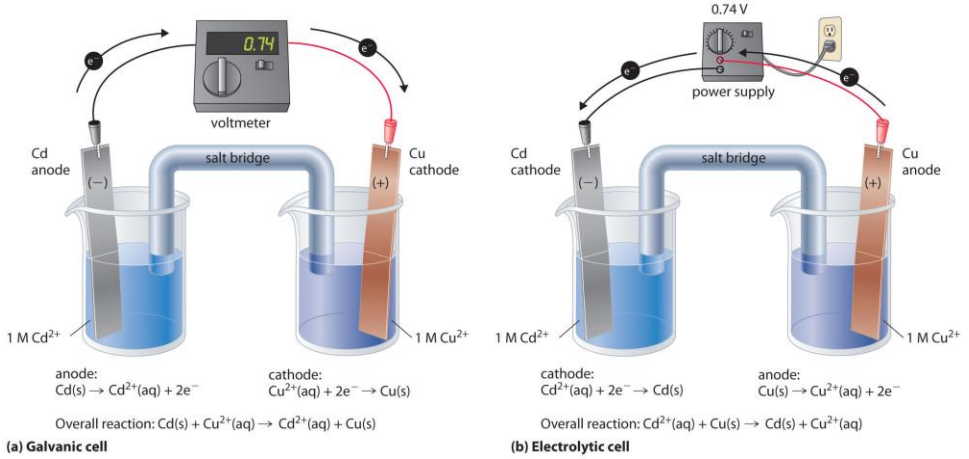
This reaction is thermodynamically spontaneous as written ($\Delta G^\circ < 0$):

Equation 19.104

$$DG° = - nFE \square cell = - (2 mole-)[96,486$$
$$J/(V \cdot mol)](0.74V) = - 140\ kJ\ (per\ mole\ Cd)$$

In this direction, the system is acting as a galvanic cell.

Figure 19.21 *An Applied Voltage Can Reverse the Flow of Electrons in a Galvanic Cd/Cu Cell*



(a) When compartments that contain a Cd electrode immersed in 1 M $Cd^{2+}(aq)$ and a Cu electrode immersed in 1 M $Cu^{2+}(aq)$ are connected to create a galvanic cell, Cd(s) is spontaneously oxidized to $Cd^{2+}(aq)$ at the anode, and $Cu^{2+}(aq)$ is spontaneously reduced to Cu(s) at the cathode. The potential of the galvanic cell is 0.74 V. (b) Applying an external potential greater than 0.74 V in the reverse direction forces electrons to flow from the Cu electrode [which is now the anode, at which metallic Cu(s) is oxidized to $Cu^{2+}(aq)$] and into the Cd electrode [which is now the cathode, at which $Cd^{2+}(aq)$ is reduced to Cd(s)]. The anode in an electrolytic cell is positive because electrons are flowing from it, whereas the cathode is negative because electrons are flowing into it.

The reverse reaction, the reduction of Cd^{2+} by Cu, is thermodynamically nonspontaneous and will occur only with an *input* of 140 kJ. We can force the reaction to proceed in the reverse direction by applying an electrical potential greater than 0.74 V from an external power supply. The applied voltage forces electrons through the circuit in the reverse direction, converting a galvanic cell to an electrolytic cell. Thus the copper electrode is now the anode (Cu is oxidized), and the cadmium electrode is now the cathode (Cd^{2+} is reduced) (part (b) in Figure 19.21 "An Applied Voltage Can Reverse the Flow of Electrons in a Galvanic Cd/Cu Cell"). The signs of the cathode and the anode have switched to reflect the flow of electrons in the circuit. The half-reactions that occur at the cathode and the anode are as follows:

Equation 19.105

$$cathode: Cd2+(aq)+2e- \rightarrow Cd(s) \quad E°cathode = -0.40\ V$$

Equation 19.106

$$anode: Cu(s) \rightarrow Cu2+(aq)+2e- \quad E°anode = 0.34\ V$$

Equation 19.107

$$overall: Cd2+(aq)+Cu(s) \rightarrow Cd(s)+Cu2+(aq) \quad E°cell = -0.74\ V$$

Because $E°_{cell} < 0$, the overall reaction—the reduction of Cd^{2+} by Cu—clearly cannot occur spontaneously and proceeds only when sufficient electrical energy is applied. The differences between galvanic and electrolytic cells are summarized in Table 19.3 "Comparison of Galvanic and Electrolytic Cells".

Table 19.3 Comparison of Galvanic and Electrolytic Cells

Property	Galvanic Cell	Electrolytic Cell
ΔG	< 0	> 0
E_{cell}	> 0	< 0
Electrode Process		

Property	Galvanic Cell	Electrolytic Cell
anode	oxidation	oxidation
cathode	reduction	reduction
Sign of Electrode		
anode	−	+
cathode	+	−

Electrolytic Reactions

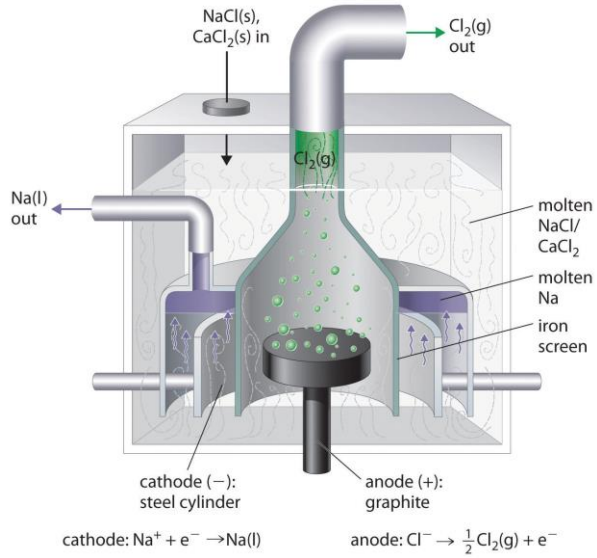
At sufficiently high temperatures, ionic solids melt to form liquids that conduct electricity extremely well due to the high concentrations of ions. If two inert electrodes are inserted into molten NaCl, for example, and an electrical potential is applied, Cl^- is oxidized at the anode, and Na^+ is reduced at the cathode. The overall reaction is as follows:

Equation 19.108

$$2NaCl(l) \rightarrow 2Na(l) + Cl_2(g)$$

This is the reverse of the formation of NaCl from its elements. The product of the reduction reaction is *liquid* sodium because the melting point of sodium metal is 97.8°C, well below that of NaCl (801°C). Approximately 20,000 tons of sodium metal are produced commercially in the United States each year by the electrolysis of molten NaCl in a *Downs cell* (Figure 19.22 "A Downs Cell for the Electrolysis of Molten NaCl"). In this specialized cell, $CaCl_2$ (melting point = 772°C) is first added to the NaCl to lower the melting point of the mixture to about 600°C, thereby lowering operating costs.

Figure 19.22 *A Downs Cell for the Electrolysis of Molten NaCl*



The electrolysis of a molten mixture of NaCl and $CaCl_2$ results in the formation of elemental sodium and chlorine gas. Because sodium is a liquid under these conditions and liquid sodium is less dense than molten sodium chloride, the sodium floats to the top of the melt and is collected in concentric capped iron cylinders surrounding the cathode. Gaseous chlorine collects in the inverted cone over the anode. An iron screen separating the cathode and anode compartments ensures that the molten sodium and gaseous chlorine do not come into contact.

Similarly, in the *Hall–Heroult process* used to produce aluminum commercially, a molten mixture of about 5% aluminum oxide (Al_2O_3; melting point = 2054°C) and 95% cryolite (Na_3AlF_6; melting point = 1012°C) is electrolyzed at about 1000°C, producing molten aluminum at the cathode and CO_2 gas at the carbon anode. The overall reaction is as follows:

Equation 19.109

$$2Al_2O_3(l) + 3C(s) \rightarrow 4Al(l) + 3CO_2(g)$$

Oxide ions react with oxidized carbon at the anode, producing $CO_2(g)$.

There are two important points to make about these two commercial processes and about the electrolysis of molten salts in general.

1. The electrode potentials for molten salts are likely to be very different from the standard cell potentials listed in Table 19.2 "Standard Potentials for Selected Reduction Half-Reactions at 25°C" and Chapter 29 "Appendix E: Standard Reduction Potentials at 25°C", which are compiled for the reduction of the hydrated ions in aqueous solutions under standard conditions.
2. Using a mixed salt system means there is a possibility of competition between different electrolytic reactions. When a mixture of NaCl and $CaCl_2$ is electrolyzed, Cl^- is oxidized because it is the only anion present, but either Na^+ or Ca^{2+} can be reduced. Conversely, in the Hall–Heroult process, only one cation is present that can be reduced (Al^{3+}), but there are three species that can be oxidized: C, O^{2-}, and F^-.

   In the Hall–Heroult process, C is oxidized instead of O^{2-} or F^- because oxygen and fluorine are more electronegative than carbon, which means that C is a weaker oxidant than either O_2 or F_2. Similarly, in the Downs cell, we might expect electrolysis of a NaCl/$CaCl_2$ mixture to produce calcium rather than sodium because Na is slightly less electronegative than Ca (χ = 0.93 versus 1.00, respectively), making Na easier to

oxidize and, conversely, Na^+ more difficult to reduce. In fact, the reduction of Na^+ to Na is the observed reaction. In cases where the electronegativities of two species are similar, other factors, such as the formation of complex ions, become important and may determine the outcome.

EXAMPLE 14

If a molten mixture of $MgCl_2$ and KBr is electrolyzed, what products will form at the cathode and the anode, respectively?

Given: identity of salts

Asked for: electrolysis products

Strategy:

A List all the possible reduction and oxidation products. Based on the electronegativity values shown in Figure 7.5 "Definitions of the Atomic Radius", determine which species will be reduced and which species will be oxidized.

B Identify the products that will form at each electrode.

Solution:

A The possible reduction products are Mg and K, and the possible oxidation products are Cl_2 and Br_2. Because Mg is more electronegative than K (χ = 1.31 versus 0.82), it is likely that Mg will be reduced rather than K. Because Cl is more electronegative than Br (3.16 versus 2.96), Cl_2 is a stronger oxidant than Br_2.

B Electrolysis will therefore produce Br_2 at the anode and Mg at the cathode.

Exercise

Predict the products if a molten mixture of $AlBr_3$ and LiF is electrolyzed.

Answer: Br_2 and Al

Electrolysis can also be used to drive the thermodynamically nonspontaneous decomposition of water into its constituent elements: H_2 and O_2. However, because pure water is a very poor electrical conductor, a small amount of an ionic solute (such as H_2SO_4 or Na_2SO_4) must first be added to increase its electrical conductivity. Inserting inert electrodes into the solution and applying a voltage between them will result in the rapid evolution of bubbles of H_2 and O_2 (Figure 19.23 "The Electrolysis of Water"). The reactions that occur are as follows:

Equation 19.110

$$cathode: 2H+(aq)+2e- \rightarrow H2(g) \quad E \square cathode = 0\ V$$

Equation 19.111

$$anode: 2H2O(l) \rightarrow O2(g) + 4H + (aq) + 4e - \quad E \square anode = 1.23\ V$$

Equation 19.112

$$overall: 2H2O(l) \rightarrow O2(g) + 2H2(g) \quad E \square cell = -1.23\ V$$

For a system that contains an electrolyte such as Na_2SO_4, which has a negligible effect on the ionization equilibrium of liquid water, the pH of the solution will be 7.00 and $[H^+] = [OH^-] = 1.0 \times 10^{-7}$. Assuming th

$$at\ PO2 = PH2 =$$

1 atm, we can use the standard potentials and Equation 19.64 to calculate *E* for the overall reaction:

Equation 19.113

$$EcellEcell = E \square cell - (0.0591\ Vn) log(PO2P2H2)$$
$$= -1.23\ V - (0.0591\ V4) log(1) = -1.23\ V$$

Thus E_{cell} is −1.23 V, which is the value of $E°_{cell}$ if the reaction is carried out in the presence of 1 M H^+ rather than at pH 7.0.

In practice, a voltage about 0.4–0.6 V greater than the calculated value is needed to electrolyze water. This added voltage, called an overvoltage, represents the additional driving force required to overcome barriers such as the large activation energy for the formation of a gas at a metal surface. Overvoltages are needed in all electrolytic processes, which explain why, for example, approximately 14 V must be applied to recharge the 12 V battery in your car.

In general, any metal that does *not* react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation. The *p*-block metals and most of the transition metals are in this category, but metals in high oxidation states, which form oxoanions, cannot be reduced to the metal by simple electrolysis. Active metals, such as aluminum and those of groups 1 and 2, react so readily with water that they can be prepared only by the electrolysis of molten salts. Similarly, any nonmetallic element that does not readily oxidize water to O_2 can be prepared by the electrolytic oxidation of an aqueous solution that contains an appropriate anion. In practice, among the nonmetals, only F_2 cannot be prepared using this method. Oxoanions of nonmetals in their highest oxidation states, such as NO_3^-, SO_4^{2-}, PO_4^{3-}, are usually difficult to reduce electrochemically and usually behave like spectator ions that remain in solution during electrolysis.

Note the Pattern

In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation.

Electroplating

In a process called electroplating, a layer of a second metal is deposited on the metal electrode that acts as the cathode during electrolysis. Electroplating is used to enhance the appearance of metal objects and protect them from corrosion. Examples of electroplating include the chromium layer found on many bathroom fixtures or (in earlier days) on the bumpers and hubcaps of cars, as well as the thin layer of precious metal that coats silver-plated dinnerware or jewelry. In all cases, the basic concept is the same. A schematic view of an apparatus for electroplating silverware and a photograph of a commercial electroplating cell are shown in Figure 19.24 "Electroplating".

(a) Electroplating uses an electrolytic cell in which the object to be plated, such as a fork, is immersed in a solution of the metal to be deposited. The object being plated acts as the cathode, on which the desired metal is deposited in a thin layer, while the anode usually consists of the metal that is being deposited (in this case, silver) that maintains the solution concentration as it dissolves. (b) In this commercial electroplating apparatus, a large number of objects can be plated simultaneously by lowering the rack into the Ag^+ solution and applying the correct potential.

The half-reactions in electroplating a fork, for example, with silver are as follows:

Equation 19.114

$$cathode\ (fork):$$

$$Ag^+(aq) + e^- \rightarrow Ag(s)$$

$$E°cathode = 0.80\ V$$

Equation 19.19

$$anode\ (silver\ bar)$$

$$: Ag(s) \rightarrow Ag^+(aq)$$

$$E°anode = 0.80\ V$$

The overall reaction is the transfer of silver metal from one electrode (a silver bar acting as the anode) to another (a fork acting as the cathode). Because $E°_{cell}$ = 0 V, it takes only a small applied voltage to drive the electroplating process. In practice, various other substances may be added to the plating solution to

control its electrical conductivity and regulate the concentration of free metal ions, thus ensuring a smooth, even coating.

Quantitative Considerations

If we know the stoichiometry of an electrolysis reaction, the amount of current passed, and the length of time, we can calculate the amount of material consumed or produced in a reaction. Conversely, we can use stoichiometry to determine the combination of current and time needed to produce a given amount of material.

The quantity of material that is oxidized or reduced at an electrode during an electrochemical reaction is determined by the stoichiometry of the reaction and the amount of charge that is transferred. For example, in the reaction $Ag^+(aq) + e^- \rightarrow Ag(s)$, 1 mol of electrons reduces 1 mol of Ag^+ to Ag metal. In contrast, in the reaction $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$, 1 mol of electrons reduces only 0.5 mol of Cu^{2+} to Cu metal. Recall that the charge on 1 mol of electrons is 1 faraday (1 *F*), which is equal to 96,486 C. We can therefore calculate the number of moles of electrons transferred when a known current is passed through a cell for a given period of time. The total charge (C) transferred is the product of the current (A) and the time (*t*, in seconds):

Equation 19.116

$$C = A \times t$$

The stoichiometry of the reaction and the total charge transferred enable us to calculate the amount of product formed during an electrolysis reaction or the amount of metal deposited in an electroplating process.

For example, if a current of 0.60 A passes through an aqueous solution of $CuSO_4$ for 6.0 min, the total number of coulombs of charge that passes through the cell is as follows:

Equation 19.117

$$charge = (0.60\ A)(6.0\ min)(60\ s/min) = 220\ A \times s = 220\ C$$

The number of moles of electrons transferred to Cu^{2+} is therefore

Equation 19.118

$$moles\ e^- = 220\ C\,96,486\ C/mol = 2.3 \times 10^{-3}\ mol\ e^-$$

Because two electrons are required to reduce a single Cu^{2+} ion, the total number of moles of Cu produced is half the number of moles of electrons transferred, or 1.2×10^{-3} mol. This corresponds to 76 mg of Cu. In

commercial electrorefining processes, much higher currents (greater than or equal to 50,000 A) are used, corresponding to approximately 0.5 F/s, and reaction times are on the order of 3–4 weeks.

EXAMPLE 15

A silver-plated spoon typically contains about 2.00 g of Ag. If 12.0 h are required to achieve the desired thickness of the Ag coating, what is the average current per spoon that must flow during the electroplating process, assuming an efficiency of 100%?

Given: mass of metal, time, and efficiency

Asked for: current required

Strategy:

A Calculate the number of moles of metal corresponding to the given mass transferred.

B Write the reaction and determine the number of moles of electrons required for the electroplating process.

C Use the definition of the faraday to calculate the number of coulombs required. Then convert coulombs to current in amperes.

Solution:

A We must first determine the number of moles of Ag corresponding to 2.00 g of Ag:

$$moles\ Ag = 2.00\ g 107.868\ g/mol$$
$$= 1.85 \times 10^{-2}\ mol\ Ag$$

B The reduction reaction is $Ag^+(aq) + e^- \rightarrow Ag(s)$, so 1 mol of electrons produces 1 mol of silver.

C Using the definition of the faraday,

The current in amperes needed to deliver this amount of charge in 12.0 h is therefore

$$amperes = 1.78 \times 10^{3}\ C(12.0\ h)(60 min/h)(60\ s/min)$$
$$= 4.12 \times 10^{-2}\ C/s = 4.12 \times 10^{-2}\ A$$

Because the electroplating process is usually much less than 100% efficient (typical values are closer to 30%), the actual current necessary is greater than 0.1 A.

Exercise

A typical aluminum soft-drink can weighs about 29 g. How much time is needed to produce this amount of Al(s) in the Hall–Heroult process, using a current of 15 A to reduce a molten Al_2O_3/Na_3AlF_6 mixture?

Answer: 5.8 h

Summary

In **electrolysis**, an external voltage is applied to drive a nonspontaneous reaction. A Downs cell is used to produce sodium metal from a mixture of salts, and the Hall–Heroult process is used to produce aluminum commercially. Electrolysis can also be used to produce H_2 and O_2 from water. In practice, an additional voltage, called an **overvoltage**, must be applied to overcome factors such as a large activation energy and a junction potential. **Electroplating** is the process by which a second metal is deposited on a metal surface, thereby enhancing an object's appearance or providing protection from corrosion. The amount of material consumed or produced in a reaction can be calculated from the stoichiometry of an electrolysis reaction, the amount of current passed, and the duration of the electrolytic reaction.

KEY TAKEAWAYS

- In electrolysis, an external voltage is applied to drive a nonspontaneous reaction.
- The quantity of material oxidized or reduced can be calculated from the stoichiometry of the reaction and the amount of charge transferred.

KEY EQUATION

Relationship of charge, current and time

Equation 19.116: $C = A \times t$

CONCEPTUAL PROBLEMS

1. Why might an electrochemical reaction that is thermodynamically favored require an overvoltage to occur?
2. How could you use an electrolytic cell to make quantitative comparisons of the strengths of various oxidants and reductants?
3. Why are mixtures of molten salts, rather than a pure salt, generally used during electrolysis?
4. Two solutions, one containing $Fe(NO_3)_2 \cdot 6H_2O$ and the other containing the same molar concentration of $Fe(NO_3)_3 \cdot 6H_2O$, were electrolyzed under identical conditions. Which solution produced the most metal? Justify your answer.

NUMERICAL PROBLEMS

1. The electrolysis of molten salts is frequently used in industry to obtain pure metals. How many grams of metal are deposited from these salts for each mole of electrons?

a. $AlCl_3$

b. $MgCl_2$

c. $FeCl_3$

2. Electrolysis is the most direct way of recovering a metal from its ores. However, the $Na^+(aq)/Na(s)$, $Mg^{2+}(aq)/Mg(s)$, and $Al^{3+}(aq)/Al(s)$ couples all have standard electrode potentials ($E°$) more negative than the reduction potential of water at pH 7.0 (−0.42 V), indicating that these metals can never be obtained by electrolysis of aqueous solutions of their salts. Why? What reaction would occur instead?
3. What volume of chlorine gas at standard temperature and pressure is evolved when a solution of $MgCl_2$ is electrolyzed using a current of 12.4 A for 1.0 h?
4. What mass of copper metal is deposited if a 5.12 A current is passed through a $Cu(NO_3)_2$ solution for 1.5 h.
5. What mass of PbO_2 is reduced when a current of 5.0 A is withdrawn over a period of 2.0 h from a lead storage battery?
6. Electrolysis of $Cr^{3+}(aq)$ produces $Cr^{2+}(aq)$. If you had 500 mL of a 0.15 M solution of $Cr^{3+}(aq)$, how long would it take to reduce the Cr^{3+} to Cr^{2+} using a 0.158 A current?
7. Predict the products obtained at each electrode when aqueous solutions of the following are electrolyzed.

a. $AgNO_3$

b. RbI

8. Predict the products obtained at each electrode when aqueous solutions of the following are electrolyzed.

a. $MgBr_2$

b. $Hg(CH_3CO_2)_2$

c. $Al_2(SO_4)_3$

ANSWERS

1.

2.

3. 5.2 L

4.

5.

6.

7.

a. cathode: Ag(s); anode: $O_2(g)$;

b. cathode: $H_2(g)$; anode: $I_2(s)$

19.8 End-of-Chapter Material

APPLICATION PROBLEMS

Problems marked with a ♦ involve multiple concepts.

1. The percent efficiency of a fuel cell is defined as $\Delta G°/\Delta H° \times 100$. If hydrogen gas were distributed for domestic and industrial use from a central electrolysis facility, the gas could be piped to consumers much as methane is piped today. Conventional nuclear power stations have an efficiency of 25%–30%. Use tabulated data to calculate the efficiency of a fuel cell in which the reaction $H_2(g) + 1/2O_2(g) \rightarrow H_2O(g)$ occurs under standard conditions.
2. ♦ You are about to run an organic reaction and need a strong oxidant. Although you have BrO_3^- at your disposal, you prefer to use MnO_4^-. You notice you also have MnO_2in the lab.

a. Predict whether you will be able to synthesize MnO_4^- using the materials available to you.

b. Write the overall reaction for the synthesis of MnO_4^-.

c. What is $\Delta G°$ for this reaction?

d. What is the equilibrium constant?

3. It is possible to construct a galvanic cell using amalgams as electrodes, each containing different concentrations of the same metal. One example is the $Pb(Hg)(a_1)|\ PbSO_4(soln)|\ Pb(Hg)(a_2)$ cell, in which a_1 and a_2 represent the concentrations of lead in the amalgams. No chemical change occurs; rather, the reaction transfers lead from one amalgam to the other, thus altering the Pb concentration in both amalgams. Write an equation for E for such a cell.
4. ♦ The oldest known metallurgical artifacts are beads made from alloys of copper, produced in Egypt, Mesopotamia, and the Indus Valley around 3000 BC. To determine the copper content of alloys such as brass, a sample is dissolved in nitric acid to obtain $Cu^{2+}(aq)$, and then the pH is adjusted to 7.0. Excess KI is used to reduce the Cu^{2+} to $Cu^+$with concomitant oxidation of I^- to I_2. The iodine that is produced is then titrated with thiosulfate solution to determine the amount of Cu^{2+} in the original solution. The following reactions are involved in the procedure:

a. $Cu^{2+}(aq) + I^-(aq) + e^- \rightarrow CuI(s)$; $E° = 0.86$ V

b. $S_4O_6^{2-}(aq) + 2e^- \rightarrow 2S_2O_3^{2-}(aq)$; $E° = 0.08$ V

c. $NO_3^-(aq) + 2H^+(aq) + 2e^- \rightarrow NO_2^-(aq) + H_2O(l)$; $E° = 0.94$ V

d. $I_2(s) + 2e^- \rightarrow 2I^-(aq)$; $E° = 0.54$ V

e. Write a balanced chemical equation for the reaction between nitric acid and Cu(s).

f. What is $E°_{cell}$ for this reaction?

g. What is $E°_{cell}$ for the reaction between thiosulfate and iodine?

h. When the pH of the copper(ll) solution is adjusted to 7.0, what is E for reduction of nitrate?

i. Why is it necessary to adjust the pH of the copper(II) solution before adding KI?

j. Use tabulated data to explain why rust (Fe_2O_3) is a contaminant that renders this method useless in determining Cu concentrations.

5. The biological electron transport chain provides for an orderly, stepwise transfer of electrons. Both NADH (reduced nicotinamide adenine dinucleotide) and $FADH_2$ (reduced flavin adenine dinucleotide) are energy-rich molecules that liberate a large amount of energy during oxidation. Free energy released during the transfer of electrons from either of these molecules to oxygen drives the synthesis of ATP (adenosine triphosphate) formed during respiratory metabolism. The reactions are as follows:

$$NADH + H + + 12O2FADH2 + 12O2 \rightarrow NAD + + H2O \rightarrow$$

$$FAD + H2ODG°'DG°' = - 52.6\ kcal / mol = - 43.4\ kcal / mol$$

The standard potential ($E°'$) for a biological process is defined at pH = 7.0.

a. What is $E°'_{cell}$ for each reaction?

b. What is the reduction potential of NAD^+ at pH 7.0?

c. What is the reduction potential of FAD at pH 7.0?

6. While working at a nuclear reactor site, you have been put in charge of reprocessing spent nuclear fuel elements. Your specific task is to reduce Pu(VI) to elemental Pu without reducing U(VI) to elemental U. You have the following information at your disposal:

$$E°E°UO22 + PuO22 + - \rightarrow 0.05UO2 +$$

$$- \rightarrow 0.91PuO2 + - \rightarrow 0.62U4 + - \rightarrow 1.17Pu4 + - \rightarrow$$

$$- - 0.61U3 + - \rightarrow 0.98Pu3 + - \rightarrow$$

$$- - - - -1.85U - \rightarrow - - - - - -2.03$$

$$Pu$$

Use tabulated data to decide what reductant will accomplish your task in an acidic solution containing 1.0 M concentrations of both UO_2^{2+} and PuO_2^{2+}.

7. Stainless steels typically contain 11% Cr and are resistant to corrosion because of the formation of an oxide layer that can be approximately described as $FeCr_2O_4$, where the iron is Fe(II). The protective layer forms

when Cr(II) is oxidized to Cr(III) and Fe is oxidized to Fe(II). Explain how this film prevents the corrosion of Fe to rust, which has the formula Fe_2O_3.

8. ♦ Ion-selective electrodes are powerful tools for measuring specific concentrations of ions in solution. For example, they are used to measure iodide in milk, copper-ion levels in drinking water, fluoride concentrations in toothpastes, and the silver-ion concentration in photographic emulsions and spent fixing solutions. Describe how ion-selective electrodes work and then propose a design for an ion-selective electrode that can be used for measuring water hardness (Ca^{2+}, Mg^{2+}) in water-conditioning systems.
9. ♦ Enzymes are proteins that catalyze a specific reaction with a high degree of specificity. An example is the hydrolysis of urea by urease:

$$NH2CONH2+2H2O+H+--\rightarrow---urease2NH4++HCO3-$$

An enzyme electrode for measuring urea concentrations can be made by coating the surface of a glass electrode with a gel that contains urease.

a. Explain what occurs when the electrode is placed in contact with a solution that contains urea.
b. What species diffuses through the gel?
c. What would be an effective reference electrode?

10. Gas-sensing electrodes can be constructed using a combination electrode that is surrounded by a gas-permeable membrane. For example, to measure CO_2, a pH electrode and a reference electrode are placed in solution on the "inner" side of a CO_2-permeable membrane, and the sample solution is placed on the "external" side. As CO_2diffuses through the membrane, the pH of the internal solution changes due to the reaction $CO_2(g) + H_2O(l) \rightarrow HCO_3^-(aq) + H^+(aq)$. Thus the pH of the internal solution varies directly with the CO_2 pressure in the external sample. Ammonia electrodes operate in the same manner. Describe an electrode that would test for ammonia levels in seawater.
11. US submarines that are not nuclear powered use a combination of batteries and diesel engines for their power. When submerged, they are battery driven; when on the surface, they are diesel driven. Why are batteries not used when submarines are on the surface?
12. List some practical considerations in designing a battery to power an electric car.
13. ♦ It is possible to run a digital clock using the power supplied by two potatoes. The clock is connected to two wires: one is attached to a copper plate, and the other is attached to a zinc plate. Each plate is pushed into a

different potato; when a wire connects the two potatoes, the clock begins to run as if it were connected to a battery.

a. Draw a cell diagram of the potato clock.

b. Explain why the clock runs.

14. ♦ The silver–zinc battery has the highest energy density of any rechargeable battery available today. Its use is presently limited to military applications, primarily in portable communications, aerospace, and torpedo-propulsion systems. The disadvantages of these cells are their limited life (they typically last no more than about 2 yr) and their high cost, which restricts their use to situations in which cost is only a minor factor. The generally accepted equations representing this type of battery are as follows:

a. $2AgO(s) + Zn(s) + H2O(l) \rightarrow Ag2O(s) + Zn(OH)2(aq) \quad E° = 1.85\ V$

$Ag2O(s) + Zn(s) + H2O(l) \rightarrow 2Ag(s) + Zn(OH)2(aq) \quad E° = 1.59\ V$ Write the overall cell reaction and calculate $E°_{cell}$.

b. If the cell is 75% efficient, what is the maximum amount of work that can be generated from this type of battery?

c. Use tabulated data to calculate the maximum work that can be generated by a lead storage cell. If a silver–zinc battery is operating at 100% efficiency, how do the two batteries compare?

15. All metals used in boats and ships are subject to corrosion, particularly when the vessels are operated in salt water, which is a good electrolyte. Based on the data in the following table, where potentials are measured using a glass electrode, explain why

a. iron or steel should not be used in bolts in a lead ballast keel.

b. ordinary brass should not be used as a structural fastening, particularly below the waterline.

c. an aluminum hull should not be painted with a copper-based antifouling paint.

d. magnesium sacrificial anodes are preferred over zinc when a vessel is kept in fresh water.

e. Monel (an alloy that contains mostly nickel and copper) is preferred over stainless steel for freshwater tanks.

Metal	*E* versus Ag/AgCl (V)
titanium	0.02

Metal	*E* versus Ag/AgCl (V)
Monel [Ni(Cu)]	−0.06
Ni(Al) bronze	−0.16
lead	−0.20
manganese bronze	−0.29
brass	−0.30
copper	−0.31
tin	−0.31
stainless steel	−0.49
aluminum	−0.87
zinc	−1.00
magnesium	−1.60

16. Parents often coat a baby's first shoes with copper to preserve them for posterity. A conducting powder, such as graphite, is rubbed on the shoe, and then copper is electroplated on the shoe. How much copper is deposited on a shoe if the electrolytic process is run for 60 min at 1.2 A from a 1.0 M solution of $CuSO_4$?
17. Before 1886, metallic aluminum was so rare that a bar of it was displayed next to the Crown Jewels at the Paris Exposition of 1855. Today, aluminum is obtained commercially from aluminum oxide by the Hall–Heroult process, an electrolytic process that uses molten Al_2O_3 and cryolite (Na_3AlF_6). As the operation proceeds, molten Al sinks to the bottom of the cell. The overall reaction is $2Al_2O_3(l) + 3C(s) \rightarrow 4Al(l) + 3CO_2(g)$; however, the process is only approximately 90% efficient.

a. Why is cryolite added to the Al_2O_3?

b. How much aluminum is deposited if electrodeposition occurs for 24 h at 1.8 A?

18. ♦ One of the most important electrolytic processes used in industry is the electrolytic reduction of acrylonitrile (CH_2CHCN) to adiponitrile [$NC(CH_2)_4CN$]. The product is then hydrogenated to hexamethylenediamine [$H_2N(CH_2)_6NH_2$], a key component of one form of nylon. Using this process, Monsanto produces about 200,000 metric tons of adiponitrile annually. The cathode reaction in the electrochemical cell is as follows:

$$2CH_2CHCN + 2H^+ + 2e^- \rightarrow NC(CH_2)_4CN$$

The cost of electricity makes this an expensive process. Calculate the total number of kilowatt-hours of electricity used by Monsanto each year in this process, assuming a continuous applied potential of 5.0 V and an electrochemical efficiency of 50%. (One kilowatt-hour equals 3.6×10^3 kJ.)

19. ♦ Compact discs (CDs) are manufactured by electroplating. Information is stored on a CD master in a pattern of "pits" (depressions, which correspond to an audio track) and "lands" (the raised areas between depressions). A laser beam cuts the pits into a plastic or glass material. The material is cleaned, sprayed with $[Ag(NH_3)_2]^+$, and then washed with a formaldehyde solution that reduces the complex and leaves a thin silver coating. Nickel is electrodeposited on the disk and then peeled away to produce a master disk, which is used to stamp copies.

a. Write the half-reactions that correspond to the electrodeposition reaction.

b. If a CD has a radius of 12 cm and an interior hole with a diameter of 2.5 cm, how long does it take to deposit a 50 µm layer of nickel on one side of the CD using a 1.0 M solution of $NiSO_4$ and a current of 0.80 A?

20. ♦ Calculate the total amount of energy consumed in the electrolysis reaction used to make the 16×10^6 metric tons of aluminum produced annually worldwide, assuming a continuous applied potential of 5.0 V and an efficiency of 50%. Express your answer in kilojoules and in kilowatt-hours. (See Problem 19 for the conversion between kilowatt-hours and kilojoules.)

ANSWERS

1.

2.

3.

4.

5.

a. $E°_{cell}$ = 1.14 V for NADH; 0.94 V for $FADH_2$

b. −0.32 V

c. −0.12 V

6.

7.

8.

9.

10.

11.

12.

13.

14.

15.

16.

17.

18.

19.

a. $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$; $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$

b. 22 hrs

20.

Chapter 20

20.1 The Components of the Nucleus

LEARNING OBJECTIVE

1. To understand the factors that affect nuclear stability.

Although most of the known elements have at least one isotope whose atomic nucleus is stable indefinitely, all elements have isotopes that are unstable and disintegrate, or*decay*, at measurable rates by emitting radiation. Some elements have no stable isotopes and eventually decay to other elements. In contrast to the chemical reactions that were the main focus of earlier chapters and are due to changes in the arrangements of the valence electrons of atoms, the process of nuclear decay results in changes inside an atomic nucleus. We begin our discussion of nuclear reactions by reviewing the conventions used to describe the components of the nucleus.

The Atomic Nucleus

As you learned in Chapter 1 "Introduction to Chemistry", each element can be represented by the notation XZA, where A, the mass number, is the sum of the number of protons and the number of neutrons, and Z, the atomic number, is the number of protons. The protons and neutrons that make up the nucleus of an atom are callednucleons, and an atom with a particular number of protons and neutrons is called anuclide. Nuclides with the same number of protons but different numbers of neutrons are called **isotopes**. Isotopes can also be represented by an alternative notation that uses the name of the element followed by the mass number, such as carbon-12. The stable isotopes of oxygen, for example, can be represented in any of the following ways:

$$XZA : XA : element - A : O816O16oxygen$$

$$- 16O817O17oxygen - 17O818O18oxygen - 18$$

Because the number of neutrons is equal to $A - Z$, we see that the first isotope of oxygen has 8 neutrons, the second isotope 9 neutrons, and the third isotope 10 neutrons. Isotopes of all naturally occurring elements on Earth are present in nearly fixed proportions, with each proportion constituting an isotope's *natural abundance*. For example, in a typical terrestrial sample of oxygen, 99.76% of the O atoms is oxygen-16, 0.20% is oxygen-18, and 0.04% is oxygen-17.

Any nucleus that is unstable and decays spontaneously is said to be radioactive, emitting subatomic particles and electromagnetic radiation. The emissions are collectively called *radioactivity* and can be measured. Isotopes that emit radiation are called radioisotopes. As you learned in Chapter 14 "Chemical Kinetics", the rate at which radioactive decay occurs is characteristic of the isotope and is generally reported as a **half-life** ($t_{1/2}$), the amount of time required for half of the initial number of nuclei present to decay in a first-order reaction. (For more information on half-life, seeChapter 14 "Chemical Kinetics", Section 14.5 "Half-Lives and Radioactive Decay Kinetics".) An isotope's half-life can range from fractions of a second to billions of years and, among other applications, can be used to measure the age of ancient objects. Example 1 and its corresponding exercise review the calculations involving radioactive decay rates and half-lives.

EXAMPLE 1

Fort Rock Cave in Oregon is the site where archaeologists discovered several Indian sandals, the oldest ever found in Oregon. Analysis of the ^{14}C content of the sagebrush used to make the sandals gave an average decay rate of 5.1 disintegrations per minute (dpm) per gram of carbon. The current $^{14}C/^{12}C$ ratio in

living organisms is 1.3×10^{-12}, with a decay rate of 15 dpm/g C. How long ago was the sagebrush in the sandals cut? The half-life of ^{14}C is 5730 yr.

Given: radioisotope, current $^{14}C/^{12}C$ ratio, initial decay rate, final decay rate, and half-life

Asked for: age

Strategy:

A Use Equation 14.30 to calculate N_0/N, the ratio of the number of atoms of ^{14}C originally present in the sample to the number of atoms now present.

B Substitute the value for the half-life of ^{14}C into Equation 14.28 to obtain the rate constant for the reaction.

C Substitute the calculated values for N_0/N and the rate constant into Equation 14.32to obtain the elapsed time t.

Solution:

We can use the integrated rate law for a first-order nuclear reaction (Equation 14.32) to calculate the amount of time that has passed since the sagebrush was cut to make the sandals:

$$ln\ NN0 = - kt$$

A From Equation 14.30, we know that $A = kN$. We can therefore use the initial and final activities ($A_0 = 15$ and $A = 5.1$) to calculate N_0/N:

$$A0A = kN0kN = N0N = 155.1$$

B Now we can calculate the rate constant k from the half-life of the reaction (5730 yr) using Equation 14.28:

$$t1/2 = 0.693k$$

Rearranging this equation to solve for k,

$$k = 0.693t1/2 = 0.6935730\ yr = 1.21´\ 10 - 4yr - 1$$

C Substituting the calculated values into the equation for t,

$$t = ln(N0/N)k = ln(15/5.1)1.21´\ 10 - 4\ yr - 1 = 8900\ yr$$

Thus the sagebrush in the sandals is about 8900 yr old.

Exercise

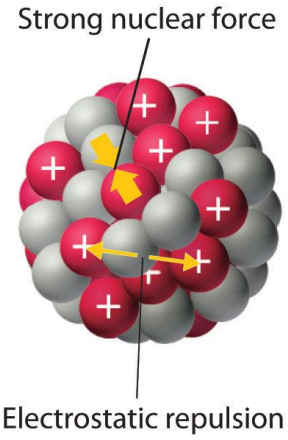
While trying to find a suitable way to protect his own burial chamber, the ancient Egyptian pharaoh Sneferu developed the pyramid, a burial structure that protected desert graves from thieves and exposure to wind. Analysis of the ^{14}C content of several items in pyramids built during his reign gave an average decay rate of 8.6 dpm/g C. When were the objects in the chamber created?

Answer: about 4600 yr ago, or about 2600 BC

Nuclear Stability

As discussed in Chapter 1 "Introduction to Chemistry", the nucleus of an atom occupies a tiny fraction of the volume of an atom and contains the number of protons and neutrons that is characteristic of a given isotope. Electrostatic repulsions would normally cause the positively charged protons to repel each other, but the nucleus does not fly apart because of the strong nuclear force, an extremely powerful but very short-range attractive force between nucleons (Figure 20.1 "Competing Interactions within the Atomic Nucleus"). All stable nuclei except the hydrogen-1 nucleus (^{1}H) contain at least one neutron to overcome the electrostatic repulsion between protons. As the number of protons in the nucleus increases, the number of neutrons needed for a stable nucleus increases even more rapidly. Too many protons (or too few neutrons) in the nucleus result in an imbalance between forces, which leads to nuclear instability.

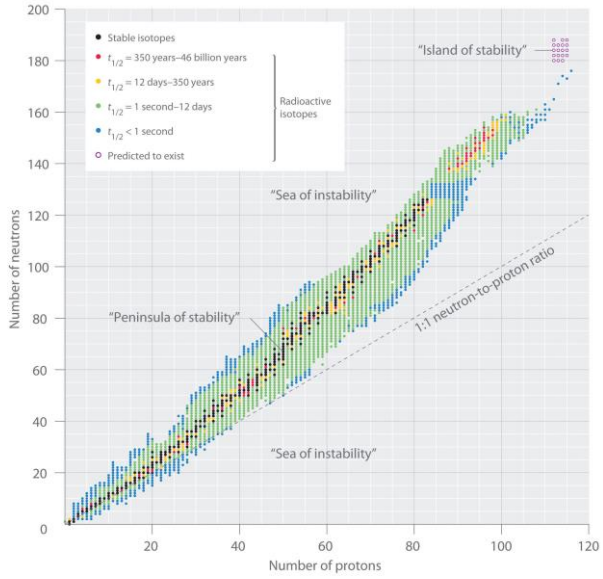
Figure 20.1 *Competing Interactions within the Atomic Nucleus*



Electrostatic repulsions between positively charged protons would normally cause the nuclei of atoms (except H) to fly apart. In stable atomic nuclei, these repulsions are overcome by the strong nuclear force, a short-range but powerful attractive interaction between nucleons. If the attractive interactions due to the strong nuclear force are weaker than the electrostatic repulsions between protons, the nucleus is unstable, and it will eventually decay.

The relationship between the number of protons and the number of neutrons in stable nuclei, arbitrarily defined as having a half-life longer than 10 times the age of Earth, is shown graphically in Figure 20.2 "The Relationship between Nuclear Stability and the Neutron-to-Proton Ratio". The stable isotopes form a “peninsula of stability” in a “sea of instability.” Only two stable isotopes, ^{1}H and ^{3}He, have a neutron-to-proton ratio less than 1. Several stable isotopes of light atoms have a neutron-to-proton ratio equal to 1 (e.g., $H24e,\ B510,\ and\ C2040a$). *All* other stable nuclei have a higher neutron-to-proton ratio, which increases steadily to about 1.5 for the heaviest nuclei. Regardless of the number of neutrons, however, all elements with $Z > 83$ are unstable and radioactive.

Figure 20.2 The Relationship between Nuclear Stability and the Neutron-to-Proton Ratio

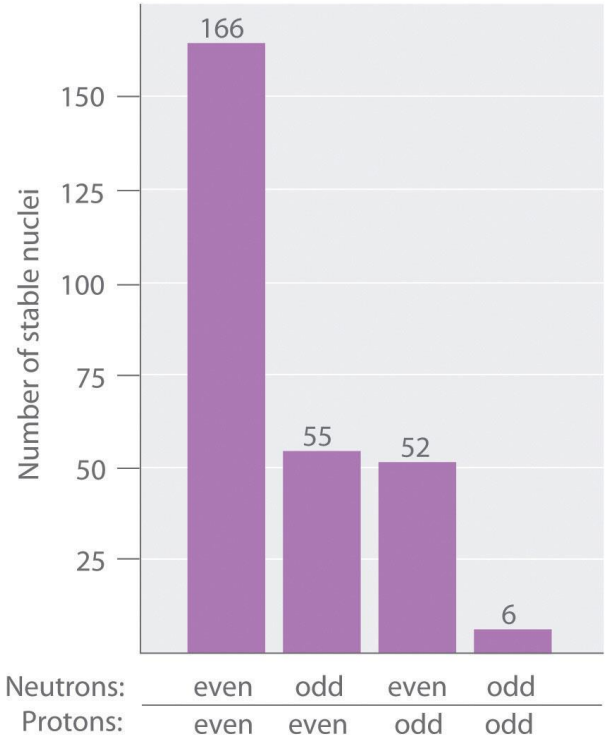


In this plot of the number of neutrons versus the number of protons, each black point corresponds to a stable nucleus. In this classification, a stable nucleus is arbitrarily defined as one with a half-life longer than 46 billion years (10 times the age of Earth). As the number of protons (the atomic number) increases, the number of neutrons required for a stable nucleus increases even more rapidly. Isotopes shown in red, yellow, green, and blue are progressively less stable and more radioactive; the farther an isotope is from the diagonal band of stable isotopes, the shorter its half-life. The purple dots indicate superheavy nuclei that are predicted to be relatively stable, meaning that they are expected to be radioactive but to have relatively long half-lives. In most cases, these elements have not yet been observed or synthesized.

Data source: National Nuclear Data Center, Brookhaven National Laboratory, Evaluated Nuclear Structure Data File (ENSDF), Chart of Nuclides,http://www.nndc.bnl.gov/chart.

As shown in Figure 20.3 "The Relationship between the Number of Protons and the Number of Neutrons and Nuclear Stability", more than half of the stable nuclei (166 out of 279) have *even* numbers of both neutrons and protons; only 6 of the 279 stable nuclei do not have odd numbers of both. Moreover, certain numbers of neutrons or protons result in especially stable nuclei; these are the so-called *magic numbers* 2, 8, 20, 50, 82, and 126. For example, tin ($Z = 50$) has 10 stable isotopes, but the elements on either side of tin in the periodic table, indium ($Z = 49$) and antimony ($Z = 51$), have only 2 stable isotopes each. Nuclei with magic numbers of *both* protons *and* neutrons are said to be “doubly magic” and are even more stable. Examples of elements with doubly magic nuclei are $^{4}_{2}He$, with 2 protons and 2 neutrons, and $^{208}_{82}Pb$, with 82 protons and 126 neutrons, which is the heaviest known stable isotope of any element.

Figure 20.3 The Relationship between the Number of Protons and the Number of Neutrons and Nuclear Stability



Most stable nuclei contain even numbers of both neutrons and protons.

The pattern of stability suggested by the magic numbers of nucleons is reminiscent of the stability associated with the closed-shell electron configurations of the noble gases in group 18 and has led to the

hypothesis that the nucleus contains shells of nucleons that are in some ways analogous to the shells occupied by electrons in an atom. As shown in Figure 20.2 "The Relationship between Nuclear Stability and the Neutron-to-Proton Ratio", the “peninsula” of stable isotopes is surrounded by a “reef” of radioactive isotopes, which are stable enough to exist for varying lengths of time before they eventually decay to produce other nuclei.

EXAMPLE 2

Classify each nuclide as stable or radioactive.

a. *a.* $P1530$ *b.* $T4398c$

b. tin-118

a. $P1530$

Given: mass number and atomic number

Asked for: predicted nuclear stability

Strategy:

Use the number of protons, the neutron-to-proton ratio, and the presence of even or odd numbers of neutrons and protons to predict the stability or radioactivity of each nuclide.

Solution:

a. This isotope of phosphorus has 15 neutrons and 15 protons, giving a neutron-to-proton ratio of 1.0. Although the atomic number, 15, is much less than the value of 83 above which all nuclides are unstable, the neutron-to-proton ratio is less than that expected for stability for an element with this mass. As shown in Figure 20.2 "The Relationship between Nuclear Stability and the Neutron-to-Proton Ratio", its neutron-to-proton ratio should be greater than 1. Moreover, this isotope has an odd number of both neutrons and protons, which also tends to make a nuclide unstable. Consequently, $P1530$ *is* predicted to be radioactive, and it is.

b. This isotope of technetium has 55 neutrons and 43 protons, giving a neutron-to-proton ratio of 1.28, which places $T4398c$ *near*

c. the edge of the band of stability. The atomic number, 55, is much less than the value of 83 above which all isotopes are unstable. These facts suggest that $T4398c$ *might be stable. However,* $T4398c$ *has*

d. an odd number of both neutrons and protons, a combination that seldom gives a stable nucleus. Consequently, $T4398c\ is$

e. predicted to be radioactive, and it is.

f. Tin-118 has 68 neutrons and 50 protons, for a neutron-to-proton ratio of 1.36. As in part b, this value and the atomic number both suggest stability. In addition, the isotope has an *even* number of both neutrons and protons, which tends to increase nuclear stability. Most important, the nucleus has 50 protons, and 50 is one of the magic numbers associated with especially stable nuclei. Thu $s\ S50118nshould$

g. be particularly stable.

h. This nuclide has an atomic number of 94. Because all nuclei with $Z > 83$ are unstable , $P94239u\ must$

i. be radioactive.

Exercise

Classify each nuclide as stable or radioactive.

$a.\quad T90232h$

$b.C2040a$

$c.O815$

$L57139a$

Answer:

a. radioactive

b. stable

c. radioactive

d. stable

Superheavy Elements

In addition to the "peninsula of stability," Figure 20.2 "The Relationship between Nuclear Stability and the Neutron-to-Proton Ratio" shows a small "island of stability" that is predicted to exist in the upper right corner. This island corresponds to thesuperheavy elements, with atomic numbers near the magic number 126. Because the next magic number for neutrons should be 184, it was suggested that an element

with 114 protons and 184 neutrons might be stable enough to exist in nature. Although these claims were met with skepticism for many years, since 1999 a few atoms of isotopes with $Z = 114$ and $Z = 116$ have been prepared and found to be surprisingly stable. One isotope of element 114 lasts 2.7 seconds before decaying, described as an "eternity" by nuclear chemists. Moreover, there is recent evidence for the existence of a nucleus with $A = 292$ that was found in ^{232}Th. With an estimated half-life greater than 10^8 years, the isotope is particularly stable. Its measured mass is consistent with predictions for the mass of an isotope with $Z = 122$. Thus a number of relatively long-lived nuclei may well be accessible among the superheavy elements.

Summary

Subatomic particles of the nucleus (protons and neutrons) are called **nucleons**. A **nuclide** is an atom with a particular number of protons and neutrons. An unstable nucleus that decays spontaneously is **radioactive**, and its emissions are collectively called *radioactivity*. Isotopes that emit radiation are called **radioisotopes**. Each nucleon is attracted to other nucleons by the **strong nuclear force**. Stable nuclei generally have even numbers of both protons and neutrons and a neutron-to-proton ratio of at least 1. Nuclei that contain *magic numbers* of protons and neutrons are often especially stable. **Superheavy elements**, with atomic numbers near 126, may even be stable enough to exist in nature.

KEY TAKEAWAY

- Nuclei with magic numbers of neutrons or protons are especially stable, as are those nuclei that are doubly magic.

CONCEPTUAL PROBLEMS

1. What distinguishes a nuclear reaction from a chemical reaction? Use an example of each to illustrate the differences.
2. What do chemists mean when they say a substance is *radioactive*?
3. What characterizes an isotope? How is the mass of an isotope of an element related to the atomic mass of the element shown in the periodic table?
4. In a typical nucleus, why does electrostatic repulsion between protons not destabilize the nucleus? How does the neutron-to-proton ratio affect the stability of an isotope? Why are all isotopes with $Z > 83$ unstable?
5. What is the significance of a *magic number* of protons or neutrons? What is the relationship between the number of stable isotopes of an element and whether the element has a magic number of protons?

6. Do you expect Bi to have a large number of stable isotopes? Ca? Explain your answers.
7. Potassium has three common isotopes, ^{39}K, ^{40}K, and ^{41}K, but only potassium-40 is radioactive (a beta emitter). Suggest a reason for the instability of ^{40}K.
8. Samarium has 11 relatively stable isotopes, but only 4 are nonradioactive. One of these 4 isotopes is ^{144}Sm, which has a lower neutron-to-proton ratio than lighter, radioactive isotopes of samarium. Why is ^{144}Sm more stable?

ANSWERS

1.
2.
3.
4.
5. Isotopes with magic numbers of protons and/or neutrons tend to be especially stable. Elements with magic numbers of protons tend to have more stable isotopes than elements that do not.
6.
7. Potassium-40 has 19 protons and 21 neutrons. Nuclei with odd numbers of both protons and neutrons tend to be unstable. In addition, the neutron-to-proton ratio is very low for an element with this mass, which decreases nuclear stability.
8.

NUMERICAL PROBLEMS

1. Write the nuclear symbol for each isotope *using XZA notation*.

a. chlorine-39
b. lithium-8
c. osmium-183
d. zinc-71

2. Write the nuclear symbol for each isotope u*sing XZA notation.*

a. lead-212
b. helium-5
c. oxygen-19
d. plutonium-242

3. Give the number of protons, the number of neutrons, and the neutron-to-proton ratio for each isotope.

a. iron-57

b. ^{185}W

c. potassium-39

d. ^{131}Xe

4. Give the number of protons, the number of neutrons, and the neutron-to-proton ratio for each isotope.

a. technetium-99*m*

b. ^{140}La

c. radium-227

d. ^{208}Bi

5. Which of these nuclides do you expect to be radioactive? Explain your reasoning.

a. ^{20}Ne

b. tungsten-184

c. ^{106}Ti

6. Which of these nuclides do you expect to be radioactive? Explain your reasoning.

a. ^{107}Ag

b. ^{50}V

c. lutetium-176

ANSWERS

1.

a. $C1739l$

b. $L38i$

c. $O76183s$

d. $Z3071n$

2.

a. 26 protons; 31 neutrons; 1.19

b. 74 protons; 111 neutrons; 1.50

c. 19 protons; 20 neutrons; 1.05

d. 54 protons; 77 neutrons; 1.43

Chapter 20
Nuclear Chemistry

Until now, you have studied chemical processes in which atoms share or transfer electrons to form new compounds, leaving the atomic nuclei largely unaffected. In this chapter, we examine some properties of the atomic nucleus and the changes that can occur in atomic nuclei.

Nuclear reactions differ from other chemical processes in one critical way: in a nuclear reaction, the identities of the elements change. In addition, nuclear reactions are often accompanied by the release of enormous amounts of energy, as much as a *billion* times more than the energy released by chemical reactions. Moreover, the yields and rates of a nuclear reaction are generally unaffected by changes in temperature, pressure, or the presence of a catalyst.

We begin by examining the structure of the atomic nucleus and the factors that determine whether a particular nucleus is stable or decays spontaneously to another element. We then discuss the major kinds of nuclear decay reactions, as well as the properties and uses of the radiation emitted when nuclei decay. You will learn how radioactive emissions can be used to study the mechanisms of chemical reactions and biological processes and how to calculate the amount of energy released during a nuclear reaction. You will also discover why houses are tested for radon gas, how radiation is used to probe organs such as the brain, and how the energy from nuclear reactions can be harnessed to produce electricity. Last, we explore the nuclear chemistry that takes place in stars, and we describe the role that stars play in producing most of the elements in the universe.

20.1 The Components of the Nucleus

LEARNING OBJECTIVE

1. To understand the factors that affect nuclear stability.

Although most of the known elements have at least one isotope whose atomic nucleus is stable indefinitely, all elements have isotopes that are unstable and disintegrate, or*decay*, at measurable rates by emitting radiation. Some elements have no stable isotopes and eventually decay to other elements. In contrast to the chemical reactions that were the main focus of earlier chapters and are due to changes in the arrangements of the valence electrons of atoms, the process of nuclear decay results in changes inside an atomic nucleus. We begin our discussion of nuclear reactions by reviewing the conventions used to describe the components of the nucleus.

The Atomic Nucleus

As you learned in Chapter 1 "Introduction to Chemistry", each element can be represented by the notation XZA, where A, the mass number, is the sum of the number of protons and the number of neutrons, and Z, the atomic number, is the number of protons. The protons and neutrons that make up the nucleus of an atom are callednucleons, and an atom with a particular number of protons and neutrons is called anuclide. Nuclides with the same number of protons but different numbers of neutrons are called **isotopes**. Isotopes can also be represented by an alternative notation that uses the name of the element followed by the mass number, such as carbon-12. The stable isotopes of oxygen, for example, can be represented in any of the following ways:

$$XZA : XA : element - A : O816O16oxygen$$

$$- 16O817O17oxygen - 17O818O18oxygen - 18$$

Because the number of neutrons is equal to $A - Z$, we see that the first isotope of oxygen has 8 neutrons, the second isotope 9 neutrons, and the third isotope 10 neutrons. Isotopes of all naturally occurring elements on Earth are present in nearly fixed proportions, with each proportion constituting an isotope's *natural abundance*. For example, in a typical terrestrial sample of oxygen, 99.76% of the O atoms is oxygen-16, 0.20% is oxygen-18, and 0.04% is oxygen-17.

Any nucleus that is unstable and decays spontaneously is said to be radioactive, emitting subatomic particles and electromagnetic radiation. The emissions are collectively called *radioactivity* and can be measured. Isotopes that emit radiation are called radioisotopes. As you learned in Chapter 14 "Chemical Kinetics", the rate at which radioactive decay occurs is characteristic of the isotope and is generally reported as a **half-life** ($t_{1/2}$), the amount of time required for half of the initial number of nuclei present to decay in a first-order reaction. (For more information on half-life, seeChapter 14 "Chemical Kinetics", Section 14.5 "Half-Lives and Radioactive Decay Kinetics".) An isotope's half-life can range from fractions of a second to billions of years and, among other applications, can be used to measure the age of ancient objects. Example 1 and its corresponding exercise review the calculations involving radioactive decay rates and half-lives.

EXAMPLE 1

Fort Rock Cave in Oregon is the site where archaeologists discovered several Indian sandals, the oldest ever found in Oregon. Analysis of the ^{14}C content of the sagebrush used to make the sandals gave an average decay rate of 5.1 disintegrations per minute (dpm) per gram of carbon. The current $^{14}C/^{12}C$ ratio in

living organisms is 1.3×10^{-12}, with a decay rate of 15 dpm/g C. How long ago was the sagebrush in the sandals cut? The half-life of ^{14}C is 5730 yr.

Given: radioisotope, current $^{14}C/^{12}C$ ratio, initial decay rate, final decay rate, and half-life

Asked for: age

Strategy:

A Use Equation 14.30 to calculate N_0/N, the ratio of the number of atoms of ^{14}C originally present in the sample to the number of atoms now present.

B Substitute the value for the half-life of ^{14}C into Equation 14.28 to obtain the rate constant for the reaction.

C Substitute the calculated values for N_0/N and the rate constant into Equation 14.32to obtain the elapsed time t.

Solution:

We can use the integrated rate law for a first-order nuclear reaction (Equation 14.32) to calculate the amount of time that has passed since the sagebrush was cut to make the sandals:

$$ln\ NN0 = - kt$$

A From Equation 14.30, we know that $A = kN$. We can therefore use the initial and final activities ($A_0 = 15$ and $A = 5.1$) to calculate N_0/N:

$$A0A = kN0kN = N0N = 155.1$$

B Now we can calculate the rate constant k from the half-life of the reaction (5730 yr) using Equation 14.28:

$$t1/2 = 0.693k$$

Rearranging this equation to solve for k,

$$k = 0.693t1/2 = 0.6935730\ yr = 1.21´\ 10 - 4yr - 1$$

C Substituting the calculated values into the equation for t,

$$t = ln(N0/N)k = ln(15/5.1)1.21´\ 10 - 4\ yr - 1 = 8900\ yr$$

Thus the sagebrush in the sandals is about 8900 yr old.

Exercise

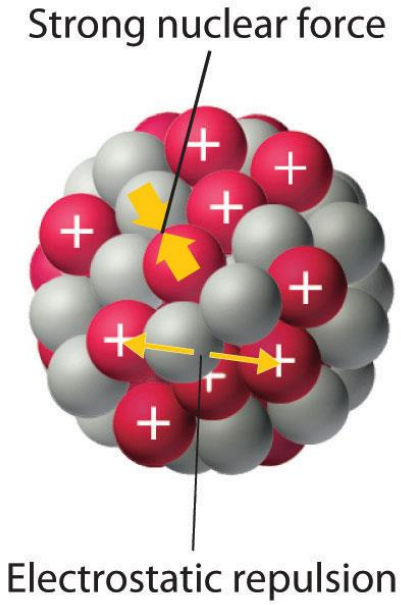
While trying to find a suitable way to protect his own burial chamber, the ancient Egyptian pharaoh Sneferu developed the pyramid, a burial structure that protected desert graves from thieves and exposure to wind. Analysis of the ^{14}C content of several items in pyramids built during his reign gave an average decay rate of 8.6 dpm/g C. When were the objects in the chamber created?

Answer: about 4600 yr ago, or about 2600 BC

Nuclear Stability

As discussed in Chapter 1 "Introduction to Chemistry", the nucleus of an atom occupies a tiny fraction of the volume of an atom and contains the number of protons and neutrons that is characteristic of a given isotope. Electrostatic repulsions would normally cause the positively charged protons to repel each other, but the nucleus does not fly apart because of the strong nuclear force, an extremely powerful but very short-range attractive force between nucleons (Figure 20.1 "Competing Interactions within the Atomic Nucleus"). All stable nuclei except the hydrogen-1 nucleus (^{1}H) contain at least one neutron to overcome the electrostatic repulsion between protons. As the number of protons in the nucleus increases, the number of neutrons needed for a stable nucleus increases even more rapidly. Too many protons (or too few neutrons) in the nucleus result in an imbalance between forces, which leads to nuclear instability.

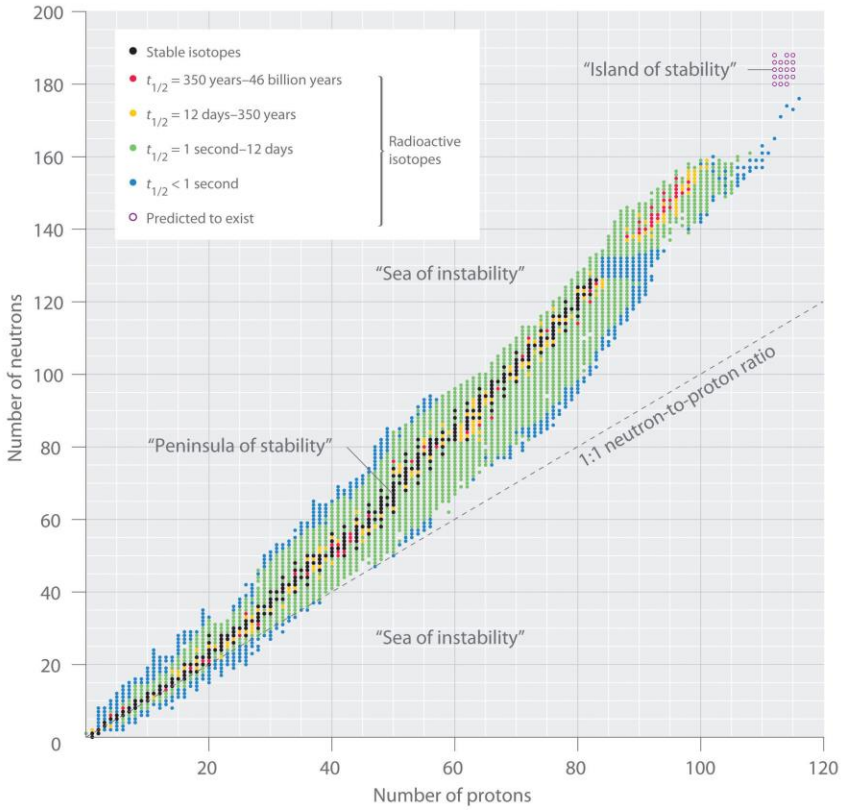
Figure 20.1 *Competing Interactions within the Atomic Nucleus*



Electrostatic repulsions between positively charged protons would normally cause the nuclei of atoms (except H) to fly apart. In stable atomic nuclei, these repulsions are overcome by the strong nuclear force, a short-range but powerful attractive interaction between nucleons. If the attractive interactions due to the strong nuclear force are weaker than the electrostatic repulsions between protons, the nucleus is unstable, and it will eventually decay.

The relationship between the number of protons and the number of neutrons in stable nuclei, arbitrarily defined as having a half-life longer than 10 times the age of Earth, is shown graphically in Figure 20.2 "The Relationship between Nuclear Stability and the Neutron-to-Proton Ratio". The stable isotopes form a “peninsula of stability” in a “sea of instability.” Only two stable isotopes, ^{1}H and ^{3}He, have a neutron-to-proton ratio less than 1. Several stable isotopes of light atoms have a neutron-to-proton ratio equal to 1 (e.g., $H24e$, $B510$, *and* $C2040a$). *All* other stable nuclei have a higher neutron-to-proton ratio, which increases steadily to about 1.5 for the heaviest nuclei. Regardless of the number of neutrons, however, all elements with $Z > 83$ are unstable and radioactive.

Figure 20.2 *The Relationship between Nuclear Stability and the Neutron-to-Proton Ratio*



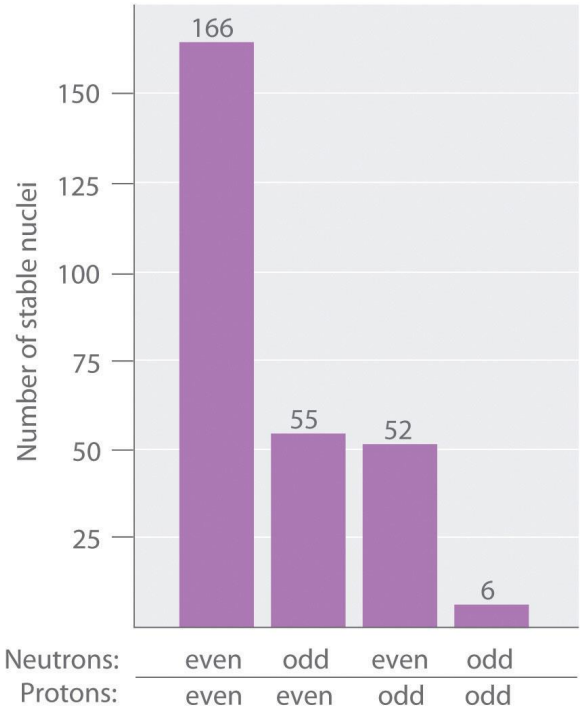
In this plot of the number of neutrons versus the number of protons, each black point corresponds to a stable nucleus. In this classification, a stable nucleus is arbitrarily defined as one with a half-life longer than 46 billion years (10 times the age of Earth). As the number of protons (the atomic number) increases, the number of neutrons required for a stable nucleus increases even more rapidly. Isotopes shown in red, yellow, green, and blue are progressively less stable and more radioactive; the farther an isotope is from the diagonal band of stable isotopes, the shorter its half-life. The purple dots indicate superheavy nuclei that are predicted to be relatively stable, meaning that they are expected to be radioactive but to have relatively long half-lives. In most cases, these elements have not yet been observed or synthesized.

Data source: National Nuclear Data Center, Brookhaven National Laboratory, Evaluated Nuclear Structure Data File (ENSDF), Chart of Nuclides,http://www.nndc.bnl.gov/chart.

As shown in Figure 20.3 "The Relationship between the Number of Protons and the Number of Neutrons and Nuclear Stability", more than half of the stable nuclei (166 out of 279) have *even* numbers of both neutrons and protons; only 6 of the 279 stable nuclei do not have odd numbers of both. Moreover, certain numbers of neutrons or protons result in especially stable nuclei; these are the so-called *magic*

numbers 2, 8, 20, 50, 82, and 126. For example, tin ($Z = 50$) has 10 stable isotopes, but the elements on either side of tin in the periodic table, indium ($Z = 49$) and antimony ($Z = 51$), have only 2 stable isotopes each. Nuclei with magic numbers of *both* protons *and* neutrons are said to be “doubly magic” and are even more stable. Examples of elements with doubly magic nuclei *are* $^{4}_{2}He$, *with* 2 *protons and* 2 *neutrons*, *and* $^{208}_{82}Pb$, *with* 82 protons and 126 neutrons, which is the heaviest known stable isotope of any element.

Figure 20.3 *The Relationship between the Number of Protons and the Number of Neutrons and Nuclear Stability*



Most stable nuclei contain even numbers of both neutrons and protons.

The pattern of stability suggested by the magic numbers of nucleons is reminiscent of the stability associated with the closed-shell electron configurations of the noble gases in group 18 and has led to the hypothesis that the nucleus contains shells of nucleons that are in some ways analogous to the shells occupied by electrons in an atom. As shown in Figure 20.2 "The Relationship between Nuclear Stability and the Neutron-to-Proton Ratio", the “peninsula” of stable isotopes is surrounded by a “reef” of radioactive isotopes, which are stable enough to exist for varying lengths of time before they eventually decay to produce other nuclei.

EXAMPLE 2

Classify each nuclide as stable or radioactive.

a. $P1530$

b. $T4398c$ tin-118

d. $P94239u$

Given: mass number and atomic number

Asked for: predicted nuclear stability

Strategy:

Use the number of protons, the neutron-to-proton ratio, and the presence of even or odd numbers of neutrons and protons to predict the stability or radioactivity of each nuclide.

Solution:

a. This isotope of phosphorus has 15 neutrons and 15 protons, giving a neutron-to-proton ratio of 1.0. Although the atomic number, 15, is much less than the value of 83 above which all nuclides are unstable, the neutron-to-proton ratio is less than that expected for stability for an element with this mass. As shown in Figure 20.2 "The Relationship between Nuclear Stability and the Neutron-to-Proton Ratio", its neutron-to-proton ratio should be greater than 1. Moreover, this isotope has an odd number of both neutrons and protons, which also tends to make a nuclide unstable. Consequently, $P1530$ *is predicted*

b. to be radioactive, and it is.

c. This isotope of technetium has 55 neutrons and 43 protons, giving a neutron-to-proton ratio of 1.28, which *places* $T4398c$ *near* the edge of the band of stability. The atomic number, 55, is much less than the value of 83 above which all isotopes are unstable. These facts suggest *that* $T4398c$ *might* be stable. However, $T4398c$ *has* an odd number of both neutrons and protons, a combination that seldom gives a stable nucleus. Consequently, $T4398c$ *is predicted* to be radioactive, and it is.

d. Tin-118 has 68 neutrons and 50 protons, for a neutron-to-proton ratio of 1.36. As in part b, this value and the atomic number both suggest stability. In addition, the isotope has an *even* number of both neutrons and protons, which tends to increase nuclear stability. Most important, the nucleus has 50 protons, and 50 is one of the magic numbers associated with especially stable nuclei. Thus $S50118n$*should be particularly*

e. stable.

f. This nuclide has an atomic number of 94. Because all nuclei with $Z > 83$ are *unstable*, $P94239u$ must be radioactive.

Exercise

Classify each nuclide as stable or radioactive.

$O815$

$L57139a$

Answer:

a. radioactive

b. stable

c. radioactive

d. stable

Superheavy Elements

In addition to the "peninsula of stability," Figure 20.2 "The Relationship between Nuclear Stability and the Neutron-to-Proton Ratio" shows a small "island of stability" that is predicted to exist in the upper right corner. This island corresponds to thesuperheavy elements, with atomic numbers near the magic number 126. Because the next magic number for neutrons should be 184, it was suggested that an element with 114 protons and 184 neutrons might be stable enough to exist in nature. Although these claims were met with skepticism for many years, since 1999 a few atoms of isotopes with $Z = 114$ and $Z = 116$ have been prepared and found to be surprisingly stable. One isotope of element 114 lasts 2.7 seconds before decaying, described as an "eternity" by nuclear chemists. Moreover, there is recent evidence for the existence of a nucleus with$A = 292$ that was found in ^{232}Th. With an estimated half-life greater than 10^8 years, the isotope is particularly stable. Its measured mass is consistent with predictions for the mass of an isotope with $Z = 122$. Thus a number of relatively long-lived nuclei may well be accessible among the superheavy elements.

Summary

Subatomic particles of the nucleus (protons and neutrons) are called **nucleons**. A**nuclide** is an atom with a particular number of protons and neutrons. An unstable nucleus that decays spontaneously is **radioactive**, and its emissions are collectively called *radioactivity*. Isotopes that emit radiation are

called**radioisotopes**. Each nucleon is attracted to other nucleons by the **strong nuclear force**. Stable nuclei generally have even numbers of both protons and neutrons and a neutron-to-proton ratio of at least 1. Nuclei that contain *magic numbers* of protons and neutrons are often especially stable. **Superheavy elements**, with atomic numbers near 126, may even be stable enough to exist in nature.

KEY TAKEAWAY

- Nuclei with magic numbers of neutrons or protons are especially stable, as are those nuclei that are doubly magic.

CONCEPTUAL PROBLEMS

1. What distinguishes a nuclear reaction from a chemical reaction? Use an example of each to illustrate the differences.
2. What do chemists mean when they say a substance is *radioactive*?
3. What characterizes an isotope? How is the mass of an isotope of an element related to the atomic mass of the element shown in the periodic table?
4. In a typical nucleus, why does electrostatic repulsion between protons not destabilize the nucleus? How does the neutron-to-proton ratio affect the stability of an isotope? Why are all isotopes with $Z > 83$ unstable?
5. What is the significance of a *magic number* of protons or neutrons? What is the relationship between the number of stable isotopes of an element and whether the element has a magic number of protons?
6. Do you expect Bi to have a large number of stable isotopes? Ca? Explain your answers.
7. Potassium has three common isotopes, ^{39}K, ^{40}K, and ^{41}K, but only potassium-40 is radioactive (a beta emitter). Suggest a reason for the instability of ^{40}K.
8. Samarium has 11 relatively stable isotopes, but only 4 are nonradioactive. One of these 4 isotopes is ^{144}Sm, which has a lower neutron-to-proton ratio than lighter, radioactive isotopes of samarium. Why is ^{144}Sm more stable?

ANSWERS

1.
2.
3.
4.

5. Isotopes with magic numbers of protons and/or neutrons tend to be especially stable. Elements with magic numbers of protons tend to have more stable isotopes than elements that do not.
6.
7. Potassium-40 has 19 protons and 21 neutrons. Nuclei with odd numbers of both protons and neutrons tend to be unstable. In addition, the neutron-to-proton ratio is very low for an element with this mass, which decreases nuclear stability.
8.

NUMERICAL PROBLEMS

1. Write the nuclear symbol for each isotope *using XZA notation*
2. .

a. chlorine-39
b. lithium-8
c. osmium-183
d. zinc-71

3. Write the nuclear symbol for each isotope using *XZA notation*
4. .

a. lead-212
b. helium-5
c. oxygen-19
d. plutonium-242

5. Give the number of protons, the number of neutrons, and the neutron-to-proton ratio for each isotope.

a. iron-57
b. ^{185}W
c. potassium-39
d. ^{131}Xe

6. Give the number of protons, the number of neutrons, and the neutron-to-proton ratio for each isotope.

a. technetium-99*m*
b. ^{140}La
c. radium-227

d. ^{208}Bi

7. Which of these nuclides do you expect to be radioactive? Explain your reasoning.

a. ^{20}Ne

b. tungsten-184

c. ^{106}Ti

8. Which of these nuclides do you expect to be radioactive? Explain your reasoning.

a. ^{107}Ag

b. ^{50}V

c. lutetium-176

ANSWERS

1.

2. $C1739l$

3. $a.\ L38i\ \ O76183s$

4. $Z3071n$

5.

a. 26 protons; 31 neutrons; 1.19

b. 74 protons; 111 neutrons; 1.50

c. 19 protons; 20 neutrons; 1.05

d. 54 protons; 77 neutrons; 1.43

20.2 Nuclear Reactions

LEARNING OBJECTIVES

1. To know the different kinds of radioactive decay.
2. To balance a nuclear reaction.

The two general kinds of nuclear reactions are nuclear decay reactions and nuclear transmutation reactions. In a nuclear decay reaction, also called *radioactive decay*, an unstable nucleus emits radiation and is transformed into the nucleus of one or more other elements. The resulting *daughter nuclei* have a lower mass and are lower in energy (more stable) than the *parent nucleus* that decayed. In contrast, in anuclear transmutation reaction, a nucleus reacts with a subatomic particle or another nucleus to form a product nucleus that is *more massive* than the

starting material. As we shall see, nuclear decay reactions occur spontaneously under all conditions, but nuclear transmutation reactions occur only under very special conditions, such as the collision of a beam of highly energetic particles with a target nucleus or in the interior of stars. We begin this section by considering the different classes of radioactive nuclei, along with their characteristic nuclear decay reactions and the radiation they emit.

Note the Pattern

Nuclear decay reactions occur spontaneously under all conditions, whereas nuclear transmutation reactions are induced.

Classes of Radioactive Nuclei

The three general classes of radioactive nuclei are characterized by a different decay process or set of processes:

1. **Neutron-rich nuclei.** The nuclei on the upper left side of the band of stable nuclei in Figure 20.2 "The Relationship between Nuclear Stability and the Neutron-to-Proton Ratio" have a neutron-to-proton ratio that is too high to give a stable nucleus. These nuclei decay by a process that *converts a neutron to a proton*, thereby *decreasing* the neutron-to-proton ratio.
2. **Neutron-poor nuclei.** Nuclei on the lower right side of the band of stable nuclei have a neutron-to-proton ratio that is too low to give a stable nucleus. These nuclei decay by processes that have the net effect of *converting a proton to a neutron*, thereby *increasing* the neutron-to-proton ratio.
3. **Heavy nuclei.** With very few exceptions, heavy nuclei (those with $A \geq 200$) are intrinsically unstable regardless of the neutron-to-proton ratio, and all nuclei with $Z > 83$ are unstable. This is presumably due to the cumulative effects of electrostatic repulsions between the large number of positively charged protons, which cannot be totally overcome by the strong nuclear force, regardless of the number of neutrons present. Such nuclei tend to decay by emitting an α particle (a helium nucleus, $H24e$), which decreases the number of protons and neutrons in the original nucleus by 2. Because the neutron-to-proton ratio in an α particle is 1, the net result of alpha emission is an increase in the neutron-to-proton ratio.

Note the Pattern

Nuclear decay reactions always produce daughter nuclei that have a more favorable neutron-to- proton ratio and hence are more stable than the parent nucleus.

Nuclear Decay Reactions

Just as we use the number and type of *atoms* present to balance a chemical equation, we can use the number and type of *nucleons* present to write a balanced nuclear equation for a nuclear decay reaction. This procedure also allows us to predict the identity of either the parent or the daughter nucleus if the identity of only one is known. Regardless of the mode of decay, *the total number of nucleons is conserved* in all nuclear reactions.

To describe nuclear decay reactions, chemists have extended the *XZA notation* for nuclides to include radioactive emissions. Table 20.1 "Nuclear Decay Emissions and Their Symbols" lists the name and symbol for each type of emitted radiation. We introduced the most common of these, α and β particles and γ rays, in Chapter 1 "Introduction to Chemistry" and Chapter 14 "Chemical Kinetics". The most notable addition is the positron, a particle that has the same mass as an electron but a*positive* charge rather than a negative charge.

Table 20.1 Nuclear Decay Emissions and Their Symbols

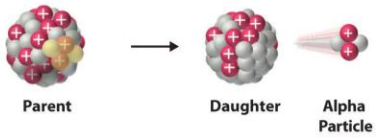
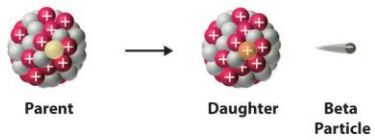
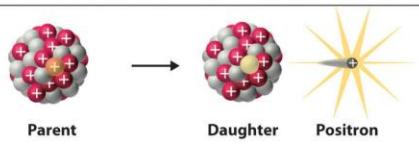
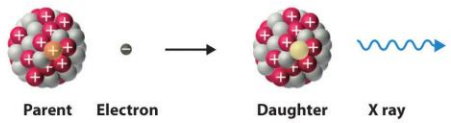
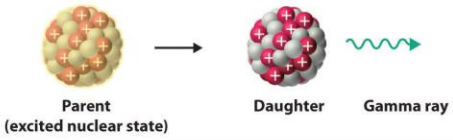
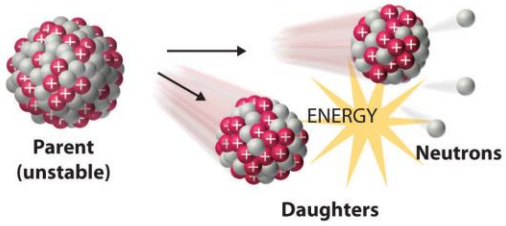
Identity	Symbol	Charge	Mass (amu)
helium nucleus	$a24$	+2	4.001506
electron	$b-10$ *or* $b-$	−1	0.000549
photon	$g00$	—	—
neutron	$n01$	0	1.008665
proton	$p11$	+1	1.007276
positron	$b+10$ *or* $b+$	+1	0.000549

Like the notation used to indicate isotopes, the upper left superscript in the symbol for a particle gives the mass number, which is the total number of protons and neutrons. For a proton or a neutron, $A = 1$. Because neither an electron nor a positron contains protons or neutrons, its mass number is 0. The numbers should not be taken literally, however, as meaning that these particles have zero mass; ejection of a beta particle (an electron) simply has a negligible effect on the mass of a nucleus.

Similarly, the lower left subscript gives the charge of the particle. Because protons carry a positive charge, $Z = +1$ for a proton. In contrast, a neutron contains no protons and is electrically neutral, so $Z = 0$. In the case of an electron, $Z = -1$, and for a positron, $Z = +1$. Because γ rays are high-energy photons, both A and Z are 0. In some cases, two different symbols are used for particles that are identical but produced in different ways. For example, the $_{-1}^{0}e$ symbol, which is usually simplified to e^-, represents a free electron or an electron associated with an *atom*, whereas the symbol $_{-1}^{0}\beta$, which is often simplified to β^-, denotes an electron that originates from within the *nucleus*, which is a β particle. Similarly, $_{2}^{4}He^{2+}$ refers to the nucleus of a helium atom, and $_{2}^{4}\alpha$ denotes an identical particle that has been ejected from a heavier nucleus.

There are six fundamentally different kinds of nuclear decay reactions, and each releases a different kind of particle or energy. The essential features of each reaction are shown in Figure 20.4 "Common Modes of Nuclear Decay". The most common are *alpha*and *beta decay* and *gamma emission*, but the others are essential to an understanding of nuclear decay reactions.

Figure 20.4 *Common Modes of Nuclear Decay*

Decay Type	Radiation Emitted	Generic Equation	Model
Alpha decay	$^{4}_{2}\alpha$	$^{A}_{Z}X \longrightarrow {}^{A-4}_{Z-2}X' + {}^{4}_{2}\alpha$	
Beta decay	$^{0}_{-1}\beta$	$^{A}_{Z}X \longrightarrow {}^{A}_{Z+1}X' + {}^{0}_{-1}\beta$	
Positron emission	$^{0}_{+1}\beta$	$^{A}_{Z}X \longrightarrow {}^{A}_{Z-1}X' + {}^{0}_{+1}\beta$	
Electron capture	X rays	$^{A}_{Z}X + {}^{0}_{-1}e \longrightarrow {}^{A}_{Z-1}X' + \text{X ray}$	
Gamma emission	$^{0}_{0}\gamma$	$^{A}_{Z}X^{*} \xrightarrow{\text{Relaxation}} {}^{A}_{Z}X' + {}^{0}_{0}\gamma$	
Spontaneous fission	Neutrons	$^{A+B+C}_{Z+Y}X \longrightarrow {}^{A}_{Z}X' + {}^{B}_{Y}X' + C\,{}^{1}_{0}n$	

Alpha Decay

Many nuclei with mass numbers greater than 200 undergo alpha (α) decay, which results in the emission of a helium-4 nucleus as an alpha (α) particl *e*, *a*24. *The* general reaction is as follows:

Equation 20.1

$$XZAparent \rightarrow X'Z - 2A - 4daughter + a24alphaparticle$$

The daughter nuclide contains two fewer protons and two fewer neutrons than the parent. Thus α-particle emission produces a daughter nucleus with a mass number $A - 4$ and a nuclear charge $Z - 2$ compared to the parent nucleus. Radium-226, for example, undergoes alpha decay to form radon-222:

Equation 20.2

$$R88226a \rightarrow R86222n + a24$$

Because nucleons are conserved in this and all other nuclear reactions, the sum of the mass numbers of the products, 222 + 4 = 226, equals the mass number of the parent. Similarly, the sum of the atomic numbers of the products, 86 + 2 = 88, equals the atomic number of the parent. Thus the nuclear equation is balanced.

Note the Pattern

Just as the total number of atoms is conserved in a chemical reaction, the total number of nucleons is conserved in a nuclear reaction.

Beta Decay

Nuclei that contain too many neutrons often undergo beta (β) decay, in which a neutron is converted to a proton and a high-energy electron that is ejected from the nucleus as a β particle:

Equation 20.3

$$n01unstableneutron\ innucleus \rightarrow p11protonretainedby\ nucleus$$
$$+b- 10beta\ particleemitted\ bynucleus$$

The general reaction for beta decay is therefore

Equation 20.4

$$XZAparent \rightarrow X'Z+1Adaughter + b- 10beta\ particle$$

Although beta decay does *not* change the mass number of the nucleus, it does result in an increase of +1 in the atomic number because of the addition of a proton in the daughter nucleus. Thus beta decay decreases the neutron-to-proton ratio, moving the nucleus toward the band of stable nuclei. For example, carbon-14 undergoes beta decay to form nitrogen-14:

Equation 20.5

$$C614 \rightarrow N714 + b- 10$$

Once again, the number of nucleons is conserved, and the charges are balanced. The parent and the daughter nuclei have the same mass number, 14, and the sum of the atomic numbers of the products is 6, which is the same as the atomic number of the carbon-14 parent.

Positron Emission

Because a positron has the same mass as an electron but opposite charge,positron emission is the opposite of beta decay. Thus positron emission is characteristic of neutron-poor nuclei, which decay by transforming a proton to a neutron and emitting a high-energy positron:

Equation 20.6

$$p11 \rightarrow n01 + b + 10$$

The general reaction for positron emission is therefore

Equation 20.7

$$XZAparent \rightarrow X'Z - 1Adaughter + b + 10positron$$

Like beta decay, positron emission does not change the mass number of the nucleus. In this case, however, the atomic number of the daughter nucleus is *lower* by 1 than that of the parent. Thus the neutron-to-proton ratio has increased, again moving the nucleus closer to the band of stable nuclei. For example, carbon-11 undergoes positron emission to form boron-11:

Equation 20.8

$$C611 \rightarrow B511 + b + 10$$

Nucleons are conserved, and the charges balance. The mass number, 11, does not change, and the sum of the atomic numbers of the products is 6, the same as the atomic number of the parent carbon-11 nuclide.

Electron Capture

A neutron-poor nucleus can decay by either positron emission orelectron capture (EC), in which an electron in an inner shell reacts with a proton to produce a neutron:

Equation 20.9

$$p11 + e - 10 \rightarrow n01$$

When a second electron moves from an outer shell to take the place of the lower-energy electron that was absorbed by the nucleus, an x-ray is emitted. The overall reaction for electron capture is thus

Equation 20.10

$$XZAparent + e - 10electron \rightarrow X'Z - 1Adaughter + x - ray$$

Electron capture does not change the mass number of the nucleus because both the proton that is lost and the neutron that is formed have a mass number of 1. As with positron emission, however, the atomic number of the daughter nucleus is *lower* by 1 than that of the parent. Once again, the neutron-to-proton ratio has increased, moving the nucleus toward the band of stable nuclei. For example, iron-55 decays by electron capture to form manganese-55, which is often written as follows:

Equation 20.11

$$F2655e \rightarrow ECM2555n + x - ray$$

The atomic numbers of the parent and daughter nuclides differ in Equation 20.11, although the mass numbers are the same. To write a balanced nuclear equation for this reaction, we must explicitly include the captured electron in the equation:

Equation 20.12

$$F2655e + e\text{ - }10 \rightarrow M2555n + x\text{ - }ray$$

Both positron emission and electron capture are usually observed for nuclides with low neutron-to-proton ratios, but the decay rates for the two processes can be very different.

Gamma Emission

Many nuclear decay reactions produce daughter nuclei that are in a nuclear excited state, which is similar to an atom in which an electron has been excited to a higher-energy orbital to give an electronic excited state. Just as an electron in an electronic excited state emits energy in the form of a photon when it returns to the ground state, a nucleus in an excited state releases energy in the form of a photon when it returns to the ground state. (For more information on electron ground states, see Chapter 6 "The Structure of Atoms".) These high-energy photons are γ rays. Gamma (γ) emissioncan occur virtually instantaneously, as it does in the alpha decay of uranium-238 to thorium-234, where the asterisk denotes an excited state:

Equation 20.13

$$U92238 \rightarrow T90234h * excitednuclearstate + a24\text{-} \rightarrow$$
$$\text{- - - - }relaxationT90234h + g00$$

If we disregard the decay event that created the excited nucleus, then

Equation 20.14

$$T88234h* \rightarrow T88234h + g00$$

or more generally,

Equation 20.15

$$XZA* \rightarrow XZA + g00$$

Gamma emission can also occur after a significant delay. For example, technetium-99*m* has a half-life of about 6 hours before emitting a γ ray to form technetium-99. (The*m* is for metastable, which is explained in Chapter 14 "Chemical Kinetics", Section 14.5 "Half-Lives and Radioactive Decay Kinetics".)

Because γ rays are energy, their emission does not affect either the mass number or the atomic number of the daughter nuclide. Gamma-ray emission is therefore the only kind of radiation that does not necessarily involve the conversion of one element to another, although it is almost always observed in conjunction with some other nuclear decay reaction.

Spontaneous Fission

Only very massive nuclei with high neutron-to-proton ratios can undergospontaneous fission, in which the nucleus breaks into two pieces that have different atomic numbers and atomic masses. This process is most important for the transactinide elements, with $Z \geq 104$. Spontaneous fission is invariably accompanied by the release of large amounts of energy, and it is usually accompanied by the emission of several neutrons as well. An example is the spontaneous fission $of\ C98254f, which$ gives a distribution of fission products; one possible set of products is shown in the following equation:

Equation 20.16

$$C98254f \rightarrow P46118d + T52132e + 410n$$

Once again, the number of nucleons is conserved. Thus the sum of the mass numbers of the products (118 + 132 + 4 = 254) equals the mass number of the reactant. Similarly, the sum of the atomic numbers of the products [46 + 52 + (4 × 0) = 98] is the same as the atomic number of the parent nuclide.

EXAMPLE 3

Write a balanced nuclear equation to describe each reaction.

a. the beta decay of $S1635$

b. the decay o $f\ H80201g$

c. by electron capture

d. the decay $of\ P1530\ by\ positron$ emission

Given: radioactive nuclide and mode of decay

Asked for: balanced nuclear equation

Strategy:

A Identify the reactants and the products from the information given.

B Use the values of *A* and *Z* to identify any missing components needed to balance the equation.

Solution:

a. **A** We know the identities of the reactant and one of the products (a β particle). We can therefore begin by writing an equation that shows the reactant and one of the products and indicates the unknown product a $s\ XZA$:

$$S1635 \rightarrow XZA + b\text{-}\ 10$$

B Because both protons and neutrons must be conserved in a nuclear reaction, the unknown product must have a mass number of $A = 35 - 0 = 35$ and an atomic number of $Z = 16 - (-1) = 17$. The element with $Z = 17$ is chlorine, so the balanced nuclear equation is as follows:

b. $S1635 \rightarrow C1735l + b\text{-}\ 10$

c. **A** We know the identities of both

reactants: $H80201g\ and\ an\ inner\ electron,\ e\text{-}\ 10.\ The$

d. reaction is as follows:

$$H80201g + e\text{-}\ 10 \rightarrow XZA$$

B Both protons and neutrons are conserved, so the mass number of the product must be $A = 201 + 0 = 201$, and the atomic number of the product must be $Z = 80 + (-1) = 79$, which corresponds to the element gold. The balanced nuclear equation is thus

e. $H80201g + e\text{-}\ 10 \rightarrow A79201u$

f. **A** As in part (a), we are given the identities of the reactant and one of the products—in this case, a positron. The unbalanced nuclear equation is therefore

$$P1530 \rightarrow XZA + b + 10$$

B The mass number of the second product is $A = 30 - 0 = 30$, and its atomic number is $Z = 15 - 1 = 14$, which corresponds to silicon. The balanced nuclear equation for the reaction is as follows:

$$P1530 \rightarrow S1430i + b + 10$$

Exercise

Write a balanced nuclear equation to describe each reaction.

a. $C611\ by$ positron emission

b. the beta decay of molybdenum-99

c. the emission of an α particle followed by gamma emission from $W74185$

Answer:

a. $C611 \rightarrow B511 + b + 10 \quad M4299o \rightarrow T4399mc + b - 10$

a. *a.* $W74185 \rightarrow H72181f + a24 + g00$

EXAMPLE 4

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

a. $T2245i$

$P94242u$

$B512$

$P94242u \text{ is expected}$

Given: nuclide

Asked for: type of nuclear decay

Strategy:

Based on the neutron-to-proton ratio and the value of *Z*, predict the type of nuclear decay reaction that will produce a more stable nuclide.

Solution:

a. This nuclide has a neutron-to-proton ratio of only 1.05, which is much less than the requirement for stability for an element with an atomic number in this range. Nuclei that have low neutron-to-proton ratios decay by converting a proton to a neutron. The two possibilities are positron emission, which converts a proton to a neutron and a positron, and electron capture, which converts a proton and a core electron to a neutron. In this case, both are observed, with positron emission occurring about 86% of the time and electron capture about 14% of the time.

b. Nuclei with $Z > 83$ are too heavy to be stable and usually undergo alpha decay, which decreases both the mass number and the atomic number.
Thus $P94242u \text{ is expected}$

c. to decay by alpha emission.

d. This nuclide has a neutron-to-proton ratio of 1.4, which is very high for a light element. Nuclei with high neutron-to-proton ratios decay by converting a neutron to

a proton and an electron. The electron is emitted as a β particle, and the proton remains in the nucleus, causing an increase in the atomic number with no change in the mass number. We therefore predict $^{512}_{\ 5}B$ *that will undergo*

e. beta decay.

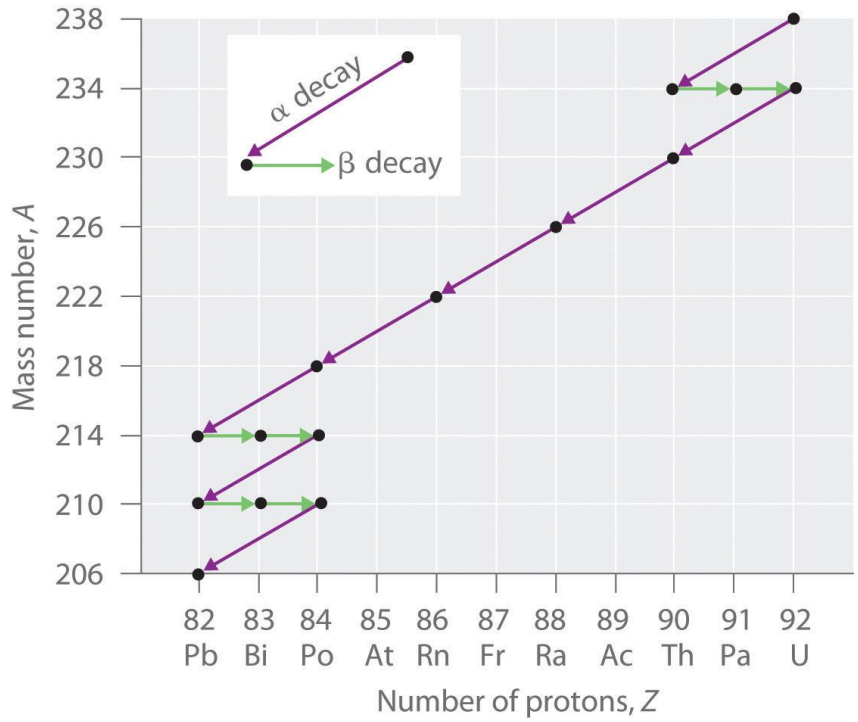
f. This is a massive nuclide, with an atomic number of 100 and a mass number much greater than 200. Nuclides with $A \geq 200$ tend to decay by alpha emission, and even heavier nuclei tend to undergo spontaneous fission. We therefore predict that $^{256}_{100}F$ *will*

g. decay by either or both of these two processes. In fact, it decays by both spontaneous fission and alpha emission, in a 97:3 ratio.

Radioactive Decay Series

The nuclei of all elements with atomic numbers greater than 83 are unstable. Thus all isotopes of all elements beyond bismuth in the periodic table are radioactive. Because alpha decay decreases Z by only 2, and positron emission or electron capture decreases$Z$ by only 1, it is impossible for any nuclide with $Z >$ 85 to decay to a stable daughter nuclide in a single step, except via nuclear fission. Consequently, radioactive isotopes with $Z > 85$ usually decay to a daughter nucleus that is radiaoctive, which in turn decays to a second radioactive daughter nucleus, and so forth, until a stable nucleus finally results. This series of sequential alpha- and beta-decay reactions is called aradioactive decay series. The most common is the uranium-238 decay series, which produces lead-206 in a series of 14 sequential alpha- and beta-decay reactions (Figure 20.5 "A Radioactive Decay Series"). Although a radioactive decay series can be written for almost any isotope with $Z > 85$, only two others occur naturally: the decay of uranium-235 to lead-207 (in 11 steps) and thorium-232 to lead-208 (in 10 steps). A fourth series, the decay of neptunium-237 to bismuth-209 in 11 steps, is known to have occurred on the primitive Earth. With a half-life of "only" 2.14 million years, all the neptunium-237 present when Earth was formed decayed long ago, and today all the neptunium on Earth is synthetic.

Figure 20.5 A Radioactive Decay Series



Three naturally occurring radioactive decay series are known to occur currently: the uranium-238 decay series, the decay of uranium-235 to lead-207, and the decay of thorium-232 to lead-208.

Due to these radioactive decay series, small amounts of very unstable isotopes are found in ores that contain uranium or thorium. These rare, unstable isotopes should have decayed long ago to stable nuclei with a lower atomic number, and they would no longer be found on Earth. Because they are generated continuously by the decay of uranium or thorium, however, their amounts have reached a steady state, in which their rate of formation is equal to their rate of decay. In some cases, the abundance of the daughter isotopes can be used to date a material or identify its origin, as described in Chapter 14 "Chemical Kinetics".

Induced Nuclear Reactions

The discovery of radioactivity in the late 19th century showed that some nuclei spontaneously transform into nuclei with a different number of protons, thereby producing a different element. When scientists realized that these naturally occurring radioactive isotopes decayed by emitting subatomic particles, they realized that—in principle—it should be possible to carry out the reverse reaction, converting a stable nucleus to another more massive nucleus by bombarding it with subatomic particles in a nuclear transmutation reaction.

The first successful nuclear transmutation reaction was carried out in 1919 by Ernest Rutherford, who showed that α particles emitted by radium could react with nitrogen nuclei to form oxygen nuclei. As shown in the following equation, a proton is emitted in the process:

Equation 20.17

$$a24 + N714 \rightarrow O817 + p11$$

Rutherford's nuclear transmutation experiments led to the discovery of the neutron. He found that bombarding the nucleus of a light target element with an α particle usually converted the target nucleus to a product that had an atomic number higher by 1 and a mass number higher by 3 than the target nucleus. Such behavior is consistent with the emission of a proton after reaction with the α particle. Very light targets such as Li, Be, and B reacted differently, however, emitting a new kind of highly penetrating radiation rather than a proton. Because neither a magnetic field nor an electrical field could deflect these high-energy particles, Rutherford concluded that they were electrically neutral. (For more information on high-energy particles, see Chapter 1 "Introduction to Chemistry".) Other observations suggested that the mass of the neutral particle was similar to the mass of the proton. In 1932, James Chadwick (Nobel Prize in Physics, 1935), who was a student of Rutherford's at the time, named these neutral particles*neutrons* and proposed that they were fundamental building blocks of the atom. The reaction that Chadwick initially used to explain the production of neutrons was as follows:

Equation 20.18

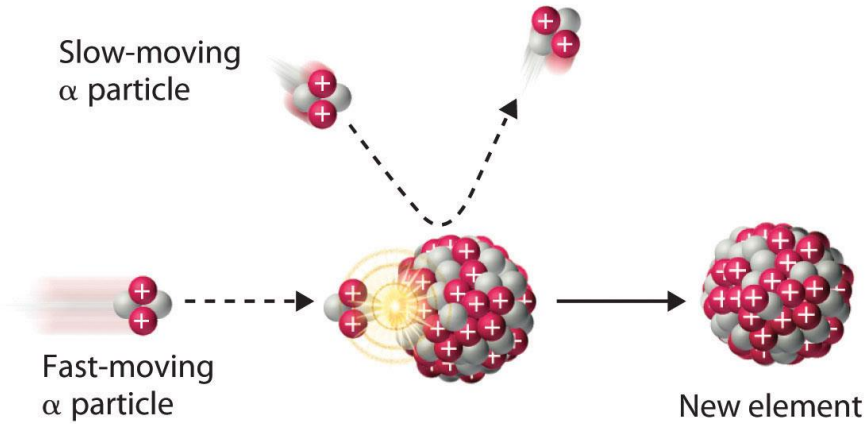
$$a24 + B49e \rightarrow C612 + n01$$

Because α particles and atomic nuclei are both positively charged, electrostatic forces cause them to repel each other. Only α particles with very high kinetic energy can overcome this repulsion and collide with a nucleus (Figure 20.6 "A Nuclear Transmutation Reaction"). Neutrons have no electrical charge, however, so they are not repelled by the nucleus. Hence bombardment with neutrons is a much easier way to prepare new isotopes of the lighter elements. In fact, carbon-14 is formed naturally in the atmosphere by bombarding nitrogen-14 with neutrons generated by cosmic rays:

Equation 20.19

$$n01 + N714 \rightarrow C614 + p11$$

Figure 20.6 *A Nuclear Transmutation Reaction*



Bombarding a target of one element with high-energy nuclei or subatomic particles can create new elements. Electrostatic repulsions normally prevent a positively charged particle from colliding and reacting with a positively charged nucleus. If the positively charged particle is moving at a very high speed, however, its kinetic energy may be great enough to overcome the electrostatic repulsions, and it may collide with the target nucleus. Such collisions can result in a nuclear transmutation reaction.

EXAMPLE 5

In 1933, Frédéric Joliot and Iréne Joliot-Curie (daughter of Marie and Pierre Curie) prepared the first artificial radioactive isotope by bombarding aluminum-27 with α particles. For each ^{27}Al that reacted, one neutron was released. Identify the product nuclide and write a balanced nuclear equation for this transmutation reaction.

Given: reactants in a nuclear transmutation reaction

Asked for: product nuclide and balanced nuclear equation

Strategy:

A Based on the reactants and one product, identify the other product of the reaction. Use conservation of mass and charge to determine the values of *Z* and *A* of the product nuclide and thus its identity.

B Write the balanced nuclear equation for the reaction.

Solution:

A Bombarding an element with α particles usually produces an element with an atomic number that is 2 greater than the atomic number of the target nucleus. Thus we expect that aluminum ($Z = 13$) will be converted to phosphorus ($Z = 15$). With one neutron released, conservation of mass requires that the mass number of the other product be 3 greater than the mass number of the target. In this case, the mass

number of the target is 27, so the mass number of the product will be 30. The second product is therefore phosphorus-30, $P1530.$

B The balanced nuclear equation for the reaction is as follows:

$A1327l + a24 \rightarrow P1530 + n01$ Exercise

Because all isotopes of technetium are radioactive and have short half-lives, it does not exist in nature. Technetium can, however, be prepared by nuclear transmutation reactions. For example, bombarding a molybdenum-96 target with deuterium $nuclei\ (H12)\ produces$ technetium-97. Identify the other product of the reaction and write a balanced nuclear equation for this transmutation reaction.

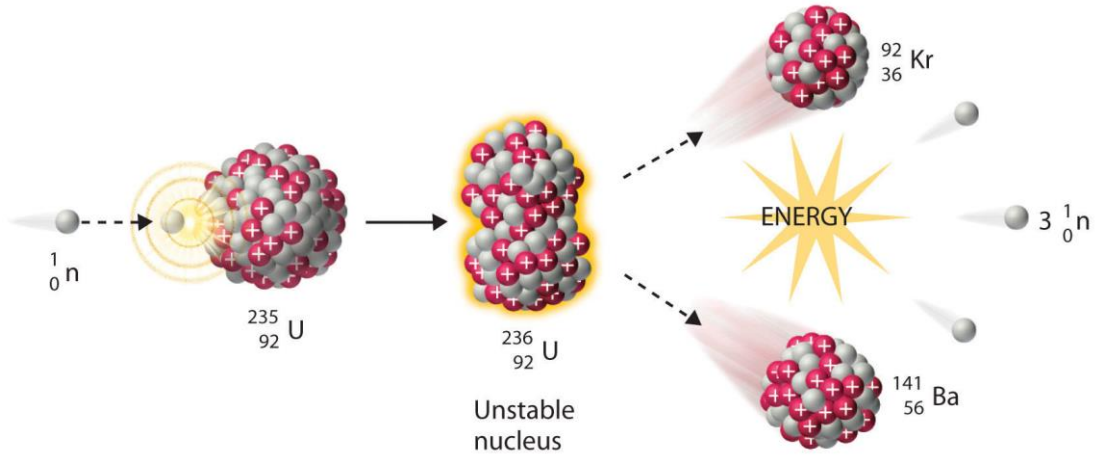
Answer: neutro $n,\ n01;\ M4296o + H12 \rightarrow T4397c + n01$

We noted earlier in this section that very heavy nuclides, corresponding to $Z \geq 104$, tend to decay by spontaneous fission. Nuclides with slightly lower values of Z, such as the isotopes of uranium ($Z = 92$) and plutonium ($Z = 94$), do not undergo spontaneous fission at any significant rate. $Some\ isotopes\ of\ these\ elements,\ however,$ $such\ as\ U92235 and\ P94239u\ undergo\ induced\ nuclear$ *fission* when they are bombarded with relatively low-energy neutrons, as shown in the following equation for uranium-235 and in Figure 20.7 "Neutron-Induced Nuclear Fission":

Equation 20.20

$$U92235 + n01 \rightarrow U92236 \rightarrow B56141a + K3692r + 3n01$$

Figure 20.7 Neutron-Induced Nuclear Fission

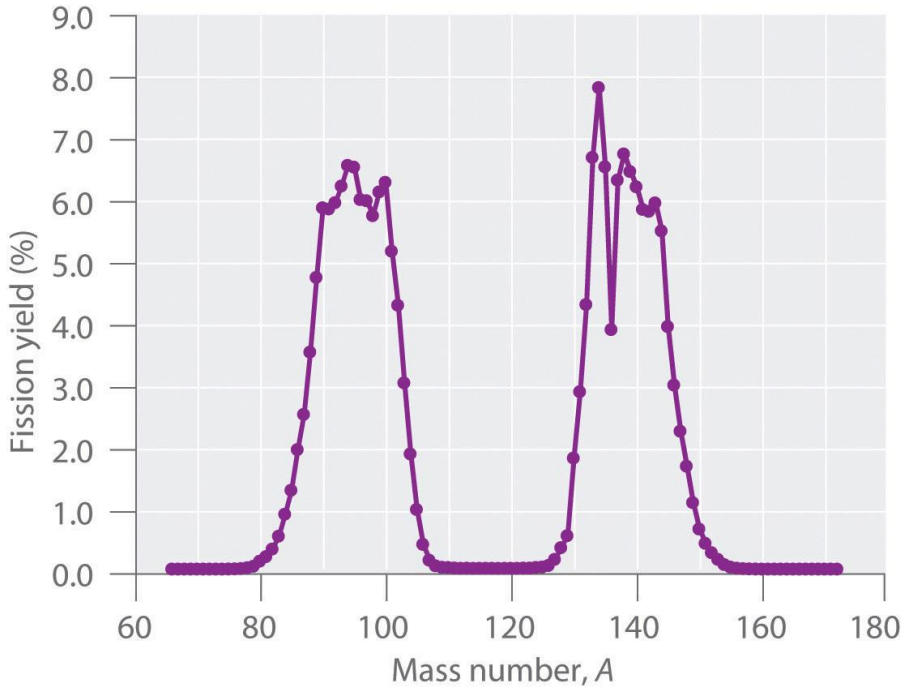


Collision of a relatively slow-moving neutron with a fissile nucleus can split it into two smaller nuclei with the same or different masses. Neutrons are also released in the process, along with a great deal of energy.

Any isotope that can undergo a nuclear fission reaction when bombarded with neutrons is called a *fissile isotope*.

During nuclear fission, the nucleus usually divides asymmetrically rather than into two equal parts, as shown in Figure 20.7 "Neutron-Induced Nuclear Fission". Moreover, every fission event of a given nuclide does not give the same products; more than 50 different fission modes have been identified for uranium-235, for example. Consequently, nuclear fission of a fissile nuclide can never be described by a single equation. Instead, as shown in Figure 20.8 "Mass Distribution of Nuclear Fission Products of ", a distribution of many pairs of fission products with different yields is obtained, but the mass ratio of each pair of fission products produced by a single fission event is always roughly 3:2.

Figure 20.8 *Mass Distribution of Nuclear Fission Products of ^{235}U*



Nuclear fission usually produces a range of products with different masses and yields, although the mass ratio of each pair of fission products from a fission event is approximately 3:2. As shown in this plot, more than 50 different fission products are known for ^{235}U.

Data source: T. R. England and B. F. Rider, Los Alamos National Laboratory, LA-UR-94-3106, ENDF-349 (1993).

Synthesis of Transuranium Elements

Uranium (Z = 92) is the heaviest naturally occurring element. Consequently, all the elements with Z > 92, the transuranium elements, are artificial and have been prepared by bombarding suitable target nuclei with smaller particles. The first of the transuranium elements to be prepared was neptunium (Z = 93), which was synthesized in 1940 by bombarding a ^{238}U target with neutrons. As shown in Equation 20.21, this reaction occurs in two steps. Initially, a neutron combines with a ^{238}U nucleus to form ^{239}U, which is unstable and undergoes beta decay to produce ^{239}Np:

Equation 20.21

$$U92238 + n01 \rightarrow U92239 \rightarrow N93239p + b - 10$$

Subsequent beta decay of ^{239}Np produces the second transuranium element, plutonium (Z = 94):

Equation 20.22

$$N93239p \rightarrow P94239u + b - 10$$

Bombarding the target with more massive nuclei creates elements that have atomic numbers significantly greater than that of the target nucleus (Table 20.2 "Some Reactions Used to Synthesize Transuranium Elements"). Such techniques have resulted in the creation of the superheavy elements 114 and 116, both of which lie in or near the "island of stability" discussed in Section 20.1 "The Components of the Nucleus".

Table 20.2 Some Reactions Used to Synthesize Transuranium Elements

$P94239u + a24 \rightarrow C96242m + n01$
$P94239u + a24 \rightarrow A95241m + p11 + n01$
$C96242m + a24 \rightarrow B97243k + p11 + 2n01$
$E99253s + a24 \rightarrow M101256d + n01$
$U92238 + C612 \rightarrow C98246f + 4n01$
$C98252f + B510 \rightarrow L103256r + 6n01$

A device called a *particle accelerator* is used to accelerate positively charged particles to the speeds needed to overcome the electrostatic repulsions between them and the target nuclei by using electrical and magnetic fields. Operationally, the simplest particle accelerator is the linear accelerator (Figure 20.9

"A Linear Particle Accelerator"), in which a beam of particles is injected at one end of a long evacuated tube. Rapid alternation of the polarity of the electrodes along the tube causes the particles to be alternately accelerated toward a region of opposite charge and repelled by a region with the same charge, resulting in a tremendous acceleration as the particle travels down the tube. A modern linear accelerator such as the Stanford Linear Accelerator (SLAC) at Stanford University is about 2 miles long.

(a) An aerial view of the SLAC, the longest linear particle accelerator in the world; the overall length of the tunnel is 2 miles. (b) Rapidly reversing the polarity of the electrodes in the tube causes the charged particles to be alternately attracted as they enter one section of the tube and repelled as they leave that section. As a result, the particles are continuously accelerated along the length of the tube.

To achieve the same outcome in less space, a particle accelerator called a *cyclotron*forces the charged particles to travel in a circular path rather than a linear one. The particles are injected into the center of a ring and accelerated by rapidly alternating the polarity of two large D-shaped electrodes above and below the ring, which accelerates the particles outward along a spiral path toward the target.

The length of a linear accelerator and the size of the D-shaped electrodes in a cyclotron severely limit the kinetic energy that particles can attain in these devices. These limitations can be overcome by using a *synchrotron*, a hybrid of the two designs. A synchrotron contains an evacuated tube similar to that of a linear accelerator, but the tube is circular and can be more than a mile in diameter (Figure 20.10 "A Synchrotron"). Charged particles are accelerated around the circle by a series of magnets whose polarities rapidly alternate.

tube characteristic of a synchrotron is 4 miles in circumference, contains 1000 superconducting magnets cooled by liquid helium, and can accelerate a beam of protons to almost the speed of light, giving them an energy greater than 1 TeV (teraelectronvolt = 10^3 GeV = 10^{12} eV) for collisions with other particles.

Summary

In **nuclear decay reactions (or radioactive decay)**, the *parent nucleus* is converted to a more stable *daughter nucleus*. Nuclei with too many neutrons decay by converting a neutron to a proton, whereas nuclei with too few neutrons decay by converting a proton to a neutron. Very heavy nuclei (with $A \geq 200$ and $Z > 83$) are unstable and tend to decay by emitting an **α particle**. When an unstable nuclide undergoes radioactive decay, the total number of nucleons is conserved, as is the total positive

charge. Six different kinds of nuclear decay reactions are known.**Alpha decay** results in the emission of an α partic*le, a*24, *and produces*

a daughter nucleus with a mass number that is lower by 4 and an atomic number that is lower by 2 than the parent nucleus. **Beta decay** converts a neutron to a proton and emits a high-energy electron, producing a daughter nucleus with the same mass number as the parent and an atomic number that is higher by 1. **Positron emission** is the opposite of beta decay and converts a proton to a neutron plus a positron. Positron emission does not change the mass number of the nucleus, but the atomic number of the daughter nucleus is lower by 1 than the parent. In **electron capture (EC)**, an electron in an inner shell reacts with a proton to produce a neutron, with emission of an x-ray. The mass number does not change, but the atomic number of the daughter is lower by 1 than the parent. In **gamma emission**, a daughter nucleus in a *nuclear excited state* undergoes a transition to a lower-energy state by emitting a γ ray. Very heavy nuclei with high neutron-to-proton ratios can undergo **spontaneous fission**, in which the nucleus breaks into two pieces that can have different atomic numbers and atomic masses with the release of neutrons. Many very heavy nuclei decay via a **radioactive decay series**—a succession of some combination of alpha- and beta-decay reactions. In**nuclear transmutation reactions**, a target nucleus is bombarded with energetic subatomic particles to give a product nucleus that is more massive than the original. All **transuranium elements**—elements with $Z > 92$—are artificial and must be prepared by nuclear transmutation reactions. These reactions are carried out in *particle accelerators* such as *linear accelerators*, *cyclotrons*, and*synchrotrons*.

KEY TAKEAWAY

- Nuclear decay reactions occur spontaneously under all conditions and produce more stable daughter nuclei, whereas nuclear transmutation reactions are induced and form a product nucleus that is more massive than the starting material.

KEY EQUATIONS

alpha decay

$$Equation\ 20.1: XZA \rightarrow X'Z - 2A - 4 + a24$$

beta decay

$$Equation\ 20.4: XZA \rightarrow X'Z + 1A + b - 10$$

positron emission

Equation 20.7: $XZA \rightarrow X'Z - 1A + b + 10$

electron capture $Equation\ 20.10: XZA + e - 10 \rightarrow X'Z - 1A + x - ray$

gamma emission

$Equation\ 20.15: XZA^* \rightarrow XZA + g00$

CONCEPTUAL PROBLEMS

1. Describe the six classifications of nuclear decay reactions. What is the most common mode of decay for elements that have heavy nuclei? Why?
2. Complete the following table for these five nuclear reactions.

	Alpha Decay	Beta Decay	Gamma Emission	Positron Emission	Electron Capture
identity of particle or radiation	helium-4 nucleus				
mass number of parent – mass number of daughter	4				
atomic number of parent – atomic number of daughter		–1			
effect on neutron-to-proton ratio		decreases			

3. What is the most common decay process for elements in row 5 of the periodic table that contain too few neutrons for the number of protons present? Why?
4. Explain the difference between the symbols e^- and β^-. What is the difference in meaning between *the symbols* $H24e$ *and* $a24$?
5. What is a mass number? Which particles have a mass number of zero?
6. What are the key differences between the equations written for chemical reactions and for nuclear reactions? How are they similar?
7. Can all the kinds of nuclear decay reactions discussed be characterized by the general equation: parent → daughter + particle? Explain your answer.

8. Which types of nuclear decay reactions conserve both mass number and atomic number? In which do the parent and daughter nuclei have the same mass number but different atomic numbers? Which do not convert one element to another?
9. Describe a radioactive decay series. How many series occur naturally? Of these, which one no longer occurs in nature? Why?
10. Only nine naturally occurring elements have an atomic number greater than 83, and all of them are radioactive. Except for some isotopes of uranium that have a very long half-life, the half-lives of the heavy elements are so short that these elements should have been completely converted to lighter, more stable elements long ago. Why are these elements still present in nature?
11. Why are neutrons preferred to protons when preparing new isotopes of the lighter elements?
12. Why are particle accelerators and cyclotrons needed to create the transuranium elements?

ANSWERS

1.
2.
3. Both positron decay and electron capture increase the neutron-to-proton ratio; electron capture is more common for heavier elements such those of row 5.
4.
5. The mass number is the sum of the numbers of protons and neutrons present. Particles with a mass number of zero include β particles (electrons) and positrons; gamma rays and x-rays also have a mass number of zero.
6.
7.
8.
9.
10.
11. Unlike protons, neutrons have no charge, which minimizes the electrostatic barrier to colliding and reacting with a positively charged nucleus.
12.

NUMERICAL PROBLEMS

1. What type of particle is emitted in each nuclear reaction?

a. $^{238}Pu \rightarrow {}^{234}U$

b. $^{32}Si \rightarrow {}^{32}P$

c. $^{18}F \rightarrow {}^{18}O$

d. $^{206}Tl \rightarrow {}^{206}Pb$

2. What type of particle is emitted in each nuclear reaction?

a. $^{230}Th \rightarrow {}^{226}Ra$

b. $^{224}Rn \rightarrow {}^{224}Fr$

c. $^{210}Bi \rightarrow {}^{206}Tl$

d. $^{36}Cl \rightarrow {}^{36}S$

3. Predict the mode of decay and write a balanced nuclear reaction for each isotope.

a. ^{235}U

b. ^{254}Es

c. ^{36}S

d. ^{99}Mo

4. Predict the mode of decay and write a balanced nuclear reaction for each isotope.

a. ^{13}N

b. ^{231}Pa

c. ^{7}Be

d. ^{77}Ge

5. Balance each nuclear reaction.

a. $^{208}Po \rightarrow \alpha + Pb$

b. $^{226}Ra \rightarrow \alpha + Rn$

c. $^{228}Th \rightarrow Ra + \alpha + \gamma$

d. $^{231}Pa \rightarrow Ac + \alpha + \gamma$

e. $Ho \rightarrow {}^{166}Er + \beta^{-} + \gamma$

f. $Ac \rightarrow {}^{226}Th + \beta^{-} + \gamma$

6. Complete each nuclear reaction.

a. $a.\quad P84210o \rightarrow P206b$

b. $A85217t \rightarrow Bi + a$

c. $a.\ \ Ra \rightarrow R86220n + a$ $^{208}Tl \rightarrow {}_{82}Pb + \beta^-$

d. $Np \rightarrow {}^{239}Pu + \beta^-$

e. $Fe \rightarrow {}^{52}Mn + \beta^+ + \gamma$

7. Write a balanced nuclear equation for each reaction.

a. β^- decay of ^{87}Rb

b. β^+ decay of ^{20}Mg

c. α decay of ^{268}Mt

8. Write a balanced nuclear equation for each reaction.

a. β^- decay of ^{45}K

b. β^+ decay of ^{41}Sc

c. α decay of ^{146}Sm

9. The decay products of several isotopes are listed here. Identify the type of radiation emitted and write a balanced nuclear equation for each.

a. $^{218}Po \rightarrow {}^{214}Pb$

b. $^{32}Si \rightarrow {}^{32}P$

c. an excited state of an iron-57 nucleus decaying to its ground state

d. conversion of thallium-204 to lead-204

10. The decay products of several isotopes are listed here. Identify the type of radiation emitted and write a balanced nuclear equation for each.

a. $^{218}Po \rightarrow {}^{218}At$

b. $^{216}Po \rightarrow {}^{212}Pb$

c. bismuth-211 converted to thallium-207

d. americium-242 converted to rhodium-107 with the emission of four neutrons

11. Predict the most likely mode of decay and write a balanced nuclear reaction for each isotope.

a. ^{238}U

b. ^{208}Po

c. ^{40}S

d. molybdenum-93*m*

12. Predict the most likely mode of decay and write a balanced nuclear reaction for each isotope.

a. ^{16}N

b. ^{224}Th

c. ^{118}In

d. ^{64}Ge

13. For each nuclear reaction, identify the type(s) of decay and write a balanced nuclear equation.

a. $^{216}Po \rightarrow ? + At$

b. $? \rightarrow \alpha + {}^{231}Pa$

c. $^{228}Th \rightarrow ? + \alpha + \gamma$

d. $^{231}Pa \rightarrow ? + \beta^{-} + \gamma$

14. For each nuclear reaction, identify the type(s) of decay and write a balanced nuclear equation.

a. $^{212}Po \rightarrow {}^{208}Pb + ?$

b. $^{192}Ir \rightarrow Pt + ?$

c. $^{241}Am \rightarrow {}^{57}Fe + {}^{184}? + ?$

d. $Ge \rightarrow {}^{77}Ge + ?$

15. Identify the parent isotope and write a balanced nuclear reaction for each process.

a. Lead-205 is formed via an alpha emission.

b. Titanium-46 is formed via beta and gamma emission.

c. Argon-36 is formed via a beta decay and a gamma emission.

16. Identify the parent isotope and write a balanced nuclear reaction for each process.

a. Iodine-130 is formed by ejecting an electron and a gamma ray from a nucleus.

b. Uranium-240 is formed by alpha decay.

c. Curium-247 is formed by releasing a helium dication and a gamma ray.

17. Write a balanced nuclear equation for each process.

a. Bromine undergoes a decay and produces a gas with an atomic mass of 80 amu.

b. An element emits two neutrons while decaying into two metals, each of which can be extracted and converted to chlorides with the formula MCl_2. The masses of the two salts are 162.9 and 210.9 g/mol, respectively.

18. Write a balanced nuclear equation for each process.

a. An unknown element emits γ rays plus particles that are readily blocked by paper. The sample also contains a substantial quantity of tin-104.
b. An unstable element undergoes two different decay reactions: beta decay to produce a material with a mass of 222 amu and alpha decay to astatine.

19. Bombarding ^{249}Cf with ^{12}C produced a transuranium element with a mass of 257 amu, plus several neutral subatomic particles. Identify the element and write a nuclear reaction for this transmutation.
20. One transuranium element, ^{253}Es, is prepared by bombarding ^{238}U with 15 neutrons. What is the other product of this reaction? Write a balanced transmutation reaction for this conversion.
21. Complete this radioactive decay series

20.3 The Interaction of Nuclear Radiation with Matter

LEARNING OBJECTIVES

1. To know the differences between ionizing and nonionizing radiation and their effects on matter.
2. To identify natural and artificial sources of radiation.

Because nuclear reactions do not typically affect the valence electrons of the atom (although electron capture draws an electron from an orbital of the lowest energy level), they do not directly cause chemical changes. Nonetheless, the particles and the photons emitted during nuclear decay are very energetic, and they can indirectly produce chemical changes in the matter surrounding the nucleus that has decayed. For instance, an α particle is an ionized helium nucleus (He^{2+}) that can act as a powerful oxidant. In this section, we describe how radiation interacts with matter and the some of the chemical and biological effects of radiation.

Ionizing versus Nonionizing Radiation

The effects of radiation on matter are determined primarily by the energy of the radiation, which depends on the nuclear decay reaction that produced it.Nonionizing radiation is relatively low in energy; when it collides with an atom in a molecule or an ion, most or all of its energy can be absorbed without causing a structural or a chemical change. Instead, the kinetic energy of the radiation is transferred to the atom or

molecule with which it collides, causing it to rotate, vibrate, or move more rapidly. Because this energy can be transferred to adjacent molecules or ions in the form of heat, many radioactive substances are warm to the touch. Highly radioactive elements such as polonium, for example, have been used as heat sources in the US space program. As long as the intensity of the nonionizing radiation is not great enough to cause overheating, it is relatively harmless, and its effects can be neutralized by cooling.

In contrast, ionizing radiation is higher in energy, and some of its energy can be transferred to one or more atoms with which it collides as it passes through matter. If enough energy is transferred, electrons can be excited to very high energy levels, resulting in the formation of positively charged ions:

Equation 20.23

$$\text{atom} + \text{ionizing radiation} \rightarrow \text{ion}^{+} + e^{-}$$

Molecules that have been ionized in this way are often highly reactive, and they can decompose or undergo other chemical changes that create a cascade of reactive molecules that can damage biological tissues and other materials (Figure 20.11 "Radiation Damage"). Because the energy of ionizing radiation is very high, we often report its energy in units such as megaelectronvolts (MeV) per particle: 1 MeV/particle = 96 billion J/mol.

The Effects of Ionizing Radiation on Matter

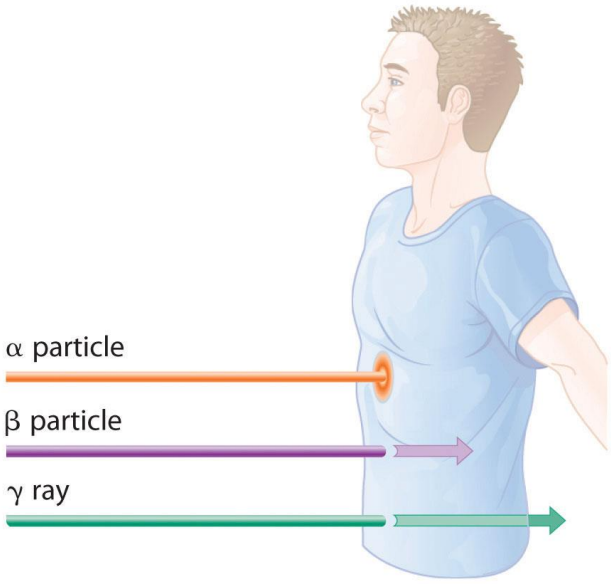
The effects of ionizing radiation depend on four factors:

1. The type of radiation, which dictates how far it can penetrate into matter
2. The energy of the individual particles or photons
3. The number of particles or photons that strike a given area per unit time
4. The chemical nature of the substance exposed to the radiation

The relative abilities of the various forms of ionizing radiation to penetrate biological tissues are illustrated inFigure 20.12 "Depth of Penetration of Ionizing Radiation". Because of its high charge and mass, α radiation interacts strongly with matter. Consequently, it does not penetrate deeply into an object, and it can be stopped by a piece of paper, clothing, or skin. In contrast, γ rays, with no charge and essentially no mass, do not interact strongly with matter and penetrate deeply into most objects, including the human body. Several inches of lead or more than 12 inches of special concrete are needed to completely stop γ rays. Because β particles are intermediate in mass and charge between α particles and γ

rays, their interaction with matter is also intermediate. Beta particles readily penetrate paper or skin, but they can be stopped by a piece of wood or a relatively thin sheet of metal.

Figure 20.12 *Depth of Penetration of Ionizing Radiation*



The depth of penetration of alpha, beta, and gamma radiation varies with the particle. Because α particles interact strongly with matter, they do not penetrate deeply into the human body. In contrast, β particles do not interact as strongly with matter and penetrate more deeply. Gamma rays, which have no charge, are stopped by only very dense materials and can pass right through the human body without being absorbed.

Because of their great penetrating ability, γ rays are by far the most dangerous type of radiation when they come from a source *outside* the body. Alpha particles, however, are the most damaging if their source is *inside* the body because internal tissues absorb all of their energy. Thus danger from radiation depends strongly on the type of radiation emitted and the extent of exposure, which allows scientists to safely handle many radioactive materials if they take precautions to avoid, for example, inhaling fine particulate dust that contains alpha emitters. Some properties of ionizing radiation are summarized in Table 20.3 "Some Properties of Ionizing Radiation".

Table 20.3 Some Properties of Ionizing Radiation

Type	Energy Range (MeV)	Penetration Distance in Water*	Penetration Distance in Air*
α particles	3–9	< 0.05 mm	< 10 cm
β particles	≤ 3	< 4 mm	1 m

Type	Energy Range (MeV)	Penetration Distance in Water*	Penetration Distance in Air*
x-rays	$<10^{-2}$	< 1 cm	< 3 m
γ rays	10^{-2}–10^{1}	< 20 cm	> 3 m
***Distance at which half of the radiation has been absorbed.**			

Wilhelm Röntgen

Born in the Lower Rhine Province of Germany, Röntgen was the only child of a cloth manufacturer and merchant. His family moved to the Netherlands where he showed no particular aptitude in school, but where he was fond of roaming the countryside. Röntgen was expelled from technical school in Utrecht after being unjustly accused of drawing a caricature of one of the teachers. He began studying mechanical engineering in Zurich, which he could enter without having the credentials of a regular student, and received a PhD at the University of Zurich in 1869. In 1876 he became professor of physics.

There are many different ways to measure radiation exposure, or the *dose*. Theroentgen (R), which measures the amount of energy absorbed by dry air, can be used to describe quantitative exposure.[1] Damage to biological tissues, however, is proportional to the amount of energy absorbed by *tissues*, not air. The most common unit used to measure the effects of radiation on biological tissue is therad (radiation absorbed dose); the SI equivalent is the *gray* (Gy). The rad is defined as the amount of radiation that causes 0.01 J of energy to be absorbed by 1 kg of matter, and the gray is defined as the amount of radiation that causes 1 J of energy to be absorbed per kilogram:

Equation 20.24

$$1\ rad = 0.010\ J/kg \qquad 1\ Gy = 1\ J/kg$$

Thus a 70 kg human who receives a dose of 1.0 rad over his or her entire body absorbs 0.010 J/70 kg = 1.4×10^{-4} J, or 0.14 mJ. To put this in perspective, 0.14 mJ is the amount of energy transferred to your skin by a 3.8×10^{-5} g droplet of boiling water. Because the energy of the droplet of water is transferred to a relatively large area of tissue, it is harmless. A radioactive particle, however, transfers its energy to a single molecule, which makes it the atomic equivalent of a bullet fired from a high-powered rifle.

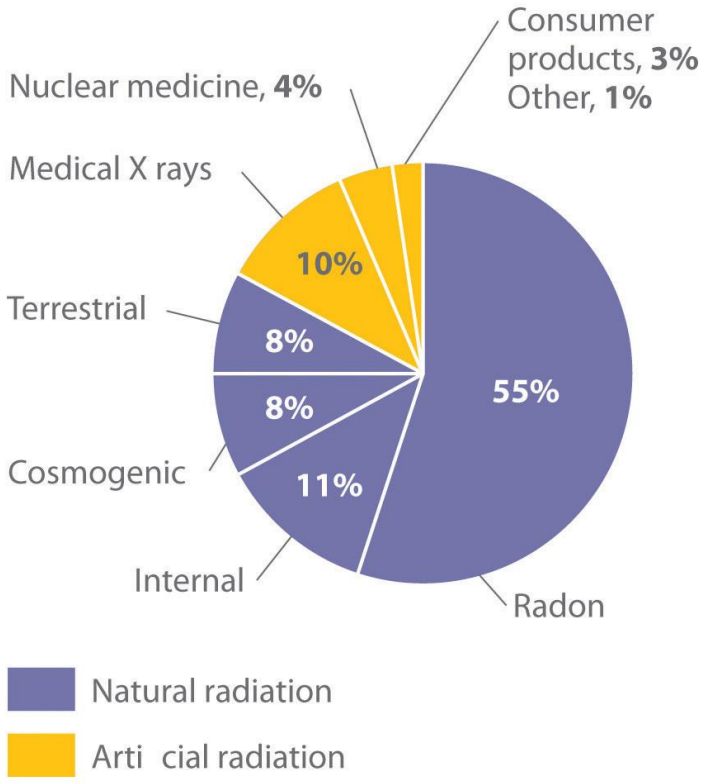
Because α particles have a much higher mass and charge than β particles or γ rays, the difference in mass between α and β particles is analogous to being hit by a bowling ball instead of a table tennis ball traveling at the same speed. Thus the amount of tissue damage caused by 1 rad of α particles is much greater than the damage caused by 1 rad of β particles or γ rays. Thus a unit called

the rem (roentgen equivalent in man)was devised to describe the *actual* amount of tissue damage caused by a given amount of radiation. The number of rems of radiation is equal to the number of rads multiplied by the *RBE* (relative biological effectiveness) factor, which is 1 for β particles, γ rays, and x-rays and about 20 for α particles. Because actual radiation doses tend to be very small, most measurements are reported in *millirems* (1 mrem = 10^{-3} rem).

Natural Sources of Radiation

We are continuously exposed to measurable background radiation from a variety of natural sources, which, on average, is equal to about 150–600 mrem/yr (Figure 20.13 "The Radiation Exposure of a Typical Adult in the United States"). One component of background radiation is *cosmic rays*, high-energy particles and γ rays emitted by the sun and other stars, which bombard Earth continuously. Because cosmic rays are partially absorbed by the atmosphere before they reach Earth's surface, the exposure of people living at sea level (about 30 mrem/yr) is significantly less than the exposure of people living at higher altitudes (about 50 mrem/yr in Denver, Colorado). Every 4 hours spent in an airplane at greater than 30,000 ft adds about 1 mrem to a person's annual radiation exposure.

Figure 20.13 *The Radiation Exposure of a Typical Adult in the United States*



The average radiation dose from natural sources for an adult in the United States is about 150–600 mrem/yr. Radon accounts for more than half of an adult's total radiation exposure, whereas background radiation (terrestrial and cosmogenic) and exposure from medical sources account for about 15% each.

Data source: Office of Civilian Radioactive Waste Management

A second component of background radiation is *cosmogenic radiation*, produced by the interaction of cosmic rays with gases in the upper atmosphere. When high-energy cosmic rays collide with oxygen and nitrogen atoms, neutrons and protons are released. These, in turn, react with other atoms to produce radioactive isotopes, such as ^{14}C:

Equation 20.25

$$N714 + n01 \rightarrow C614 + p11$$

The carbon atoms react with oxygen atoms to form CO_2, which is eventually washed to Earth's surface in rain and taken up by plants. About 1 atom in 1×10^{12} of the carbon atoms in our bodies is radioactive ^{14}C, which decays by beta emission. About 5000 ^{14}C nuclei disintegrate in your body during the 15 s or so that it takes you to read this paragraph. Tritium (^{3}H) is also produced in the upper atmosphere and falls to Earth in precipitation. The total radiation dose attributable to ^{14}C is estimated to be 1 mrem/yr, while that due to ^{3}H is about 1000 times less.

The third major component of background radiation is *terrestrial radiation*, which is due to the remnants of radioactive elements that were present on primordial Earth and their decay products. For example, many rocks and minerals in the soil contain small amounts of radioactive isotopes, such as ^{232}Th and ^{238}U, as well as radioactive daughter isotopes, such as ^{226}Ra. The amount of background radiation from these sources is about the same as that from cosmic rays (approximately 30 mrem/yr). These isotopes are also found in small amounts in building materials derived from rocks and minerals, which significantly increases the radiation exposure for people who live in brick or concrete-block houses (60–160 mrem/yr) instead of houses made of wood (10–20 mrem/yr). Our tissues also absorb radiation (about 40 mrem/yr) from naturally occurring radioactive elements that are present in our bodies. For example, the average adult contains about 140 g of potassium as the K^+ ion. Naturally occurring potassium contains 0.0117% ^{40}K, which decays by emitting both a β particle and a γ ray. In the last 20 seconds, about the time it took you to read this paragraph, approximately 40,000 ^{40}K nuclei disintegrated in your body.

By far the most important source of background radiation is *radon*, the heaviest of the noble gases (group 18). Radon-222 is produced during the decay of ^{238}U, and other isotopes of radon are produced by the decay of other heavy elements. Even though radon is chemically inert, all its isotopes are radioactive. For example, ^{222}Rn undergoes two successive alpha-decay events to give ^{214}Pb:

Equation 20.26

$$R86222n \rightarrow a24 + P84218o \rightarrow a24 + P82214b$$

Because radon is a dense gas, it tends to accumulate in enclosed spaces such as basements, especially in locations where the soil contains greater-than-average amounts of naturally occurring uranium minerals. Under most conditions, radioactive decay of radon poses no problems because of the very short range of the emitted α particle. If an atom of radon happens to be in your lungs when it decays, however, the chemically reactive daughter isotope polonium-218 can become irreversibly bound to molecules in the lung tissue. Subsequent decay of ^{218}Po releases an α particle directly into one of the cells lining the lung, and the resulting damage can eventually cause lung cancer. The ^{218}Po isotope is also readily absorbed by particles in cigarette smoke, which adhere to the surface of the lungs and can hold the radioactive isotope in place. Recent estimates suggest that radon exposure is a contributing factor in about 15% of the deaths due to lung cancer. Because of the potential health problem radon poses, many states require houses to be tested for radon before they can be sold. By current estimates, radon accounts for more than half of the radiation exposure of a typical adult in the United States.

Artificial Sources of Radiation

In addition to naturally occurring background radiation, humans are exposed to small amounts of radiation from a variety of artificial sources. The most important of these are the x-rays used for diagnostic purposes in medicine and dentistry, which are photons with much lower energy than γ rays. A single chest x-ray provides a radiation dose of about 10 mrem, and a dental x-ray about 2–3 mrem. Other minor sources include television screens and computer monitors with cathode-ray tubes, which also produce x-rays. Luminescent paints for watch dials originally used radium, a highly toxic alpha emitter if ingested by those painting the dials. Radium was replaced by tritium (^{3}H) and promethium (^{147}Pr), which emit low-energy β particles that are absorbed by the watch crystal or the glass covering the instrument. Radiation exposure from television screens, monitors, and luminescent dials totals about 2 mrem/yr. Residual fallout from previous atmospheric nuclear-weapons testing is estimated to account for about

twice this amount, and the nuclear power industry accounts for less than 1 mrem/yr (about the same as a single 4 h jet flight).

EXAMPLE 6

Calculate the annual radiation dose in rads a typical 70 kg chemistry student receives from the naturally occurring ^{40}K in his or her body, which contains about 140 g of potassium (as the K^+ ion). The natural abundance of ^{40}K is 0.0117%. Each 1.00 mol of ^{40}K undergoes 1.05×10^7 decays/s, and each decay event is accompanied by the emission of a 1.32 MeV β particle.

Given: mass of student, mass of isotope, natural abundance, rate of decay, and energy of particle

Asked for: annual radiation dose in rads

Strategy:

A Calculate the number of moles of ^{40}K present using its mass, molar mass, and natural abundance.

B Determine the number of decays per year for this amount of ^{40}K.

C Multiply the number of decays per year by the energy associated with each decay event. To obtain the annual radiation dose, use the mass of the student to convert this value to rads.

Solution:

A The number of moles of ^{40}K present in the body is the total number of potassium atoms times the natural abundance of potassium atoms present as ^{40}K divided by the atomic mass of ^{40}K:

$$moles\ 40K$$
$$= 140\ g\ K \times 0.0117\ mol\ K 40100\ mol\ K \times 1\ mol\ K 40.0\ g\ K$$
$$= 4.10 \times 10 - 4\ mol\ 40K$$

B We are given the number of atoms of ^{40}K that decay per second in 1.00 mol of ^{40}K, so the number of decays per year is as follows:

$$decaysyear = 4.10 \times 10 - 4\ mol\ 40K \times 1.05 \times 107\ decays$$
$$/s1.00\ mol\ 40K \times 60\ s1\ min \times 60\ min1\ h \times 24\ h1\ day \times 365\ days1\ yr$$

C The total energy the body receives per year from the decay of ^{40}K is equal to the total number of decays per year multiplied by the energy associated with each decay event:

$$total\ energy\ per\ year = 1.36 \times 1011 decaysyr \times 1.32 MeVdecays$$
$$\times 106 eVMeV \times 1.602 \times 10 - 19\ JeV = 2.87 \times 10 - 2\ J / yr$$

We use the definition of the rad (1 rad = 10^{-2} J/kg of tissue) to convert this figure to a radiation dose in rads. If we assume the dose is equally distributed throughout the body, then the radiation dose per year is as follows:

$$\text{radiation dose per year} = 2.87 \times 10^{-2} J/yr \, 70.0 \, kg \times 1 \, rad \, 1 \times 10^{-2} J/kg = 4.10 \times 10^{-2} \, rad/yr = 41 \, mrad/yr$$

This corresponds to almost half of the normal background radiation most people experience.

Exercise

Because strontium is chemically similar to calcium, small amounts of the Sr^{2+} ion are taken up by the body and deposited in calcium-rich tissues such as bone, using the same mechanism that is responsible for the absorption of Ca^{2+}. Consequently, the radioactive strontium (^{90}Sr) found in fission waste and released by atmospheric nuclear-weapons testing is a major health concern. A normal 70 kg human body has about 280 mg of strontium, and each mole of ^{90}Sr undergoes 4.55×10^{14} decays/s by the emission of a 0.546 MeV β particle. What would be the annual radiation dose in rads for a 70 kg person if 0.10% of the strontium ingested were ^{90}Sr?

Answer: 5.7×10^{3} rad/yr (which is 10 times the fatal dose)

Assessing the Impact of Radiation Exposure

One of the more controversial public policy issues debated today is whether the radiation exposure from artificial sources, when combined with exposure from natural sources, poses a significant risk to human health. The effects of single radiation doses of different magnitudes on humans are listed in Table 20.4 "The Effects of a Single Radiation Dose on a 70 kg Human". Because of the many factors involved in radiation exposure (length of exposure, intensity of the source, and energy and type of particle), it is difficult to quantify the specific dangers of one radioisotope versus another. Nonetheless, some general conclusions regarding the effects of radiation exposure are generally accepted as valid.

Table 20.4 The Effects of a Single Radiation Dose on a 70 kg Human

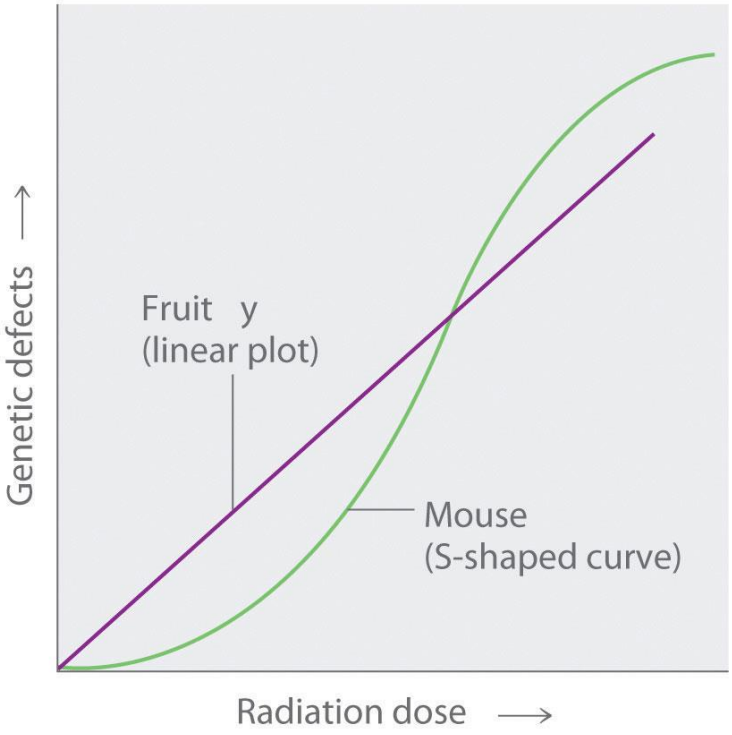
Dose (rem)	Symptoms/Effects
< 5	no observable effect
5–20	possible chromosomal damage
20–100	temporary reduction in white blood cell count
50–100	temporary sterility in men (up to a year)
100–200	mild radiation sickness, vomiting, diarrhea, fatigue; immune system suppressed; bone growth in children retarded

Dose (rem)	Symptoms/Effects
> 300	permanent sterility in women
> 500	fatal to 50% within 30 days; destruction of bone marrow and intestine
> 3000	fatal within hours

Radiation doses of 600 rem and higher are invariably fatal, while a dose of 500 rem kills half the exposed subjects within 30 days. Smaller doses (≤ 50 rem) appear to cause only limited health effects, even though they correspond to tens of years of natural radiation. This does not, however, mean that such doses have no ill effects; they may cause long-term health problems, such as cancer or genetic changes that affect offspring. The possible detrimental effects of the much smaller doses attributable to artificial sources (< 100 mrem/yr) are more difficult to assess.

The tissues most affected by large, whole-body exposures are bone marrow, intestinal tissue, hair follicles, and reproductive organs, all of which contain rapidly dividing cells. The susceptibility of rapidly dividing cells to radiation exposure explains why cancers are often treated by radiation. Because cancer cells divide faster than normal cells, they are destroyed preferentially by radiation. Long-term radiation-exposure studies on fruit flies show a linear relationship between the number of genetic defects and both the magnitude of the dose and the exposure time. In contrast, similar studies on mice show a much lower number of defects when a given dose of radiation is spread out over a long period of time rather than received all at once. Both patterns are plotted in Figure 20.14 "Two Possible Relationships between the Number of Genetic Defects and Radiation Exposure", but which of the two is applicable to humans? According to one hypothesis, mice have very low risk from low doses because their bodies have ways of dealing with the damage caused by natural radiation. At much higher doses, however, their natural repair mechanisms are overwhelmed, leading to irreversible damage. Because mice are biochemically much more similar to humans than are fruit flies, many scientists believe that this model also applies to humans. In contrast, the linear model assumes that *all* exposure to radiation is intrinsically damaging and suggests that stringent regulation of low-level radiation exposure is necessary. Which view is more accurate? The answer—while yet unknown—has extremely important consequences for regulating radiation exposure.

Figure 20.14 Two Possible Relationships between the Number of Genetic Defects and Radiation Exposure



Studies on fruit flies show a linear relationship between the number of genetic defects and the magnitude of the radiation dose and exposure time, which is consistent with a cumulative effect of radiation. In contrast, studies on mice show an S-shaped curve, which suggests that the number of defects is lower when radiation exposure occurs over a longer time. Which of these relationships is more applicable to humans is a matter of considerable debate.

Summary

The effects of radiation on matter depend on the energy of the radiation.**Nonionizing radiation** is relatively low in energy, and the energy is transferred to matter in the form of heat. **Ionizing radiation** is relatively high in energy, and when it collides with an atom, it can completely remove an electron to form a positively charged ion that can damage biological tissues. Alpha particles do not penetrate very far into matter, whereas γ rays penetrate more deeply. Common units of radiation exposure, or dose, are the **roentgen (R)**, the amount of energy absorbed by dry air, and the **rad (radiation absorbed dose)**, the amount of radiation that produces 0.01 J of energy in 1 kg of matter. The **rem (roentgen equivalent in man)** measures the actual amount of tissue damage caused by a given amount of radiation. Natural sources of radiation include *cosmic radiation*, consisting of high-energy particles and γ rays emitted by the sun and other stars;*cosmogenic radiation*, which is produced by the interaction of cosmic rays with gases in the upper atmosphere; and *terrestrial radiation*, from

radioactive elements present on primordial Earth and their decay products. The risks of ionizing radiation depend on the intensity of the radiation, the mode of exposure, and the duration of the exposure.

KEY TAKEAWAY

- Nonionizing radiation is relatively low in energy and can be used as a heat source, whereas ionizing radiation, which is higher in energy, can penetrate biological tissues and is highly reactive.

KEY EQUATION

rad

Equation 20.24: 1 rad = 0.01 J/kg

CONCEPTUAL PROBLEMS

1. Why are many radioactive substances warm to the touch? Why do many radioactive substances glow?
2. Describe the differences between nonionizing and ionizing radiation in terms of the intensity of energy emitted and the effect each has on an atom or molecule after collision. Which nuclear decay reactions are more likely to produce ionizing radiation? nonionizing radiation?
3. Would you expect nonionizing or ionizing radiation to be more effective at treating cancer? Why?
4. Historically, concrete shelters have been used to protect people from nuclear blasts. Comment on the effectiveness of such shelters.
5. Gamma rays are a very high-energy radiation, yet α particles inflict more damage on biological tissue. Why?
6. List the three primary sources of naturally occurring radiation. Explain the factors that influence the dose that one receives throughout the year. Which is the largest contributor to overall exposure? Which is the most hazardous?
7. Because radon is a noble gas, it is inert and generally unreactive. Despite this, exposure to even low concentrations of radon in air is quite dangerous. Describe the physical consequences of exposure to radon gas. Why are people who smoke more susceptible to these effects?
8. Most medical imaging uses isotopes that have extremely short half-lives. These isotopes usually undergo only one kind of nuclear decay reaction. Which kind of decay reaction is usually used? Why? Why would a short half-life be preferred in these cases?
9. Which would you prefer: one exposure of 100 rem, or 10 exposures of 10 rem each? Explain your rationale.

ANSWERS

1.
2.
3. Ionizing radiation is higher in energy and causes greater tissue damage, so it is more likely to destroy cancerous cells.
4.
5.
6.
7.
8.
9. Ten exposures of 10 rem are less likely to cause major damage.

NUMERICAL PROBLEMS

1. A 2.14 kg sample of rock contains 0.0985 g of uranium. How much energy is emitted over 25 yr if 99.27% of the uranium is ^{238}U, which has a half-life of 4.46×10^9 yr, if each decay event is accompanied by the release of 4.039 MeV? If a 180 lb individual absorbs all of the emitted radiation, how much radiation has been absorbed in rads?
2. There is a story about a "radioactive boy scout" who attempted to convert thorium-232, which he isolated from about 1000 gas lantern mantles, to uranium-233 by bombarding the thorium with neutrons. The neutrons were generated via bombarding an aluminum target with α particles from the decay of americium-241, which was isolated from 100 smoke detectors. Write balanced nuclear reactions for these processes. The "radioactive boy scout" spent approximately 2 h/day with his experiment for 2 yr. Assuming that the alpha emission of americium has an energy of 5.24 MeV/particle and that the americium-241 was undergoing 3.5×10^6 decays/s, what was the exposure of the 60.0 kg scout in rads? The intrepid scientist apparently showed no ill effects from this exposure. Why?

[1] Named after the German physicist Wilhelm Röntgen (1845–1923; Nobel Prize in Physics, 1901), who discovered x-rays. The roentgen is actually defined as the amount of radiation needed to produce an electrical charge of 2.58×10^{-4} C in 1 kg of dry air.

20.4 Thermodynamic Stability of the Atomic Nucleus

LEARNING OBJECTIVES

1. To calculate a mass-energy balance and a nuclear binding energy.

2. To understand the differences between nuclear fission and fusion.

Nuclear reactions, like chemical reactions, are accompanied by changes in energy. The energy changes in nuclear reactions, however, are enormous compared with those of even the most energetic chemical reactions. In fact, the energy changes in a typical nuclear reaction are so large that they result in a measurable change of mass. In this section, we describe the relationship between mass and energy in nuclear reactions and show how the seemingly small changes in mass that accompany nuclear reactions result in the release of enormous amounts of energy.

Mass–Energy Balance

The relationship between mass (m) and energy (E) was introduced in Chapter 6 "The Structure of Atoms" and is expressed in the following equation:

Equation 20.27

$$E = mc^2$$

where c is the speed of light (2.998×10^8 m/s), and E and m are expressed in units of joules and kilograms, respectively. Albert Einstein first derived this relationship in 1905 as part of his special theory of relativity: the mass of a particle is directly proportional to its energy. Thus according to Equation 20.27, every mass has an associated energy, and similarly, any reaction that involves a change in energy must be accompanied by a change in mass. This implies that all exothermic reactions should be accompanied by a decrease in mass, and all endothermic reactions should be accompanied by an increase in mass. Given the law of conservation of mass, how can this be true? (For more information on the conservation of mass, see Chapter 3 "Chemical Reactions".) The solution to this apparent contradiction is that *chemical reactions are indeed accompanied by changes in mass*, but these changes are simply too small to be detected.[1] For example, the chemical equation for the combustion of graphite to produce carbon dioxide is as follows:

Equation 20.28

$$C(graphite) + 12O2(g) \rightarrow CO2(g) \Delta H° = -393.5\ kJ/mol$$

Combustion reactions are typically carried out at constant pressure, and under these conditions, the heat released or absorbed is equal to ΔH. As you learned in Chapter 18 "Chemical Thermodynamics", when a reaction is carried out at constant volume, the heat released or absorbed is equal to ΔE. For most chemical reactions, however, $\Delta E \approx \Delta H$. If we rewrite Einstein's equation as

Equation 20.29

$$\Delta E = (\Delta m)c2$$

we can rearrange the equation to obtain the following relationship between the change in mass and the change in energy:

Equation 20.30

$$\Delta m = \Delta Ec2$$

Because 1 J = 1 (kg·m²)/s², the change in mass is as follows:

Equation 20.31

$$\Delta m = -393.5\ kJ/mol(2.998 \times 108\ m/s)2 = -3.935 \times 105(kg \cdot m2)$$
$$/(s2 \cdot mol)(2.998 \times 108 m/s)2 = -4.38 \times 10 - 12\ kg/mol$$

This is a mass change of about 3.6 × 10⁻¹⁰ g/g carbon that is burned, or about 100-millionths of the mass of an electron per atom of carbon. In practice, this mass change is much too small to be measured experimentally and is negligible.

In contrast, for a typical nuclear reaction, such as the radioactive decay of ¹⁴C to ¹⁴N and an electron (a β particle), there is a much larger change in mass:

Equation 20.32

$$14C \rightarrow N14 + b - 10$$

We can use the experimentally measured masses of subatomic particles and common isotopes given in Table 20.1 "Nuclear Decay Emissions and Their Symbols" andChapter 33 "Appendix I: Experimentally Measured Masses of Selected Isotopes" to calculate the change in mass directly. The reaction involves the conversion of a neutral ¹⁴C *atom* to a positively charged ¹⁴N *ion* (with six, not seven, electrons) and a negatively charged β particle (an electron), so the mass of the products is identical to the mass of a neutral ¹⁴N atom. The total change in mass during the reaction is therefore the difference between the mass of a neutral ¹⁴N atom (14.003074 amu) and the mass of a ¹⁴C atom (14.003242 amu):

Equation 20.33

$$\Delta m = massproducts - massreactants = 14.003074\ amu - 14.003242\ amu = -0.000168\ amu$$

The difference in mass, which has been released as energy, corresponds to almost one-third of an electron. The change in mass for the decay of 1 mol of ¹⁴C is −0.000168 g = −1.68 × 10⁻⁴ g = −1.68 × 10⁻⁷ kg.

Although a mass change of this magnitude may seem small, it is about 1000 times larger than the mass change for the combustion of graphite. The energy change is as follows:

Equation 20.34

$$\Delta E = (\Delta m)c2 = (-1.68 \times 10 - 7\ kg)(2.998 \times 108 m/s)2$$
$$= -1.51 \times 1010(kg \cdot m2)/s2 = -1.51 \times 1010\ J = -1.51 \times 107\ kJ$$

The energy released in this nuclear reaction is more than 100,000 times greater than that of a typical chemical reaction, even though the decay of ^{14}C is a relatively low-energy nuclear reaction.

Because the energy changes in nuclear reactions are so large, they are often expressed in kiloelectronvolts (1 keV = 10^3 eV), megaelectronvolts (1 MeV = 10^6 eV), and even gigaelectronvolts (1 GeV = 10^9 eV) per atom or particle. The change in energy that accompanies a nuclear reaction can be calculated from the change in mass using the relationship 1 amu = 931 MeV. The energy released by the decay of one atom of ^{14}C is thus

Equation 20.35

$$(-1.68 \acute{} 10 - 4amu)(931\ MeV/amu) = -0.156\ MeV = -156\ keV$$

EXAMPLE 7

Calculate the changes in mass (in atomic mass units) and energy (in joules per mole and electronvolts per atom) that accompany the radioactive decay of ^{238}U to ^{234}Th and an α particle. The α particle absorbs two electrons from the surrounding matter to form a helium atom.

Given: nuclear decay reaction

Asked for: changes in mass and energy

Strategy:

A Use the mass values in Table 20.1 "Nuclear Decay Emissions and Their Symbols" andChapter 33 "Appendix I: Experimentally Measured Masses of Selected Isotopes" to calculate the change in mass for the decay reaction in atomic mass units.

B Use Equation 20.30 to calculate the change in energy in joules per mole.

C Use the relationship between atomic mass units and megaelectronvolts to calculate the change in energy in electronvolts per atom.

Solution:

A Using particle and isotope masses from Table 20.1 "Nuclear Decay Emissions and Their Symbols" and Chapter 33 "Appendix I: Experimentally Measured Masses of Selected Isotopes", we can calculate the change in mass as follows:

$$\Delta m = mass\ products - mass\ reactants = (mass\ ^{234}Th + mass\ ^{4}He) - mass\ ^{238}U$$
$$= (234.043601\ amu + 4.002603\ amu) - 238.050788\ amu$$
$$= -0.004584\ amu$$

B Thus the change in mass for 1 mol of ^{238}U is −0.004584 g or -4.584×10^{-6} kg. The change in energy in joules per mole is as follows:

$$\Delta E = (\Delta m)c^2 = (-4.584 \times 10^{-6}\ kg)(2.998 \times 10^{8}\ m/s)^2 = -4.120 \times 10^{11}\ J/mol$$

C The change in energy in electronvolts per atom is as follows:

$$\Delta E = -4.584 \times 10^{-3}\ amu \times 931\ MeV/amu \times 1 \times 10^{6}\ eV/MeV = -4.27 \times 10^{6}\ eV/atom$$

Exercise

Calculate the changes in mass (in atomic mass units) and energy (in kilojoules per mole and kiloelectronvolts per atom) that accompany the radioactive decay of tritium (^{3}H) to ^{3}He and a β particle.

Answer: $\Delta m = -2.0 \times 10^{-5}$ amu; $\Delta E = -1.9 \times 10^{6}$ kJ/mol = −19 keV/atom

Nuclear Binding Energies

We have seen that energy changes in both chemical and nuclear reactions are accompanied by changes in mass. Einstein's equation, which allows us to interconvert mass and energy, has another interesting consequence: The mass of an atom is always less than the sum of the masses of its component particles. The only exception to this rule is hydrogen-1 (^{1}H), whose measured mass of 1.007825 amu is identical to the sum of the masses of a proton and an electron. In contrast, the experimentally measured mass of an atom of deuterium (^{2}H) is 2.014102 amu, although its calculated mass is 2.016490 amu:

Equation 20.36

$$m\,^{2}H = m_{neutron} + m_{proton} + m_{electron} = 1.008665\ amu$$
$$+1.007276\ amu + 0.000549\ amu = 2.016490\ amu$$

The difference between the sum of the masses of the components and the measured atomic mass is called the mass defect of the nucleus. Just as a molecule is more stable than its isolated atoms, a nucleus is more stable (lower in energy) than its isolated components. Consequently, when isolated nucleons assemble

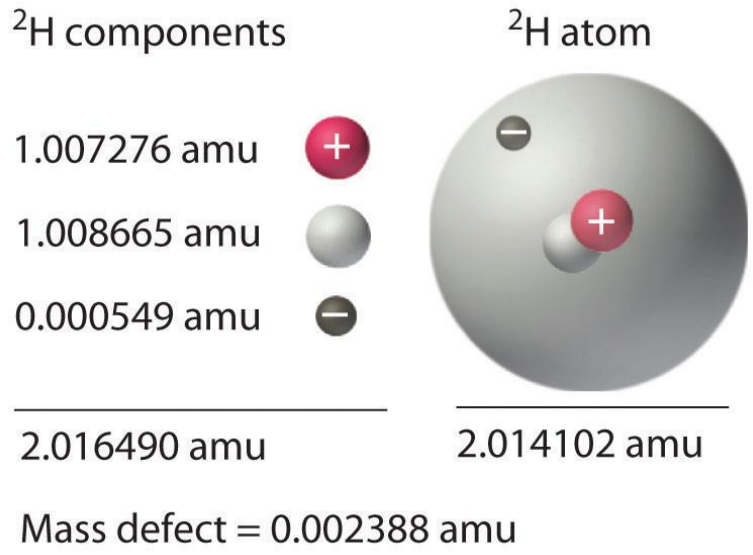
into a stable nucleus, energy is released. According to Equation 20.30, this release of energy must be accompanied by a decrease in the mass of the nucleus.

The amount of energy released when a nucleus forms from its component nucleons is the nuclear binding energy (Figure 20.15 "Nuclear Binding Energy in Deuterium"). In the case of deuterium, the mass defect is 0.002388 amu, which corresponds to a nuclear binding energy of 2.22 MeV for the deuterium nucleus. Because the magnitude of the mass defect is proportional to the nuclear binding energy, both values indicate the stability of the nucleus.

Note the Pattern

Just as a molecule is more stable (lower in energy) than its isolated atoms, a nucleus is more stable than its isolated components.

Figure 20.15 *Nuclear Binding Energy in Deuterium*



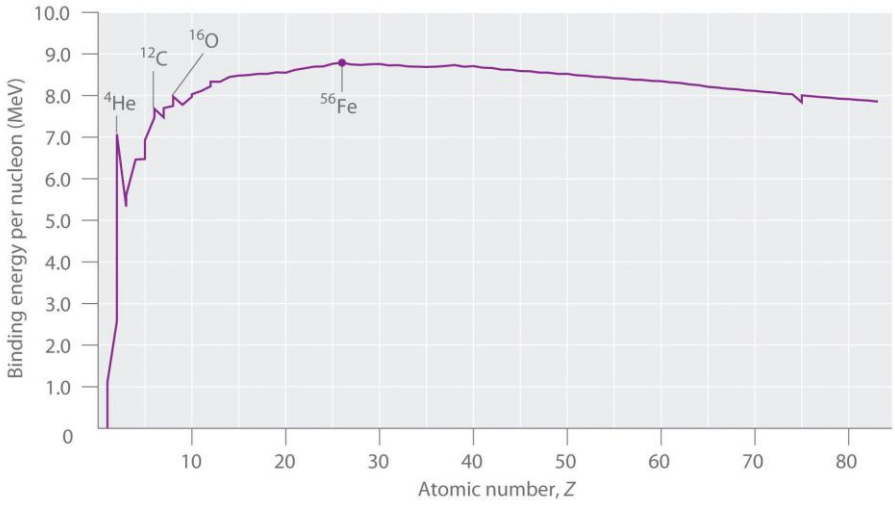
The mass of a ^{2}H atom is less than the sum of the masses of a proton, a neutron, and an electron by 0.002388 amu; the difference in mass corresponds to the nuclear binding energy. The larger the value of the mass defect, the greater the nuclear binding energy and the more stable the nucleus.

Not all nuclei are equally stable. Chemists describe the *relative* stability of different nuclei by comparing the binding energy *per nucleon*, which is obtained by dividing the nuclear binding energy by the mass number (A) of the nucleus. As shown in Figure 20.16 "The Curve of Nuclear Binding Energy", the binding energy per nucleon increases rapidly with increasing atomic number until about $Z = 26$, where it levels off to about 8–9 MeV per nucleon and then decreases slowly. The initial increase in binding energy is not a

smooth curve but exhibits sharp peaks corresponding to the light nuclei that have equal numbers of protons and neutrons (e.g., ^{4}He, ^{12}C, and ^{16}O). As mentioned earlier, these are particularly stable combinations.

Because the maximum binding energy per nucleon is reached at ^{56}Fe, all other nuclei are thermodynamically unstable with regard to the formation of ^{56}Fe. Consequently, heavier nuclei (toward the right in Figure 20.16 "The Curve of Nuclear Binding Energy") should spontaneously undergo reactions such as alpha decay, which result in a decrease in atomic number. Conversely, lighter elements (on the left in Figure 20.16 "The Curve of Nuclear Binding Energy") should spontaneously undergo reactions that result in an increase in atomic number. This is indeed the observed pattern.

Figure 20.16 *The Curve of Nuclear Binding Energy*



This plot of the average binding energy per nucleon as a function of atomic number shows that the binding energy per nucleon increases with increasing atomic number until about Z = 26, levels off, and then decreases. The sharp peaks correspond to light nuclei that have equal numbers of protons and neutrons.

Note the Pattern

Heavier nuclei spontaneously undergo nuclear reactions that decrease their atomic number. Lighter nuclei spontaneously undergo nuclear reactions that increase their atomic number.

EXAMPLE 8

Calculate the total nuclear binding energy (in megaelectronvolts) and the binding energy per nucleon for ^{56}Fe. The experimental mass of the nuclide is given in Chapter 33 "Appendix I: Experimentally Measured Masses of Selected Isotopes".

Given: nuclide and mass

Asked for: nuclear binding energy and binding energy per nucleon

Strategy:

A Sum the masses of the protons, electrons, and neutrons or, alternatively, use the mass of the appropriate number of ^{1}H atoms (because its mass is the same as the mass of one electron and one proton).

B Calculate the mass defect by subtracting the experimental mass from the calculated mass.

C Determine the nuclear binding energy by multiplying the mass defect by the change in energy in electronvolts per atom. Divide this value by the number of nucleons to obtain the binding energy per nucleon.

Solution:

A An iron-56 atom has 26 protons, 26 electrons, and 30 neutrons. We could add the masses of these three sets of particles; however, noting that 26 protons and 26 electrons are equivalent to 26 ^{1}H atoms, we can calculate the sum of the masses more quickly as follows:

$$\begin{aligned} calculated\ mass - experimental\ mass &= 26(mass\ H11) + 30(mass\ n01) \\ &= 26(1.007825)\ amu + 30(1.008665)\ amu = 56.463400\ am \\ u &= 55.934938 \end{aligned}$$

B We subtract to find the mass defect:

$$\begin{aligned} mass\ defect &= calculated\ mass - experimental\ mass \\ &= 56.463400\ amu - 55.934938\ amu = 0.528462\ amu \end{aligned}$$

C The nuclear binding energy is thus 0.528462 amu × 931 MeV/amu = 492 MeV. The binding energy per nucleon is 492 MeV/56 nucleons = 8.79 MeV/nucleon.

Exercise

Calculate the total nuclear binding energy (in megaelectronvolts) and the binding energy per nucleon for ^{238}U.

Answer: 1800 MeV/^{238}U; 7.57 MeV/nucleon

Nuclear Fission and Fusion

First discussed in Section 20.2 "Nuclear Reactions", nuclear fission is the splitting of a heavy nucleus into two lighter ones. Fission was discovered in 1938 by the German scientists Otto Hahn, Lise Meitner, and Fritz Strassmann, who bombarded a sample of uranium with neutrons in an attempt to produce new elements with $Z > 92$. They observed that lighter elements such as barium ($Z = 56$) were formed during the reaction, and they realized that such products had to originate from the neutron-induced fission of uranium-235:

Equation 20.37

$$U92235 + n01 \rightarrow B56141a + K3692r + 3n01$$

This hypothesis was confirmed by detecting the krypton-92 fission product. As discussed in Section 20.2 "Nuclear Reactions", the nucleus usually divides asymmetrically rather than into two equal parts, and the fission of a given nuclide does not give the same products every time.

In a typical nuclear fission reaction, more than one neutron is released by each dividing nucleus. When these neutrons collide with and induce fission in other neighboring nuclei, a self-sustaining series of nuclear fission reactions known as anuclear chain reaction can result (Figure 20.16 "The Curve of Nuclear Binding Energy"). For example, the fission of ^{235}U releases two to three neutrons per fission event. If absorbed by other ^{235}U nuclei, those neutrons induce additional fission events, and the rate of the fission reaction increases geometrically. Each series of events is called a *generation*. Experimentally, it is found that some minimum mass of a fissile isotope is required to sustain a nuclear chain reaction; if the mass is too low, too many neutrons are able to escape without being captured and inducing a fission reaction. The minimum mass capable of supporting sustained fission is called the critical mass. This amount depends on the purity of the material and the shape of the mass, which corresponds to the amount of surface area available from which neutrons can escape, and on the identity of the isotope. If the mass of the fissile isotope is greater than the critical mass, then under the right conditions, the resulting *supercritical mass* can release energy explosively. The enormous energy released from nuclear chain reactions is responsible for the massive destruction caused by the detonation of nuclear weapons such as fission bombs, but it also forms the basis of the nuclear power industry.

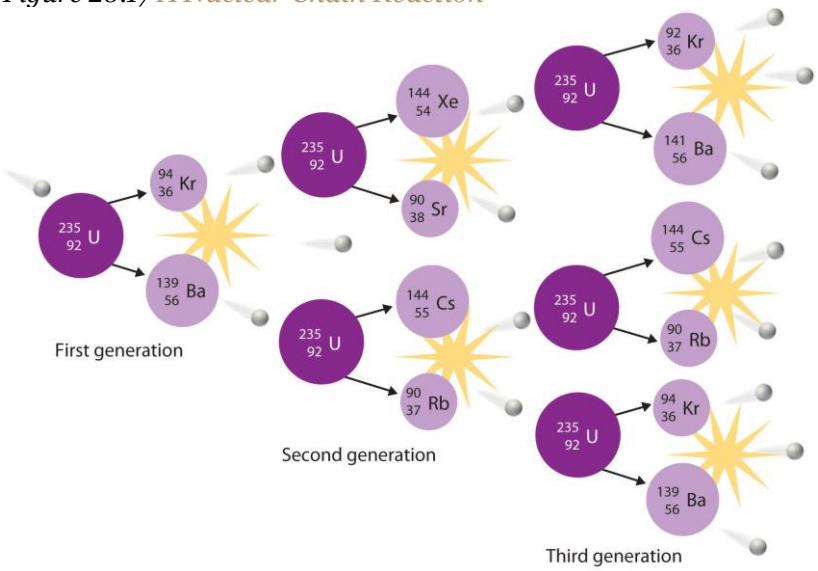
Nuclear fusion, in which two light nuclei combine to produce a heavier, more stable nucleus, is the opposite of nuclear fission. As in the nuclear transmutation reactions discussed in Section 20.2 "Nuclear

Reactions", the positive charge on both nuclei results in a large electrostatic energy barrier to fusion. This barrier can be overcome if one or both particles have sufficient kinetic energy to overcome the electrostatic repulsions, allowing the two nuclei to approach close enough for a fusion reaction to occur. The principle is similar to adding heat to increase the rate of a chemical reaction. (For more information on chemical kinetics, see Chapter 14 "Chemical Kinetics".) As shown in the plot of nuclear binding energy per nucleon versus atomic number in Figure 20.17 "A Nuclear Chain Reaction", fusion reactions are most exothermic for the lightest element. For example, in a typical fusion reaction, two deuterium atoms combine to produce helium-3, a process known as deuterium–deuterium fusion (D–D fusion):

Equation 20.38

$$2H12 \rightarrow H23e + n01$$

Figure 20.17 *A Nuclear Chain Reaction*



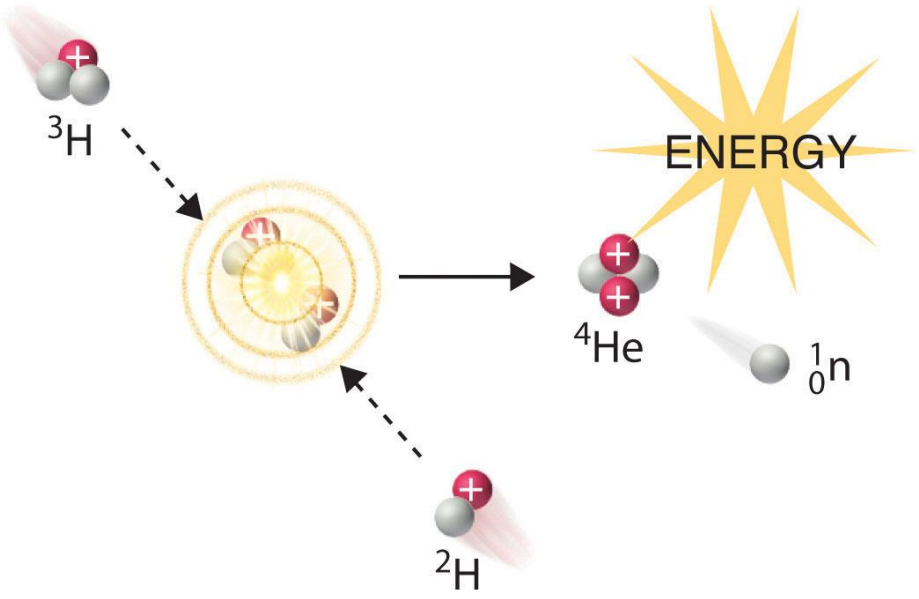
The process is initiated by the collision of a single neutron with a ^{235}U nucleus, which undergoes fission, as shown in ***Figure 20.6 "A Nuclear Transmutation Reaction"****. Because each neutron released can cause the fission of another ^{235}U nucleus, the rate of a fission reaction accelerates geometrically. Each series of events is a generation.*

In another reaction, a deuterium atom and a tritium atom fuse to produce helium-4 (Figure 20.18 "Nuclear Fusion"), a process known as deuterium–tritium fusion (D–T fusion):

Equation 20.39

$$H12 + H13 \rightarrow H24e + n01$$

Figure 20.18 Nuclear Fusion



In a nuclear fusion reaction, lighter nuclei combine to produce a heavier nucleus. As shown, fusion of ^{3}H and ^{2}H to give ^{4}He and a neutron releases an enormous amount of energy. In principle, nuclear fusion can produce much more energy than fission, but very high kinetic energy is required to overcome electrostatic repulsions between the positively charged nuclei and initiate the fusion reaction.

Initiating these reactions, however, requires a temperature comparable to that in the interior of the sun (approximately 1.5×10^{7} K). Currently, the only method available on Earth to achieve such a temperature is the detonation of a fission bomb. For example, the so-called hydrogen bomb (or H bomb) is actually a deuterium–tritium bomb (a D–T bomb), which uses a nuclear fission reaction to create the very high temperatures needed to initiate fusion of solid lithium deuteride (^{6}LiD), which releases neutrons that then react with ^{6}Li, producing tritium. The deuterium-tritium reaction releases energy explosively. Example 9 and its corresponding exercise demonstrate the enormous amounts of energy produced by nuclear fission and fusion reactions. In fact, fusion reactions are the power sources for all stars, including our sun.

EXAMPLE 9

Calculate the amount of energy (in electronvolts per atom and kilojoules per mole) released when the neutron-induced fission of ^{235}U produces ^{144}Cs, ^{90}Rb, and two neutrons:

$$U92235 + n01 \rightarrow C55144s + R3790b + 2n01$$

Given: balanced nuclear reaction

Asked for: energy released in electronvolts per atom and kilojoules per mole

Strategy:

A Following the method used in Example 7, calculate the change in mass that accompanies the reaction. Convert this value to the change in energy in electronvolts per atom.

B Calculate the change in mass per mole of ^{235}U. Then use Equation 20.29 to calculate the change in energy in kilojoules per mole.

Solution:

A The change in mass that accompanies the reaction is as follows:

$$\Delta m = mass\,products - mass\,reactants = mass(C55144s + R3790b + n01)$$
$$- mass\ U92235 = (143.932077\ amu + 89.914802\ amu + 1.008665\ amu) - 235.043930\ amu = -0.188386\ amu$$

The change in energy in electronvolts per atom is as follows:

$$DE = (-0.188386\ amu)(931\ MeV/amu) = -175\ MeV$$

B The change in mass per mol $e\ of\ U92235\ is\ -0$

.188386 g = −1.88386 × 10^{-4} kg, so the change in energy in kilojoules per mole is as follows:

$$DE = (Dm)c2 = (-1.88386 \times 10-4\ kg)(2.998 \times 108\ m/s)2$$
$$= -1.693 \times 1013\ J/mol = -1.693 \times 1010\ kJ/mol$$

Exercise

Calculate the amount of energy (in electronvolts per atom and kilojoules per mole) released when deuterium and tritium fuse to give helium-4 and a neutron:

$$H12 + H13 \rightarrow H24e + n01$$

Answer: Δ*E* = −17.6 MeV/atom = −1.697 × 10^{9} kJ/mol

Summary

Nuclear reactions are accompanied by large changes in energy, which result in detectable changes in mass. The change in mass is related to the change in energy according to Einstein's equation: $\Delta E = (\Delta m)c^2$. Large changes in energy are usually reported in kiloelectronvolts or megaelectronvolts (thousands or millions of electronvolts). With the exception of ^{1}H, the experimentally determined mass of an atom is always *less* than the sum of the masses of the component particles (protons, neutrons, and electrons) by an amount called the **mass defect** of the nucleus. The energy corresponding to the mass defect is the **nuclear binding energy**, the amount of energy released when a nucleus forms from its component particles. In **nuclear fission**, nuclei split into lighter nuclei with an accompanying release of multiple neutrons and large amounts of energy. The**critical mass** is the minimum mass required to support a self-sustaining**nuclear chain reaction**. **Nuclear fusion** is a process in which two light nuclei combine to produce a heavier nucleus plus a great deal of energy.

KEY TAKEAWAY

- Unlike a chemical reaction, a nuclear reaction results in a significant change in mass and an associated change of energy, as described by Einstein's equation.

CONCEPTUAL PROBLEMS

1. How do chemical reactions compare with nuclear reactions with respect to mass changes? Does either type of reaction violate the law of conservation of mass? Explain your answers.

2. Why is the amount of energy released by a nuclear reaction so much greater than the amount of energy released by a chemical reaction?
3. Explain why the mass of an atom is less than the sum of the masses of its component particles.
4. The stability of a nucleus can be described using two values. What are they, and how do they differ from each other?
5. In the days before true chemistry, ancient scholars (*alchemists*) attempted to find the*philosopher's stone*, a material that would enable them to turn lead into gold. Is the conversion of Pb → Au energetically favorable? Explain why or why not.
6. Describe the energy barrier to nuclear fusion reactions and explain how it can be overcome.
7. Imagine that the universe is dying, the stars have burned out, and all the elements have undergone fusion or radioactive decay. What would be the most abundant element in this future universe? Why?
8. Numerous elements can undergo fission, but only a few can be used as fuels in a reactor. What aspect of nuclear fission allows a nuclear chain reaction to occur?
9. How are transmutation reactions and fusion reactions related? Describe the main impediment to fusion reactions and suggest one or two ways to surmount this difficulty.

NUMERICAL PROBLEMS

1. Using the information provided in Chapter 33 "Appendix I: Experimentally Measured Masses of Selected Isotopes", complete each reaction and calculate the amount of energy released from each in kilojoules.

a. $^{238}Pa \rightarrow ? + \beta^-$

b. $^{216}Fr \rightarrow ? + \alpha$

c. $^{199}Bi \rightarrow ? + \beta^+$

2. Using the information provided in Chapter 33 "Appendix I: Experimentally Measured Masses of Selected Isotopes", complete each reaction and calculate the amount of energy released from each in kilojoules.

a. $^{194}Tl \rightarrow ? + \beta^+$

b. $^{171}Pt \rightarrow ? + \alpha$

c. $^{214}Pb \rightarrow ? + \beta^-$

3. Using the information provided in Chapter 33 "Appendix I: Experimentally Measured Masses of Selected Isotopes", complete each reaction and calculate the amount of energy released from each in kilojoules per mole.

a. $a.\ \ P91234a \rightarrow ?+b\text{-}\ 10$

4. $b.\ \ R88226a \rightarrow ?+a24$

5. Using the information provided in Chapter 33 "Appendix I: Experimentally Measured Masses of Selected Isotopes", complete each reaction and then calculate the amount of energy released from each in kilojoules per mole.

a. $C2760o \rightarrow ?+b\text{-}\ 10$ ($The\ mass\ of\ cobalt$-60 is 59.933817 amu.)

b. technicium-94 (mass = 93.909657 amu) undergoing fission to produce chromium-52 and potassium-40

6. Using the information provided in Chapter 33 "Appendix I: Experimentally Measured Masses of Selected Isotopes", predict whether each reaction is favorable and the amount of energy released or required in megaelectronvolts and kilojoules per mole.

a. the beta decay of bismuth-208 (mass = 207.979742 amu)

b. the formation of lead-206 by alpha decay

7. Using the information provided, predict whether each reaction is favorable and the amount of energy released or required in megaelectronvolts and kilojoules per mole.

a. alpha decay of oxygen-16

b. alpha decay to produce chromium-52

8. Calculate the total nuclear binding energy (in megaelectronvolts) and the binding energy per nucleon for ^{87}Sr if the measured mass of ^{87}Sr is 86.908877 amu.

9. Calculate the total nuclear binding energy (in megaelectronvolts) and the binding energy per nucleon for ^{60}Ni.

10. The experimentally determined mass of ^{53}Mn is 52.941290 amu. Find each of the following.

a. the calculated mass

b. the mass defect

c. the nuclear binding energy

d. the nuclear binding energy per nucleon

11. The experimentally determined mass of ^{29}S is 28.996610 amu. Find each of the following.

a. the calculated mass

b. the mass defect

c. the nuclear binding energy

d. the nuclear binding energy per nucleon

12. Calculate the amount of energy that is released by the neutron-induced fission of ^{235}U to give ^{141}Ba, ^{92}Kr (mass = 91.926156 amu), and three neutrons. Report your answer in electronvolts per atom and kilojoules per mole.
13. Calculate the amount of energy that is released by the neutron-induced fission of ^{235}U to give ^{90}Sr, ^{143}Xe, and three neutrons. Report your answer in electronvolts per atom and kilojoules per mole.
14. Calculate the amount of energy released or required by the fusion of helium-4 to produce the unstable beryllium-8 (mass = 8.00530510 amu). Report your answer in kilojoules per mole. Do you expect this to be a spontaneous reaction?
15. Calculate the amount of energy released by the fusion of ^{6}Li and deuterium to give two helium-4 nuclei. Express your answer in electronvolts per atom and kilojoules per mole.
16. How much energy is released by the fusion of two deuterium nuclei to give one tritium nucleus and one proton? How does this amount compare with the energy released by the fusion of a deuterium nucleus and a tritium nucleus, which is accompanied by ejection of a neutron? Express your answer in megaelectronvolts and kilojoules per mole. Pound for pound, which is a better choice for a fusion reactor fuel mixture?

ANSWERS

1.

a. $P91238a \rightarrow U92238 + b\text{-}\ 10;\ \text{-}\ 5.540\ \times$

b. 10^{-16} kJ

c. $F87216r \rightarrow A85212t + a24;\ \text{-}\ 1.470$

d. $\times\ 10^{-15}$ kJ

e. $B83199i \rightarrow P82199b + b + 10;\ \text{-}\ 5.458\ \times\ 10^{-16}$ kJ

2.

3.

4. $a.\quad P91234a \rightarrow U92234 + b\text{-}\ 10;\ \ 2.118\ \times\ 10^{8}\ \ kJ/mol$

5. $a.\quad R88226a \rightarrow R86222n + a24;\ \ 4.700\ \times\ 10^{8}\ \ kJ/mol$

6.

a. The beta decay of bismuth-208 to polonium is endothermic (ΔE = 1.400 MeV/atom, 1.352×10^{8} kJ/mol).

b. The formation of lead-206 by alpha decay of polonium-210 is exothermic (ΔE = −5.405 MeV/atom, -5.218×10^8 kJ/mol).

7.

8. 757 MeV/atom, 8.70 MeV/nucleon

9.

10.

a. 53.438245 amu

b. 0.496955 amu

c. 463 MeV/atom

d. 8.74 MeV/nucleon

11.

12. −173 MeV/atom; 1.67×10^{10} kJ/mol

13.

14. $\Delta E = +9.0 \times 10^6$ kJ/mol beryllium-8; no

15.

16. D–D fusion: ΔE = −4.03 MeV/tritium nucleus formed = -3.89×10^8 kJ/mol tritium; D–T fusion: ΔE = −17.6 MeV/tritium nucleus = -1.70×10^9 kJ/mol; D–T fusion

[1] This situation is similar to the wave–particle duality discussed in Chapter 6 "The Structure of Atoms". As you may recall, all particles exhibit wavelike behavior, but the wavelength is inversely proportional to the mass of the particle (actually, to its momentum, the product of its mass and velocity). Consequently, wavelike behavior is detectable only for particles with very small masses, such as electrons.

20.5 Applied Nuclear Chemistry

LEARNING OBJECTIVE

1. To understand how nuclear reactors function.

The ever-increasing energy needs of modern societies have led scientists and engineers to develop ways of harnessing the energy released by nuclear reactions. To date, all practical applications of nuclear power have been based on nuclear fission reactions. Although nuclear fusion offers many advantages in principle, technical difficulties in achieving the high energies required to initiate nuclear fusion reactions have thus far precluded using fusion for the

controlled release of energy. In this section, we describe the various types of nuclear power plants that currently generate electricity from nuclear reactions, along with some possible ways to harness fusion energy in the future. In addition, we discuss some of the applications of nuclear radiation and radioisotopes, which have innumerable uses in medicine, biology, chemistry, and industry.

Nuclear Reactors

When a critical mass of a fissile isotope is achieved, the resulting flux of neutrons can lead to a self-sustaining reaction. A variety of techniques can be used to control the flow of neutrons from such a reaction, which allows nuclear fission reactions to be maintained at safe levels. Many levels of control are required, along with a fail-safe design, because otherwise the chain reaction can accelerate so rapidly that it releases enough heat to melt or vaporize the fuel and the container, a situation that can release enough radiation to contaminate the surrounding area. Uncontrolled nuclear fission reactions are relatively rare, but they have occurred at least 18 times in the past. The most recent event resulted from the damaged Fukushima Dai-ichi plant after the March 11, 2011, earthquake and tsunami that devastated Japan. The plant used fresh water for cooling nuclear fuel rods to maintain controlled, sustainable nuclear fission. When the water supply was disrupted, so much heat was generated that a partial meltdown occurred. Radioactive iodine levels in contaminated seawater from the plant were over 4300 times the regulated safety limit. To put this in perspective, drinking one liter of fresh water with this level of contamination is the equivalent to receiving double the annual dose of radiation that is typical for a person. Dismantling the plant and decontaminating the site is estimated to require 30 years at a cost of approximately $12 billion.

There is compelling evidence that uncontrolled nuclear chain reactions occurred naturally in the early history of our planet, about 1.7 billion years ago in uranium deposits near Oklo in Gabon, West Africa (Figure 20.19 "A “Fossil Nuclear Reactor” in a Uranium Mine Near Oklo in Gabon, West Africa"). The natural abundance of ^{235}U 2 billion years ago was about 3%, compared with 0.72% today; in contrast, the “fossil nuclear reactor” deposits in Gabon now contain only 0.44% ^{235}U. An unusual combination of geologic phenomena in this region apparently resulted in the formation of deposits of essentially pure uranium oxide containing 3% ^{235}U, which coincidentally is identical to the fuel used in many modern nuclear plants. When rainwater or groundwater saturated one of these deposits, the water acted as a natural *moderator*that decreased the kinetic energy of the neutrons emitted by radioactive decay of ^{235}U, allowing the neutrons to initiate a chain reaction. As a result, the entire deposit “went critical” and became

an uncontrolled nuclear chain reaction, which is estimated to have produced about 100 kW of power. It is thought that these natural nuclear reactors operated only intermittently, however, because the heat released would have vaporized the water. Removing the water would have shut down the reactor until the rocks cooled enough to allow water to reenter the deposit, at which point the chain reaction would begin again. This on–off cycle is believed to have been repeated for more than 100,000 years, until so much ^{235}U was consumed that the deposits could no longer support a chain reaction.

In addition to the incident in Japan, another recent instance of an uncontrolled nuclear chain reaction occurred on April 25–26, 1986, at the Chernobyl nuclear power plant in the former Union of Soviet Socialist Republics (USSR; now in the Ukraine; Figure 20.20 "The Chernobyl Nuclear Power Plant"). During testing of the reactor's turbine generator, a series of mechanical and operational failures caused a chain reaction that quickly went out of control, destroying the reactor core and igniting a fire that destroyed much of the facility and released a large amount of radioactivity. Thirty people were killed immediately, and the high levels of radiation in a 20 mi radius forced nearly 350,000 people to be resettled or evacuated. In addition, the accident caused a disruption to the Soviet economy that is estimated to have cost almost $13 billion. It is somewhat surprising, however, that the long-term health effects on the 600,000 people affected by the accident appear to be much less severe than originally anticipated. Initially, it was predicted that the accident would result in tens of thousands of premature deaths, but an exhaustive study almost 20 yr after the event suggests that 4000 people will die prematurely from radiation exposure due to the accident. Although significant, in fact it represents only about a 3% increase in the cancer rate among the 600,000 people most affected, of whom about a quarter would be expected to eventually die of cancer even if the accident had not occurred.

In 1986, mechanical and operational failures during testing at the Chernobyl power plant in the USSR (now in the Ukraine) caused an uncontrolled nuclear chain reaction. The resulting fire destroyed much of the facility and severely damaged the core of the reactor, resulting in the release of large amounts of radiation that was spread over the surrounding area by the prevailing winds. The effects were devastating to the health of the population in the region and to the Soviet economy.

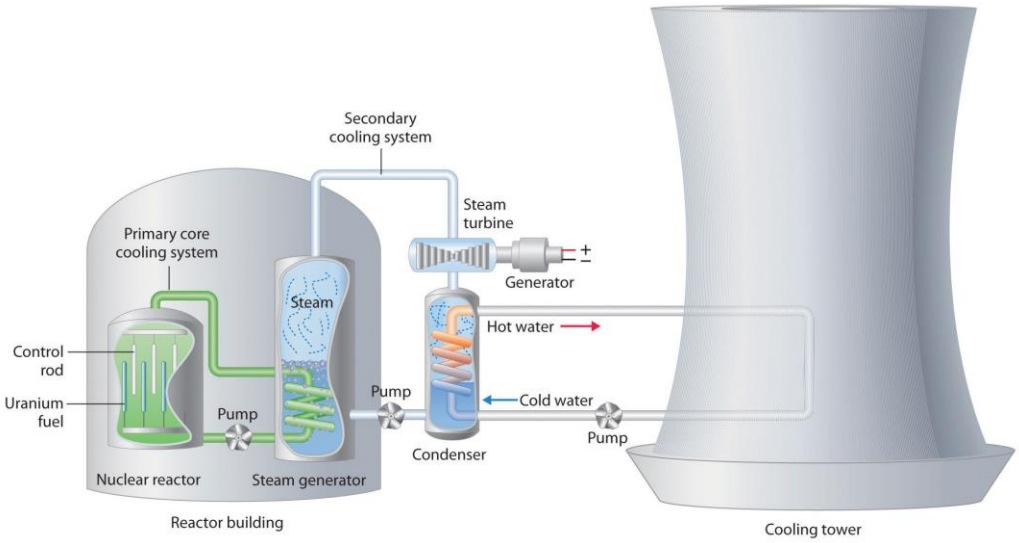
If, on the other hand, the neutron flow in a reactor is carefully regulated so that only enough heat is released to boil water, then the resulting steam can be used to produce electricity. Thus a nuclear reactor

is similar in many respects to the conventional power plants discussed in Chapter 5 "Energy Changes in Chemical Reactions", which burn coal or natural gas to generate electricity; the only difference is the source of the heat that converts water to steam.

Light-Water Reactors

We begin our description of nuclear power plants with light-water reactors, which are used extensively to produce electricity in countries such as Japan, Israel, South Korea, Taiwan, and France—countries that lack large reserves of fossil fuels. The essential components of a light-water reactor are depicted in Figure 20.21 "A Light-Water Nuclear Fission Reactor for the Production of Electric Power". All existing nuclear power plants have similar components, although different designs use different fuels and operating conditions. *Fuel rods* containing a fissile isotope in a structurally stabilized form (such as uranium oxide pellets encased in a corrosion-resistant zirconium alloy) are suspended in a cooling bath that transfers the heat generated by the fission reaction to a secondary cooling system. The heat is used to generate steam for the production of electricity. In addition, *control rods* are used to absorb neutrons and thereby control the rate of the nuclear chain reaction. Control rods are made of a substance that efficiently absorbs neutrons, such as boron, cadmium, or, in nuclear submarines, hafnium. Pulling the control rods out increases the neutron flux, allowing the reactor to generate more heat, whereas inserting the rods completely stops the reaction, a process called “scramming the reactor.”

Figure 20.21 *A Light-Water Nuclear Fission Reactor for the Production of Electric Power*



The fuel rods are made of a corrosion-resistant alloy that encases the partially enriched uranium fuel; controlled fission of ^{235}U in the fuel produces heat. Water surrounds the fuel rods and moderates the kinetic energy of the

neutrons, slowing them to increase the probability that they will induce fission. Control rods that contain elements such as boron, cadmium, or hafnium, which are very effective at absorbing neutrons, are used to control the rate of the fission reaction. A heat exchanger is used to boil water in a secondary cooling system, creating steam to drive the turbine and produce electricity. The large hyperbolic cooling tower, which is the most visible portion of the facility, condenses the steam in the secondary cooling circuit; it is often located at some distance from the actual reactor.

Despite this apparent simplicity, many technical hurdles must be overcome for nuclear power to be an efficient and safe source of energy. Uranium contains only 0.72% uranium-235, which is the only naturally occurring fissile isotope of uranium. Because this abundance is not enough to support a chain reaction, the uranium fuel must be at least partially enriched in ^{235}U, to a concentration of about 3%, for it to be able to sustain a chain reaction. At this level of enrichment, a nuclear explosion is impossible; far higher levels of enrichment (greater than or equal to 90%) are required for military applications such as nuclear weapons or the nuclear reactors in submarines. Enrichment is accomplished by converting uranium oxide to UF_6, which is volatile and contains discrete UF_6 molecules.

Because $^{235}UF_6$ and $^{238}UF_6$ have different masses, they have different rates of effusion and diffusion, and they can be separated using a gas diffusion process, as described in Chapter 10 "Gases". Another difficulty is that neutrons produced by nuclear fission are too energetic to be absorbed by neighboring nuclei, and they escape from the material without inducing fission in nearby ^{235}U nuclei. Consequently, a moderator must be used to slow the neutrons enough to allow them to be captured by other ^{235}U nuclei. High-speed neutrons are scattered by substances such as water or graphite, which decreases their kinetic energy and increases the probability that they will react with another ^{235}U nucleus. The moderator in a light-water reactor is the water that is used as the primary coolant. The system is highly pressurized to about 100 atm to keep the water from boiling at 100°C.

All nuclear reactors require a powerful cooling system to absorb the heat generated in the reactor core and create steam that is used to drive a turbine that generates electricity. In 1979, an accident occurred when the main water pumps used for cooling at the nuclear power plant at Three Mile Island in Pennsylvania stopped running, which prevented the steam generators from removing heat. Eventually, the zirconium casing of the fuel rods ruptured, resulting in a meltdown of about half of the reactor core. Although there was no loss of life and only a small release of radioactivity, the accident produced sweeping changes in

nuclear power plant operations. The US Nuclear Regulatory Commission tightened its oversight to improve safety.

The main disadvantage of nuclear fission reactors is that the spent fuel, which contains too little of the fissile isotope for power generation, is much more radioactive than the unused fuel due to the presence of many daughter nuclei with shorter half-lives than ^{235}U. The decay of these daughter isotopes generates so much heat that the spent fuel rods must be stored in water for as long as 5 yr before they can be handled. Even then, the radiation levels are so high that the rods must be stored for many, many more years to allow the daughter isotopes to decay to nonhazardous levels. How to store these spent fuel rods for hundreds of years is a pressing issue that has not yet been successfully resolved. As a result, some people are convinced that nuclear power is not a viable option for providing our future energy needs, although a number of other countries continue to rely on nuclear reactors for a large fraction of their energy.

Heavy-Water Reactors

Deuterium (^{2}H) absorbs neutrons much less effectively than does hydrogen (^{1}H), but it is about twice as effective at slowing neutrons. Consequently, a nuclear reactor that uses D_2O instead of H_2O as the moderator is so efficient that it can use *unenriched* uranium as fuel. Using a lower grade of uranium reduces operating costs and eliminates the need for plants that produce enriched uranium. Because of the expense of D_2O, however, only countries like Canada, which has abundant supplies of hydroelectric power for generating D_2O by electrolysis, have made a major investment in heavy-water reactors. (For more information on electrolysis, see Chapter 19 "Electrochemistry".)

Breeder Reactors

A *breeder reactor* is a nuclear fission reactor that produces more fissionable fuel than it consumes. This does not violate the first law of thermodynamics because the fuel produced is not the same as the fuel consumed. Under heavy neutron bombardment, the nonfissile ^{238}U isotope is converted to ^{239}Pu, which can undergo fission:

Equation 20.40

$$U92238 + n01 N93239 p \rightarrow U92239 \rightarrow N93239 p + b\text{-}\ 10 \rightarrow P94239 u + b\text{-}\ 10$$

The overall reaction is thus the conversion of nonfissile ^{238}U to fissile ^{239}Pu, which can be chemically isolated and used to fuel a new reactor. An analogous series of reactions converts nonfissile ^{232}Th to ^{233}U, which can also be used as a fuel for a nuclear reactor. Typically, about 8–10 yr are required for a breeder

reactor to produce twice as much fissile material as it consumes, which is enough to fuel a replacement for the original reactor plus a new reactor. The products of the fission of ^{239}Pu, however, have substantially longer half-lives than the fission products formed in light-water reactors.

Nuclear Fusion Reactors

Although nuclear fusion reactions, such as those in Equation 20.38 and Equation 20.39, are thermodynamically spontaneous, the positive charge on both nuclei results in a large electrostatic energy barrier to the reaction. (As you learned in Chapter 18 "Chemical Thermodynamics", thermodynamic spontaneity is unrelated to the reaction rate.) Extraordinarily high temperatures (about 1.0×10^{8}°C) are required to overcome electrostatic repulsions and initiate a fusion reaction. Even the most feasible such reaction, deuterium–tritium fusion (D–T fusion; Equation 20.39), requires a temperature of about 4.0×10^{7}°C. Achieving these temperatures and controlling the materials to be fused are extraordinarily difficult problems, as is extracting the energy released by the fusion reaction, because a commercial fusion reactor would require such high temperatures to be maintained for long periods of time. Several different technologies are currently being explored, including the use of intense magnetic fields to contain ions in the form of a dense, high-energy plasma at a temperature high enough to sustain fusion (part (a) in Figure 20.22 "Two Possible Designs for a Nuclear Fusion Reactor"). Another concept employs focused laser beams to heat and compress fuel pellets in controlled miniature fusion explosions (part (b) in Figure 20.22 "Two Possible Designs for a Nuclear Fusion Reactor").

The extraordinarily high temperatures needed to initiate a nuclear fusion reaction would immediately destroy a container made of any known material. (a) One way to avoid contact with the container walls is to use a high-energy plasma as the fuel. Because plasma is essentially a gas composed of ionized particles, it can be confined using a strong magnetic field shaped like a torus (a hollow donut). (b) Another approach to nuclear fusion is inertial confinement, which uses an icosahedral array of powerful lasers to heat and compress a tiny fuel pellet (a mixture of solid LiD and LiT) to induce fusion.

Nuclear reactions such as these are called thermonuclear reactions because a great deal of thermal energy must be invested to initiate the reaction. The amount of energy released by the reaction, however, is several orders of magnitude greater than the energy needed to initiate it. In principle, a nuclear fusion reaction should thus result in a significant net production of energy. In addition, Earth's oceans contain

an essentially inexhaustible supply of both deuterium and tritium, which suggests that nuclear fusion could provide a limitless supply of energy. Unfortunately, however, the technical requirements for a successful nuclear fusion reaction are so great that net power generation by controlled fusion has yet to be achieved.

The Uses of Radioisotopes

Nuclear radiation can damage biological molecules, thereby disrupting normal functions such as cell division (Table 20.4 "The Effects of a Single Radiation Dose on a 70 kg Human"). Because radiation is particularly destructive to rapidly dividing cells such as tumor cells and bacteria, it has been used medically to treat cancer since 1904, when radium-226 was first used to treat a cancerous tumor. Many radioisotopes are now available for medical use, and each has specific advantages for certain applications. In modern *radiation therapy*, radiation is often delivered by a source planted inside the body. For example, tiny capsules containing an isotope such as ^{192}Ir, coated with a thin layer of chemically inert platinum, are inserted into the middle of a tumor that cannot be removed surgically. The capsules are removed when the treatment is over. In some cases, physicians take advantage of the body's own chemistry to deliver a radioisotope to the desired location. For example, the thyroid glands in the lower front of the neck are the only organs in the body that use iodine. Consequently, radioactive iodine is taken up almost exclusively by the thyroid (part (a) in Figure 20.23 "Medical Imaging and Treatment with Radioisotopes"). Thus when radioactive isotopes of iodine (^{125}I or ^{131}I) are injected into the blood of a patient suffering from thyroid cancer, the thyroid glands filter the radioisotope from the blood and concentrate it in the tissue to be destroyed. In cases where a tumor is surgically inaccessible (e.g., when it is located deep in the brain), an external radiation source such as a ^{60}Co "gun" is used to aim a tightly focused beam of γ rays at it. Unfortunately, radiation therapy damages healthy tissue in addition to the target tumor and results in severe side effects, such as nausea, hair loss, and a weakened immune system. Although radiation therapy is generally not a pleasant experience, in many cases it is the only choice.

A second major medical use of radioisotopes is *medical imaging*, in which a radioisotope is temporarily localized in a particular tissue or organ, where its emissions provide a "map" of the tissue or the organ. Medical imaging uses radioisotopes that cause little or no tissue damage but are easily detected. One of the most important radioisotopes for medical imaging is ^{99m}Tc. Depending on the particular chemical form in which it is administered, technetium tends to localize in bones and soft tissues, such as the heart

or the kidneys, which are almost invisible in conventional x-rays (part (b) in Figure 20.23 "Medical Imaging and Treatment with Radioisotopes"). Some properties of other radioisotopes used for medical imaging are listed in Table 20.5 "Radioisotopes Used in Medical Imaging and Treatment".

Table 20.5 Radioisotopes Used in Medical Imaging and Treatment

Isotope	Half-Life	Tissue
^{18}F	110 min	brain
^{24}Na	15 h	circulatory system
^{32}P	14 days	eyes, liver, and tumors
^{59}Fe	45 days	blood and spleen
^{60}Co	5.3 yr	external radiotherapy
^{99}mTc	6 h	heart, thyroid, liver, kidney, lungs, and skeleton
^{125}I	59.4 days	thyroid, prostate, and brain
^{131}I	8 days	thyroid
^{133}Xe	5 days	lungs
^{201}Tl	3 days	heart

Because γ rays produced by isotopes such as ^{131}I and ^{99}mTc are emitted randomly in all directions, it is impossible to achieve high levels of resolution in images that use such isotopes. However, remarkably detailed three-dimensional images can be obtained using an imaging technique called *positron emission tomography* (*PET*). The technique uses radioisotopes that decay by positron emission, and the resulting positron is annihilated when it collides with an electron in the surrounding matter. (For more information on positron emission, see Section 20.2 "Nuclear Reactions".) In the annihilation process, both particles are converted to energy in the form of two γ rays that are emitted simultaneously and at 180° to each other:

Equation 20.41

$$b + 10 + e - 10 \rightarrow 200g$$

With PET, biological molecules that have been “tagged” with a positron-emitting isotope such as ^{18}F or ^{11}C can be used to probe the functions of organs such as the brain.

Another major health-related use of ionizing radiation is the irradiation of food, an effective way to kill bacteria such as *Salmonella* in chicken and eggs and potentially lethal strains of *Escherichia coli* in beef. Collectively, such organisms cause almost 3 million cases of food poisoning annually in the United States,

resulting in hundreds of deaths. Figure 20.24 "The Preservation of Strawberries with Ionizing Radiation" shows how irradiation dramatically extends the storage life of foods such as strawberries. Although US health authorities have given only limited approval of this technique, the growing number of illnesses caused by antibiotic-resistant bacteria is increasing the pressure to expand the scope of food irradiation.

the irradiated strawberries on the right show no visible signs of spoilage under the same conditions.

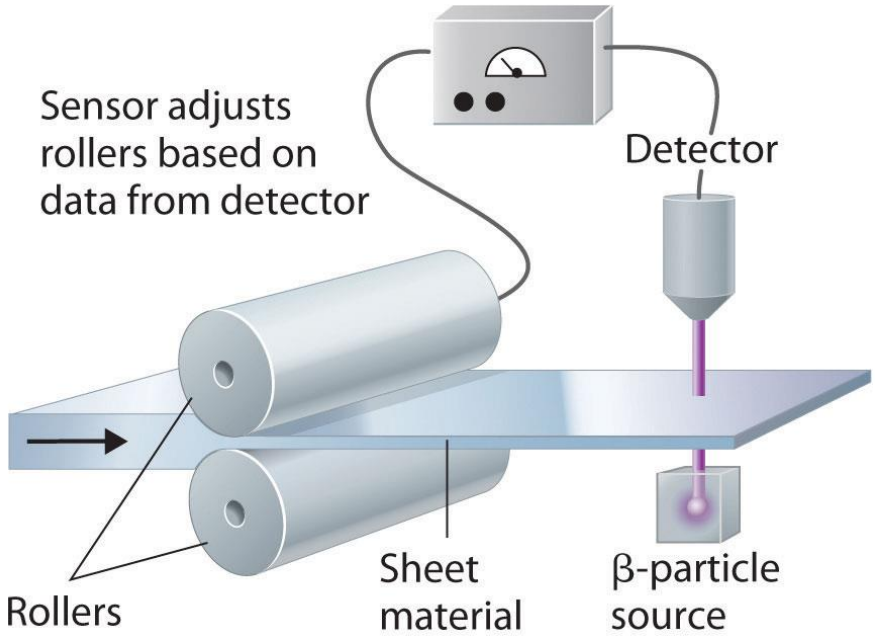
One of the more unusual effects of radioisotopes is in dentistry. Because dental enamels contain a mineral called feldspar ($KAlSi_3O_8$, which is also found in granite rocks), teeth contain a small amount of naturally occurring radioactive ^{40}K. The radiation caused by the decay of ^{40}K results in the emission of light (*fluorescence*), which gives the highly desired "pearly white" appearance associated with healthy teeth.

In a sign of how important nuclear medicine has become in diagnosing and treating illnesses, the medical community has become alarmed at the global shortage of ^{99}Tc, a radioisotope used in more than 30 million procedures a year worldwide. Two reactors that produce 60% of the world's radioactive ^{99}Mo, which decays to ^{99}Tc, are operating beyond their intended life expectancies. Moreover, because most of the reactors producing ^{99}Mo use weapons-grade uranium (^{235}U), which decays to ^{99}Mo during fission, governments are working to phase out civilian uses of technology to produce ^{99}Mo because of concerns that the technology can be used to produce nuclear weapons. Engineers are currently focused on how to make key medical isotopes with other alternatives that don't require fission. One promising option is by removing a neutron from ^{100}Mo, a stable isotope that makes up about 10% of natural molybdenum, transmuting it to ^{99}Mo.

In addition to the medical uses of radioisotopes, radioisotopes have literally hundreds of other uses. For example, smoke detectors contain a tiny amount of ^{241}Am, which ionizes the air in the detector so an electric current can flow through it. Smoke particles reduce the number of ionized particles and decrease the electric current, which triggers an alarm. Another application is the "go-devil" used to detect leaks in long pipelines. It is a packaged radiation detector that is inserted into a pipeline and propelled through the pipe by the flowing liquid. Sources of ^{60}Co are attached to the pipe at regular intervals; as the detector travels along the pipeline, it sends a radio signal each time it passes a source. When a massive leak causes the go-devil to stop, the repair crews know immediately which section of the pipeline is damaged. Finally, radioactive substances are used in gauges that measure and control the thickness of sheets and films. As

shown in Figure 20.25 "Using Radiation to Control the Thickness of a Material", thickness gauges rely on the absorption of either β particles (by paper, plastic, and very thin metal foils) or γ rays (for thicker metal sheets); the amount of radiation absorbed can be measured accurately and is directly proportional to the thickness of the material.

Figure 20.25 *Using Radiation to Control the Thickness of a Material*



Because the amount of radiation absorbed by a material is proportional to its thickness, radiation can be used to control the thickness of plastic film, tin foil, or paper. As shown, a beta emitter is placed on one side of the material being produced and a detector on the other. An increase in the amount of radiation that reaches the detector indicates a decrease in the thickness of the material and vice versa. The output of the detector can thus be used to control the thickness of the material.

Summary

In nuclear power plants, nuclear reactions generate electricity. *Light-water reactors* use enriched uranium as a fuel. They include fuel rods, a moderator, control rods, and a powerful cooling system to absorb the heat generated in the reactor core. *Heavy-water rea*ctors use unenriched uranium as a fuel because they use D_2O as the moderator, which scatters and slows neutrons much more effectively than H_2O. A *breeder reactor* produces more fissionable fuel than it consumes. A *nuclear fusion reactor* requires very high temperatures. Fusion reactions are **thermonuclear reactions** because they

require high temperatures for initiation. Radioisotopes are used in both radiation therapy and *medical imaging*.

KEY TAKEAWAY

- All practical applications of nuclear power have been based on nuclear fission reactions, which nuclear power plants use to generate electricity.

CONCEPTUAL PROBLEMS

1. In nuclear reactors, two different but interrelated factors must be controlled to prevent a mishap that could cause the release of unwanted radiation. How are these factors controlled?
2. What are the three principal components of a nuclear reactor? What is the function of each component?
3. What is meant by the term *enrichment* with regard to uranium for fission reactors? Why does the fuel in a conventional nuclear reactor have to be "enriched"?
4. The plot in a recent spy/action movie involved the threat of introducing stolen "weapons-grade" uranium, which consists of 93.3% ^{235}U, into a fission reactor that normally uses a fuel containing about 3% ^{235}U. Explain why this could be catastrophic.
5. Compare a heavy-water reactor with a light-water reactor. Why are heavy-water reactors less widely used? How do these two reactor designs compare with a breeder reactor?
6. Conventional light-water fission reactors require enriched fuel. An alternative reactor is the so-called heavy-water reactor. The components of the two different reactors are the same except that instead of using water (H_2O), the moderator in a heavy-water reactor is D_2O, known as "heavy water." Because D_2O is more efficient than H_2O at slowing neutrons, heavy-water reactors do not require fuel enrichment to support fission. Why is D_2O more effective at slowing neutrons, and why does this allow unenriched fuels to be used?
7. Isotopes emit γ rays in random directions. What difficulties do these emissions present for medical imaging? How are these difficulties overcome?
8. If you needed to measure the thickness of 1.0 mm plastic sheets, what type of radiation would you use? Would the radiation source be the same if you were measuring steel of a similar thickness? What is your rationale? Would you want an isotope with a long or short half-life for this device?

ANSWERS

1. Neutron flow is regulated by using control rods that absorb neutrons, whereas the speed of the neutrons produced by fission is controlled by using a moderator that slows the neutrons enough to allow them to react with nearby fissile nuclei.
2.
3.
4.
5.
6.
7. It is difficult to pinpoint the exact location of the nucleus that decayed. In contrast, the collision of a positron with an electron causes both particles to be annihilated, and in the process, two gamma rays are emitted in opposite directions, which makes it possible to identify precisely where a positron emitter is located and to create detailed images of tissues.
8.

NUMERICAL PROBLEMS

1. Palladium-103, which decays via electron capture and emits x-rays with an energy of 3.97×10^{-2} MeV, is often used to treat prostate cancer. Small pellets of the radioactive metal are embedded in the prostate gland. This provides a localized source of radiation to a very small area, even though the tissue absorbs only about 1% of the x-rays. Due to its short half-life, all of the palladium will decay to a stable isotope in less than a year. If a doctor embeds 50 pellets containing 2.50 mg of ^{103}Pd in the prostate gland of a 73.9 kg patient, what is the patient's radiation exposure over the course of a year?
2. Several medical treatments use cobalt-60*m*, which is formed by bombarding cobalt with neutrons to produce a highly radioactive *gamma* emitter that undergoes 4.23×10^{16}emissions/(s·kg) of pure cobalt-60. The energy of the gamma emission is 5.86×10^{-2}MeV. Write the balanced nuclear equation for the formation of this isotope. Is this a transmutation reaction? If a 55.3 kg patient received a 0.50 s exposure to a 0.30 kg cobalt-60 source, what would the exposure be in rads? Predict the potential side effects of this dose.

20.6 The Origin of the Elements

LEARNING OBJECTIVE

1. To understand how nuclear transmutation reactions lead to the formation of the elements in stars and how they can be used to synthesize transuranium elements.

The relative abundances of the elements in the known universe vary by more than 12 orders of magnitude. For the most part, these differences in abundance cannot be explained by differences in nuclear stability. Although the ^{56}Fe nucleus is the most stable nucleus known, the most abundant element in the known universe is not iron, but hydrogen (^{1}H), which accounts for about 90% of all atoms. In fact, ^{1}H is the raw material from which all other elements are formed.

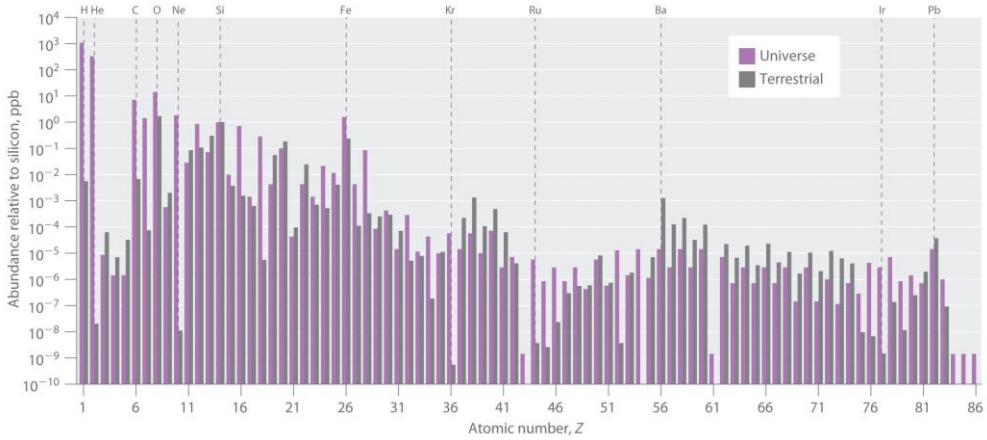
In this section, we explain why ^{1}H and ^{2}He together account for at least 99% of all the atoms in the known universe. We also describe the nuclear reactions that take place in stars, which transform one nucleus into another and create all the naturally occurring elements.

Relative Abundances of the Elements on Earth and in the Known Universe

The relative abundances of the elements in the known universe and on Earth relative to silicon are shown in Figure 20.26 "The Relative Abundances of the Elements in the Universe and on Earth". The data are estimates based on the characteristic emission spectra of the elements in stars, the absorption spectra of matter in clouds of interstellar dust, and the approximate composition of Earth as measured by geologists. The data inFigure 20.26 "The Relative Abundances of the Elements in the Universe and on Earth"illustrate two important points. First, except for hydrogen, the most abundant elements have *even* atomic numbers. Not only is this consistent with the trends in nuclear stability discussed in Section 20.1 "The Components of the Nucleus", but it also suggests that heavier elements are formed by combining helium nuclei ($Z = 2$). Second, the relative abundances of the elements in the known universe and on Earth are often very different, as indicated by the data in Table 20.6 "Relative Abundances of Elements on Earth and in the Known Universe" for some common elements. Some of these differences are easily explained. For example, nonmetals such as H, He, C, N, O, Ne, and Kr are much less abundant relative to silicon on Earth than they are in the rest of the universe. These elements are either noble gases (He, Ne, and Kr) or elements that form volatile hydrides, such as NH_3, CH_4, and H_2O. Because Earth's gravity is not strong enough to hold such light substances in the atmosphere, these elements have been slowly diffusing into outer space ever since our planet was formed. Argon is an exception; it is relatively abundant on Earth compared with the other noble gases because it is continuously produced in rocks by the radioactive decay of isotopes such as ^{40}K. In contrast, many metals, such as Al, Na, Fe, Ca, Mg, K, and Ti, are relatively abundant on Earth because they form nonvolatile compounds, such as oxides, that cannot escape into space. Other metals, however, are much *less* abundant on Earth than in the universe;

some examples are Ru and Ir. You may recall from Chapter 1 "Introduction to Chemistry" that the anomalously high iridium content of a 66-million-year-old rock layer was a key finding in the development of the asteroid-impact theory for the extinction of the dinosaurs. This section explains some of the reasons for the great differences in abundances of the metallic elements.

Figure 20.26 *The Relative Abundances of the Elements in the Universe and on Earth*



In this logarithmic plot, the relative abundances of the elements relative to that of silicon (arbitrarily set equal to 1) in the universe (green bars) and on Earth (purple bars) are shown as a function of atomic number. Elements with even atomic numbers are generally more abundant in the universe than elements with odd atomic numbers. Also, the relative abundances of many elements in the universe are very different from their relative abundances on Earth.

Table 20.6 Relative Abundances of Elements on Earth and in the Known Universe

Terrestrial/Universal Element	Abundance Ratio
H	0.0020
He	2.4×10^{-8}
C	0.36
N	0.02
O	46
Ne	1.9×10^{-6}
Na	1200
Mg	48
Al	1600
Si	390

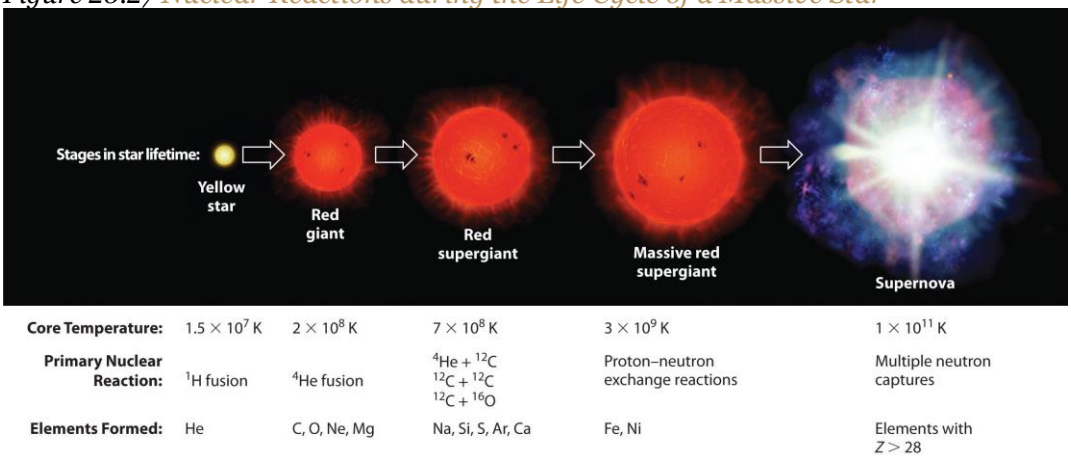
Terrestrial/Universal Element	Abundance Ratio
S	0.84
K	5000
Ca	710
Ti	2200
Fe	57

All the elements originally present on Earth (and on other planets) were synthesized from hydrogen and helium nuclei in the interiors of stars that have long since exploded and disappeared. Six of the most abundant elements in the universe (C, O, Ne, Mg, Si, and Fe) have nuclei that are integral multiples of the helium-4 nucleus, which suggests that helium-4 is the primary building block for heavier nuclei.

Synthesis of the Elements in Stars

Elements are synthesized in discrete stages during the lifetime of a star, and some steps occur only in the most massive stars known (Figure 20.27 "Nuclear Reactions during the Life Cycle of a Massive Star"). Initially, all stars are formed by the aggregation of interstellar "dust," which is mostly hydrogen. As the cloud of dust slowly contracts due to gravitational attraction, its density eventually reaches about 100 g/cm^3, and the temperature increases to about 1.5×10^7 K, forming a dense plasma of ionized hydrogen nuclei. At this point, self-sustaining nuclear reactions begin, and the star "ignites," creating a *yellow star* like our sun.

Figure 20.27 *Nuclear Reactions during the Life Cycle of a Massive Star*



At each stage in the lifetime of a star, a different fuel is used for nuclear fusion, resulting in the formation of different elements. Fusion of hydrogen to give helium is the primary fusion reaction in young stars. As the star ages, helium accumulates and begins to "burn," undergoing fusion to form

heavier elements such as carbon and oxygen. As the adolescent star matures, significant amounts of iron and nickel are formed by fusion of the heavier elements formed previously. The heaviest elements are formed only during the final death throes of the star—the formation of a nova or supernova.

In the first stage of its life, the star is powered by a series of nuclear fusion reactions that convert hydrogen to helium:

Equation 20.42

$$H11 + H11H12 + H11H23e + H23e \rightarrow H12 + b + 10$$
$$\rightarrow H23e + g00 \rightarrow H24e + 2H11$$

The overall reaction is the conversion of four hydrogen nuclei to a helium-4 nucleus, which is accompanied by the release of two positrons, two γ rays, and a great deal of energy:

Equation 20.43

$$4H11 \rightarrow H24e + 2b + 10 + 2g00$$

These reactions are responsible for most of the enormous amount of energy that is released as sunlight and solar heat. It takes several billion years, depending on the size of the star, to convert about 10% of the hydrogen to helium.

Once large amounts of helium-4 have been formed, they become concentrated in the core of the star, which slowly becomes denser and hotter. At a temperature of about 2×10^8 K, the helium-4 nuclei begin to fuse, producing beryllium-8:

Equation 20.44

$$2H24e \rightarrow B48e$$

Although beryllium-8 has both an even mass number and an even atomic number, the low neutron-to-proton ratio makes it *very* unstable, decomposing in only about 10^{-16} s. Nonetheless, this is long enough for it to react with a third helium-4 nucleus to form carbon-12, which is very stable. Sequential reactions of carbon-12 with helium-4 produce the elements with even numbers of protons and neutrons up to magnesium-24:

Equation 20.45

$$B48e- \rightarrow H24eC612- \rightarrow H24eO816-$$
$$\rightarrow H24eN1020e- \rightarrow H24eM1224g$$

So much energy is released by these reactions that it causes the surrounding mass of hydrogen to expand, producing a *red giant* that is about 100 times larger than the original yellow star.

As the star expands, heavier nuclei accumulate in its core, which contracts further to a density of about 50,000 g/cm^3, so the core becomes even hotter. At a temperature of about 7×10^8 K, carbon and oxygen nuclei undergo nuclear fusion reactions to produce sodium and silicon nuclei:

Equation 20.46

$$C612 + C612 \rightarrow N1123a + H11$$

Equation 20.47

$$C612 + O816 \rightarrow S1428i + g00$$

At these temperatures, carbon-12 reacts with helium-4 to initiate a series of reactions that produce more oxygen-16, neon-20, magnesium-24, and silicon-28, as well as heavier nuclides such as sulfur-32, argon-36, and calcium-40:

Equation 20.48

$$C612 - \rightarrow H24eO816 - \rightarrow H24eN1020e - \rightarrow H24eM1224g - \rightarrow H24eS1428i - \rightarrow H24eS1632 - \rightarrow H24eA1836r - \rightarrow H24eC2040a$$

The energy released by these reactions causes a further expansion of the star to form a*red supergiant*, and the core temperature increases steadily. At a temperature of about 3×10^9 K, the nuclei that have been formed exchange protons and neutrons freely. This equilibration process forms heavier elements up to iron-56 and nickel-58, which have the most stable nuclei known.

The Formation of Heavier Elements in Supernovas

None of the processes described so far produces nuclei with $Z > 28$. All naturally occurring elements heavier than nickel are formed in the rare but spectacular cataclysmic explosions called *supernovas* (Figure 20.27 "Nuclear Reactions during the Life Cycle of a Massive Star"). When the fuel in the core of a very massive star has been consumed, its gravity causes it to collapse in about 1 s. As the core is compressed, the iron and nickel nuclei within it disintegrate to protons and neutrons, and many of the protons capture electrons to form neutrons. The resulting *neutron star* is a dark object that is so dense that atoms no longer exist. Simultaneously, the energy released by the collapse of the core causes the supernova to explode in what is arguably the single most violent event in the universe. The force of the explosion blows most of the star's matter into space, creating a gigantic and rapidly expanding dust cloud, or *nebula* (Figure 20.28 "A Supernova"). During the extraordinarily short duration of this event, the

concentration of neutrons is so great that multiple neutron-capture events occur, leading to the production of the heaviest elements and many of the less stable nuclides. Under these conditions, for example, an iron-56 nucleus can absorb as many as 64 neutrons, briefly forming an extraordinarily unstable iron isotope that can then undergo multiple rapid β-decay processes to produce tin-120:

Equation 20.49

$$F2656e + 64n01 \rightarrow F26120e \rightarrow S50120n + 24b - 10$$

A view of the remains of Supernova 1987A, located in the Large Magellanic Cloud, showing the circular halo of expanding debris produced by the explosion. Multiple neutron-capture events occur during a supernova explosion, forming both the heaviest elements and many of the less stable nuclides.

Although a supernova occurs only every few hundred years in a galaxy such as the Milky Way, these rare explosions provide the only conditions under which elements heavier than nickel can be formed. The force of the explosions distributes these elements throughout the galaxy surrounding the supernova, and eventually they are captured in the dust that condenses to form new stars. Based on its elemental composition, our sun is thought to be a second- or third-generation star. It contains a considerable amount of cosmic debris from the explosion of supernovas in the remote past.

EXAMPLE 10

The reaction of two carbon-12 nuclei in a carbon-burning star can produce elements other than sodium. Write a balanced nuclear equation for the formation of

a. magnesium-24.

b. neon-20 from two carbon-12 nuclei.

Given: reactant and product nuclides

Asked for: balanced nuclear equation

Strategy:

Use conservation of mass and charge to determine the type of nuclear reaction that will convert the reactant to the indicated product. Write the balanced nuclear equation for the reaction.

Solution:

a. A magnesium-24 nucleus (Z = 12, A = 24) has the same nucleons as two carbon-12 nuclei (Z = 6, A = 12). The reaction is therefore a fusion of two carbon-12 nuclei, and no other particles are produced: $C612 + C612 \rightarrow M1224g.$

b. The neon-20 product has $Z = 10$ and $A = 20$. The conservation of mass requires that the other product have $A = (2 \times 12) - 20 = 4$; because of conservation of charge, it must have $Z = (2 \times 6) - 10 = 2$. These are the characteristics of an α particle. The reaction is the $refore\ C612 + C612 \rightarrow N1020e + a24.$

c.

Exercise

How many neutrons must an iron-56 nucleus absorb during a supernova explosion to produce an arsenic-75 nucleus? Write a balanced nuclear equation for the reaction.

Answer : 19 *neutrons*; $F2656e + 19n01$
$\rightarrow F2675e \rightarrow A3375s + 7b - 10$

Summary

By far the most abundant element in the universe is hydrogen. The fusion of hydrogen nuclei to form helium nuclei is the major process that fuels young stars such as the sun. Elements heavier than helium are formed from hydrogen and helium in the interiors of stars. Successive fusion reactions of helium nuclei at higher temperatures create elements with even numbers of protons and neutrons up to magnesium and then up to calcium. Eventually, the elements up to iron-56 and nickel-58 are formed by exchange processes at even higher temperatures. Heavier elements can only be made by a process that involves multiple neutron-capture events, which can occur only during the explosion of a supernova.

KEY TAKEAWAYS

- Hydrogen and helium are the most abundant elements in the universe.
- Heavier elements are formed in the interior of stars via multiple neutron-capture events.

CONCEPTUAL PROBLEMS

1. Why do scientists believe that hydrogen is the building block of all other elements? Why do scientists believe that helium-4 is the building block of the heavier elements?
2. How does a star produce such enormous amounts of heat and light? How are elements heavier than Ni formed?
3. Propose an explanation for the observation that elements with even atomic numbers are more abundant than elements with odd atomic numbers.

4. During the lifetime of a star, different reactions that form different elements are used to power the fusion furnace that keeps a star "lit." Explain the different reactions that dominate in the different stages of a star's life cycle and their effect on the temperature of the star.
5. A line in a popular song from the 1960s by Joni Mitchell stated, "We are stardust…." Does this statement have any merit or is it just poetic? Justify your answer.
6. If the laws of physics were different and the primary element in the universe were boron-11 ($Z = 5$), what would be the next four most abundant elements? Propose nuclear reactions for their formation.

ANSWER

1.
2.
3. The raw material for all elements with $Z > 2$ is helium ($Z = 2$), and fusion of helium nuclei will always produce nuclei with an even number of protons.
4.
5.
6.

NUMERICAL PROBLEMS

1. Write a balanced nuclear reaction for the formation of each isotope.

a. ^{27}Al from two ^{12}C nuclei

b. ^{9}Be from two ^{4}He nuclei

2. At the end of a star's life cycle, it can collapse, resulting in a supernova explosion that leads to the formation of heavy elements by multiple neutron-capture events. Write a balanced nuclear reaction for the formation of each isotope during such an explosion.

a. ^{106}Pd from nickel-58

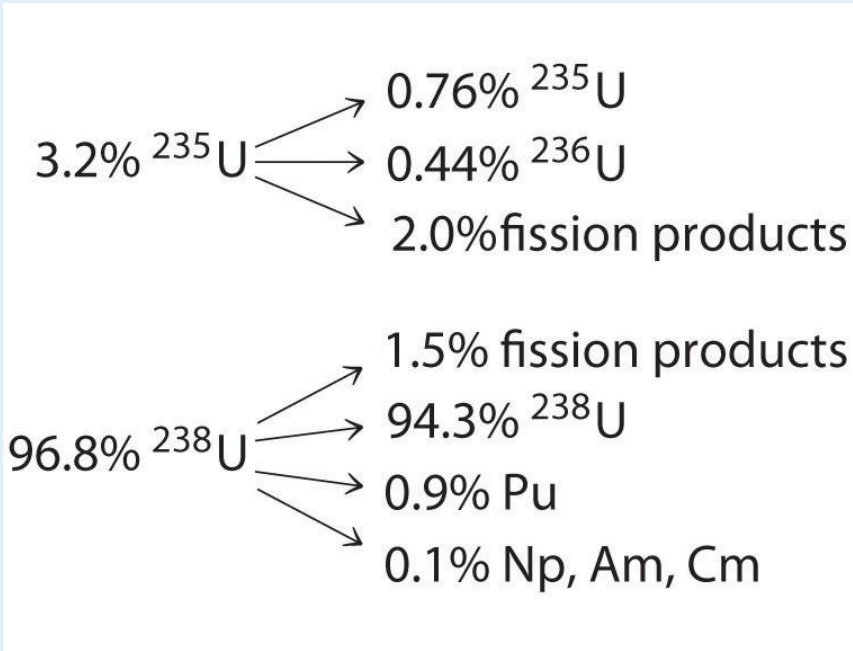
b. selenium-79 from iron-56

3. When a star reaches middle age, helium-4 is converted to short-lived beryllium-8 (mass = 8.00530510 amu), which reacts with another helium-4 to produce carbon-12. How much energy is released in each reaction (in megaelectronvolts)? How many atoms of helium must be "burned" in this process to produce the same amount of energy obtained from the fusion of 1 mol of hydrogen atoms to give deuterium?

20.7 End-of-Chapter Material

APPLICATION PROBLEMS

1. Until the 1940s, uranium glazes were popular on ceramic dishware. One brand, Fiestaware, had bright orange glazes that could contain up to 20% uranium by mass. Although this practice is less common today due to the negative association of radiation, it is still possible to buy Depression-era glassware that is quite radioactive. Aqueous solutions in contact with this "hot" glassware can reach uranium concentrations up to 10 ppm by mass. If 1.0 g of uranium undergoes 1.11×10^7 decays/s, each to an α particle with an energy of 4.03 MeV, what would be your exposure in rem and rad if you drank 1.0 L of water that had been sitting for an extended time in a Fiestaware pitcher? Assume that the water and contaminants are excreted only after 18 h and that you weigh 70.0 kg.
2. Neutrography is a technique used to take the picture of an object using a beam of neutrons. How does the penetrating power of a neutron compare with alpha, beta, and gamma radiation? Do you expect similar penetration for protons? How would the biological damage of each particle compare with the other types of radiation? (Recall that a neutron's mass is approximately 2000 times the mass of an electron.)
3. Spent fuel elements in a nuclear reactor contain radioactive fission products in addition to heavy metals. The conversion of nuclear fuel in a reactor is shown here:



Neglecting the fission products, write balanced nuclear reactions for the conversion of the original fuel to each product.

4. The first atomic bomb used ^{235}U as a fissile material, but there were immense difficulties in obtaining sufficient quantities of pure ^{235}U. A second fissile element, plutonium, was discovered in 1940, and it rapidly became important as a nuclear fuel. This element was produced by irradiating ^{238}U with neutrons in a nuclear reactor. Complete the series that produced plutonium, all isotopes of which are fissile:
5. $U92238 + n01 \rightarrow U \rightarrow Np \rightarrow Pu$
6. Boron neutron capture therapy is a potential treatment for many diseases. As the name implies, when boron-10, one of the naturally occurring isotopes of boron, is bombarded with neutrons, it absorbs a neutron and emits an α particle. Write a balanced nuclear reaction for this reaction. One advantage of this process is that neutrons cause little damage on their own, but when they are absorbed by boron-10, they can cause localized emission of alpha radiation. Comment on the utility of this treatment and its potential difficulties.
7. An airline pilot typically flies approximately 80 h per month. If 75% of that time is spent at an altitude of about 30,000 ft, how much radiation is that pilot receiving in one month? over a 30 yr career? Is the pilot receiving toxic doses of radiation?
8. At a breeder reactor plant, a 72 kg employee accidentally inhaled 2.8 mg of ^{239}Pu dust. The isotope decays by alpha decay and has a half-life of 24,100 yr. The energy of the emitted α particles is 5.2 MeV, and the dust stays in the employee's body for 18 h.

a. How many plutonium atoms are inhaled?
b. What is the energy absorbed by the body?
c. What is the physical dose in rads?
d. What is the dose in rems? Will the dosage be fatal?

9. For many years, the standard source for radiation therapy in the treatment of cancer was radioactive ^{60}Co, which undergoes beta decay to ^{60}Ni and emits two γ rays, each with an energy of 1.2 MeV. Show the sequence of nuclear reactions. If the half-life for beta decay is 5.27 yr, how many ^{60}Co nuclei are present in a typical source undergoing 6000 dps that is used by hospitals? The mass of ^{60}Co is 59.93 amu.
10. It is possible to use radioactive materials as heat sources to produce electricity. These radioisotope thermoelectric generators (RTGs) have been used in spacecraft and many other applications. Certain Cold War–era Russian-made RTGs used a 5.0 kg strontium-90 source. One mole of strontium-90 releases β

particles with an energy of 0.545 MeV and undergoes 2.7×10^{13} decays/s. How many watts of power are available from this RTG (1 watt = 1 J/s)?

11. Potassium consists of three isotopes (potassium-39, potassium-40, and potassium-41). Potassium-40 is the least abundant, and it is radioactive, decaying to argon-40, a stable, nonradioactive isotope, by the emission of a β particle with a half-life of precisely 1.25×10^9 yr. Thus the ratio of potassium-40 to argon-40 in any potassium-40–containing material can be used to date the sample. In 1952, fragments of an early hominid, *Meganthropus*, were discovered near Modjokerto in Java. The bone fragments were lying on volcanic rock that was believed to be the same age as the bones. Potassium–argon dating on samples of the volcanic material showed that the argon-40-to-potassium-40 molar ratio was 0.00281:1. How old were the rock fragments? Could the bones also be the same age? Could radiocarbon dating have been used to date the fragments?

ANSWERS

1. 6.6×10^{-3} rad; 0.13 rem
2.
3.

$$U92235 + n01 \rightarrow U92236 + g$$

$$U92238 + n01 \rightarrow U92239 + g$$

4. $U92239 \rightarrow N93239p + b - 10$
5. $N93239p \rightarrow P94239u + b - 10$
6. $P94239u \rightarrow A95239m + b - 10$
7. $A95239m \rightarrow C96239m + b - 10$
8.
9.
10.

a. 7.1×10^{18} atoms of Pu

b. 0.35 J

c. 0.49 rad

d. 9.8 rem; this dose is unlikely to be fatal.

11.

12. 130 W

13.

Chapter 21

Periodic Trends and the *s*-Block Elements

In previous chapters, we used the principles of chemical bonding, thermodynamics, and kinetics to provide a conceptual framework for understanding the chemistry of the elements. Beginning in Chapter 21 "Periodic Trends and the ", we use the periodic table to guide our discussion of the properties and reactions of the elements and the synthesis and uses of some of their commercially important compounds. We begin this chapter with a review of periodic trends as an introduction, and then we describe the chemistry of hydrogen and the other *s*-block elements. In Chapter 22 "The ", we consider the chemistry of the *p*-block elements; Chapter 23 "The " presents the transition metals, in which the *d*-subshell is being filled. In this chapter, you will learn why potassium chloride is used as a substitute for sodium chloride in a low-sodium diet, why cesium is used as a photosensor, why the heating elements in electric ranges are coated with magnesium oxide, and why exposure to a radioactive isotope of strontium is more dangerous for children than for adults.

21.1 Overview of Periodic Trends

LEARNING OBJECTIVE

1. To know important periodic trends in several atomic properties.

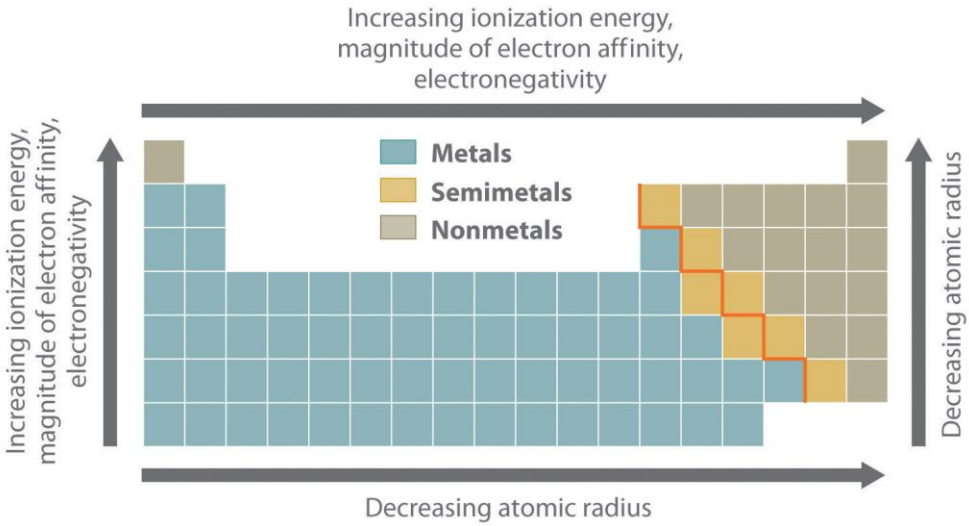
As we begin our summary of periodic trends, recall from Chapter 7 "The Periodic Table and Periodic Trends" that the single most important unifying principle in understanding the chemistry of the elements is the systematic increase in atomic number, accompanied by the orderly filling of atomic orbitals by electrons, which leads to periodicity in such properties as atomic and ionic size, ionization energy, electronegativity, and electron affinity. The same factors also lead to periodicity in valence electron configurations, which for each group results in similarities in oxidation states and the formation of compounds with common stoichiometries.

The most important periodic trends in atomic properties are summarized in Figure 21.1 "Summary of Periodic Trends in Atomic Properties". Recall from Chapter 7 "The Periodic Table and Periodic Trends" that these trends are based on periodic variations in a single fundamental property, the effective nuclear charge (Z_{eff}), which increases from left to right and from top to bottom in the periodic table (Figure 6.29 "Orbital Energy Level Diagram for a Typical Multielectron Atom").

The diagonal line in Figure 21.1 "Summary of Periodic Trends in Atomic Properties"separates the metals (to the left of the line) from the nonmetals (to the right of the line). Because metals have relatively low electronegativities, they tend

to lose electrons in chemical reactions to elements that have relatively high electronegativities, forming compounds in which they have positive oxidation states. Conversely, nonmetals have high electronegativities, and they therefore tend to gain electrons in chemical reactions to form compounds in which they have negative oxidation states. The semimetals lie along the diagonal line dividing metals and nonmetals. It is not surprising that they tend to exhibit properties and reactivities intermediate between those of metals and nonmetals. Because the elements of groups 13, 14, and 15 span the diagonal line separating metals and nonmetals, their chemistry is more complex than predicted based solely on their valence electron configurations.

Figure 21.1 *Summary of Periodic Trends in Atomic Properties*



Ionization energies, the magnitude of electron affinities, and electronegativities generally increase from left to right and from bottom to top. In contrast, atomic size decreases from left to right and from bottom to top. Consequently, the elements in the upper right of the periodic table are the smallest and most electronegative; the elements in the bottom left are the largest and least electronegative. The semimetals lie along the diagonal line separating the metals from the nonmetals and exhibit intermediate properties.

Unique Chemistry of the Lightest Elements

The chemistry of the second-period element of each group (n = 2: Li, Be, B, C, N, O, and F) differs in many important respects from that of the heavier members, or *congeners*, of the group. Consequently, the elements of the third period (n = 3: Na, Mg, Al, Si, P, S, and Cl) are generally more representative of the group to which they belong. The anomalous chemistry of second-period elements results from three important characteristics: small radii, energetically unavailable d orbitals, and a tendency to form pi (π) bonds with other atoms.

Note the Pattern

In contrast to the chemistry of the second-period elements, the chemistry of the third-period elements is more representative of the chemistry of the respective group.

Due to their small radii, second-period elements have electron affinities that are less negative than would be predicted from general periodic trends. When an electron is added to such a small atom, increased electron–electron repulsions tend to destabilize the anion. Moreover, the small sizes of these elements prevent them from forming compounds in which they have more than four nearest neighbors. Thus BF_3 forms only the four-coordinate, tetrahedral BF_4^- ion, whereas under the same conditions AlF_3forms the six-coordinate, octahedral AlF_6^{3-} ion. Because of the smaller atomic size, simple binary ionic compounds of second-period elements also have more covalent character than the corresponding compounds formed from their heavier congeners. The very small cations derived from second-period elements have a high charge-to-radius ratio and can therefore polarize the filled valence shell of an anion. As such, the bonding in such compounds has a significant covalent component, giving the compounds properties that can differ significantly from those expected for simple ionic compounds. As an example, LiCl, which is partially covalent in character, is much more soluble than NaCl in solvents with a relatively low dielectric constant, such as ethanol (ε = 25.3 versus 80.1 for H_2O).

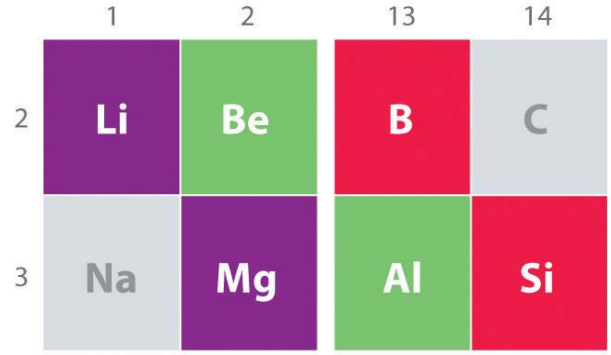
Because *d* orbitals are never occupied for principal quantum numbers less than 3, the valence electrons of second-period elements occupy 2*s* and 2*p* orbitals only. The energy of the 3*d* orbitals far exceeds the energy of the 2*s* and 2*p* orbitals, so using them in bonding is energetically prohibitive. Consequently, electron configurations with more than four electron pairs around a central, second-period element are simply not observed.[1]

One of the most dramatic differences between the lightest main group elements and their heavier congeners is the tendency of the second-period elements to form species that contain multiple bonds. For example, N is just above P in group 15: N_2 contains an N≡N bond, but each phosphorus atom in tetrahedral P_4 forms three P–P bonds. This difference in behavior reflects the fact that within the same group of the periodic table, the relative energies of the π bond and the sigma (σ) bond differ. A C=C bond, for example, is approximately 80% stronger than a C–C bond. In contrast, an Si=Si bond, with less *p*-orbital overlap between the valence orbitals of the bonded atoms because of the larger atomic size, is only about 40% stronger than an Si–Si bond. Consequently, compounds that contain both multiple and single

C to C bonds are common for carbon, but compounds that contain only sigma Si–Si bonds are more energetically favorable for silicon and the other third-period elements.

Another important trend to note in main group chemistry is the chemical similarity between the lightest element of one group and the element immediately below and to the right of it in the next group, a phenomenon known as the *diagonal effect* (Figure 21.2 "The Diagonal Effect") There are, for example, significant similarities between the chemistry of Li and Mg, Be and Al, and B and Si. Both $BeCl_2$ and $AlCl_3$ have substantial covalent character, so they are somewhat soluble in nonpolar organic solvents. In contrast, although Mg and Be are in the same group, $MgCl_2$ behaves like a typical *ionic halide* due to the lower electronegativity and larger size of magnesium.

Figure 21.2 *The Diagonal Effect*



The properties of the lightest element in a group are often more similar to those of the element below and to the right in the periodic table. For instance, the chemistry of lithium is more similar to that of magnesium in group 2 than it is to the chemistry of sodium, the next member in group 1.

The Inert-Pair Effect

The inert-pair effect refers to the empirical observation that the heavier elements of groups 13–17 often have oxidation states that are lower by 2 than the maximum predicted for their group. For example, although an oxidation state of +3 is common for group 13 elements, the heaviest element in group 13, thallium (Tl), is more likely to form compounds in which it has a +1 oxidation state. There appear to be two major reasons for the inert-pair effect: increasing ionization energies and decreasing bond strengths.

Note the Pattern

In moving down a group in the *p*-block, increasing ionization energies and decreasing bond strengths result in an inert-pair effect.

The ionization energies increase because filled $(n - 1)d$ or $(n - 2)f$ subshells are relatively poor at shielding electrons in *ns* orbitals. Thus the two electrons in the *ns*subshell experience an unusually high effective nuclear charge, so they are strongly attracted to the nucleus, reducing their participation in bonding. It is therefore substantially more difficult than expected to remove these ns^2 electrons, as shown inTable 21.1 "Ionization Energies (" by the difference between the first ionization energies of thallium and aluminum. Because Tl is less likely than Al to lose its two ns^2 electrons, its most common oxidation state is +1 rather than +3.

Table 21.1 Ionization Energies (*I*) and Average M–Cl Bond Energies for the Group 13 Elements

Element	Electron Configuration	I_1(kJ/mol)	$I_1 + I_2 + I_3$(kJ/mol)	Average M–Cl Bond Energy (kJ/mol)
B	[He] $2s^2 2p^1$	801	6828	536
Al	[Ne] $3s^2 3p^1$	578	5139	494
Ga	[Ar] $3d^{10} 4s^2 4p^1$	579	5521	481
In	[Kr] $4d^{10} 5s^2 p^1$	558	5083	439
Tl	[Xe] $4f^{14} 5d^{10} 6s^2 p^1$	589	5439	373

Source of data: John A. Dean, Lange's Handbook of Chemistry, 15th ed. (New York: McGraw-Hill, 1999).

Going down a group, the atoms generally became larger, and the overlap between the valence orbitals of the bonded atoms decreases. Consequently, bond strengths tend to decrease down a column. As shown by the M–Cl bond energies listed in Table 21.1 "Ionization Energies (", the strength of the bond between a group 13 atom and a chlorine atom decreases by more than 30% from B to Tl. Similar decreases are observed for the atoms of groups 14 and 15.

The net effect of these two factors—increasing ionization energies and decreasing bond strengths—is that in going down a group in the *p*-block, the additional energy released by forming two additional bonds eventually is not great enough to compensate for the additional energy required to remove the two ns^2 electrons.

EXAMPLE 1

Based on the positions of the group 13 elements in the periodic table and the general trends outlined in this section,

a. classify these elements as metals, semimetals, or nonmetals.

b. predict which element forms the most stable compounds in the +1 oxidation state.

c. predict which element differs the most from the others in its chemistry.

d. predict which element of another group will exhibit chemistry most similar to that of Al.

Given: positions of elements in the periodic table

Asked for: classification, oxidation-state stability, and chemical reactivity

Strategy:

From the position of the diagonal line in the periodic table separating metals and nonmetals, classify the group 13 elements. Then use the trends discussed in this section to compare their relative stabilities and chemical reactivities.

Solution:

a. Group 13 spans the diagonal line separating the metals from the nonmetals. Although Al and B both lie on the diagonal line, only B is a semimetal; the heavier elements are metals.

b. All five elements in group 13 have an ns^2np^1 valence electron configuration, so they are expected to form ions with a +3 charge from the loss of all valence electrons. The inert-pair effect should be most important for the heaviest element (Tl), so it is most likely to form compounds in an oxidation state that is lower by 2. Thus the +1 oxidation state is predicted to be most important for thallium.

c. Among the main group elements, the lightest member of each group exhibits unique chemistry because of its small size resulting in a high concentration of charge, energetically unavailable *d* orbitals, and a tendency to form multiple bonds. In group 13, we predict that the chemistry of boron will be quite different from that of its heavier congeners.

d. Within the *s* and *p* blocks, similarities between elements in different groups are most marked between the lightest member of one group and the element of the next group immediately below and to the right of it. These elements exhibit similar electronegativities and charge-to-radius ratios. Because Al is the second member of group 13, we predict that its chemistry will be most similar to that of Be, the lightest member of group 2.

Exercise

Based on the positions of the group 14 elements C, Si, Ge, Sn, and Pb in the periodic table and the general trends outlined in this section,

a. classify these elements as metals, semimetals, or nonmetals.
b. predict which element forms the most stable compounds in the +2 oxidation state.
c. predict which element differs the most from the others in its chemistry.
d. predict which element of group 14 will be chemically most similar to a group 15 element.

Answer:

a. nonmetal: C; semimetals: Si and Ge; metals: Sn and Pb
b. Pb is most stable as M^{2+}.
c. C is most different.
d. C and P are most similar in chemistry.

Summary

The most important unifying principle in describing the chemistry of the elements is that the systematic increase in atomic number and the orderly filling of atomic orbitals lead to periodic trends in atomic properties. The most fundamental property leading to periodic variations is the **effective nuclear charge (*Z*eff)**. Because of the position of the diagonal line separating metals and nonmetals in the periodic table, the chemistry of groups 13, 14, and 15 is relatively complex. The second-period elements (n = 2) in each group exhibit unique chemistry compared with their heavier congeners because of their smaller radii, energetically unavailable *d* orbitals, and greater ability to form π bonds with other atoms. Increasing ionization energies and decreasing bond strengths lead to the **inert-pair effect**, which causes the heaviest elements of groups 13–17 to have a stable oxidation state that is lower by 2 than the maximum predicted for their respective groups.

KEY TAKEAWAY

- The chemistry of the third-period element in a group is most representative of the chemistry of the group because the chemistry of the second-period elements is dominated by their small radii, energetically unavailable *d* orbitals, and tendency to form π bonds with other atoms.

CONCEPTUAL PROBLEMS

1. List three physical properties that are important in describing the behavior of the main group elements.
2. Arrange K, Cs, Sr, Ca, Ba, and Li in order of

a. increasing ionization energy.

b. increasing atomic size.

c. increasing electronegativity.

3. Arrange Rb, H, Be, Na, Cs, and Ca in order of

a. decreasing atomic size.

b. decreasing magnitude of electron affinity.

4. Which periodic trends are affected by Z_{eff}? Based on the positions of the elements in the periodic table, which element would you expect to have the highest Z_{eff}? the lowest Z_{eff}?
5. Compare the properties of the metals and nonmetals with regard to their electronegativities and preferred oxidation states.
6. Of Ca, Br, Li, N, Zr, Ar, Sr, and S, which elements have a greater tendency to form positive ions than negative ions?
7. Arrange As, O, Ca, Sn, Be, and Sb in order of decreasing metallic character.
8. Give three reasons the chemistry of the second-period elements is generally not representative of their groups as a whole.
9. Compare the second-period elements and their heavier congeners with regard to

a. magnitude of electron affinity.

b. coordination number.

c. the solubility of the halides in nonpolar solvents.

10. The heavier main group elements tend to form extended sigma-bonded structures rather than multiple bonds to other atoms. Give a reasonable explanation for this tendency.
11. What is the diagonal effect? How does it explain the similarity in chemistry between, for example, boron and silicon?
12. Although many of the properties of the second- and third-period elements in a group are quite different, one property is similar. Which one?

13. Two elements are effective additives to solid rocket propellant: beryllium and one other element that has similar chemistry. Based on the position of beryllium in the periodic table, identify the second element.
14. Give two reasons for the inert-pair effect. How would this phenomenon explain why Sn^{2+} is a better reducing agent than Pb^{2+}?
15. Explain the following trend in electron affinities: Al (−41.8 kJ/mol), Si (−134.1 kJ/mol), P (−72.0 kJ/mol), and S (−200.4 kJ/mol).
16. Using orbital energy arguments, explain why electron configurations with more than four electron pairs around the central atom are not observed for second-period elements.

ANSWERS

1.
2.
3.

a. Cs > Rb > Ca > Na > Be > H
b. H > Na > Rb > Cs > Ca > Be

4.
5.
6.
7. Ca > Be > Sn > Sb > As > O
8.
9.
10.
11.
12.
13. aluminum
14.
15. The magnitude of electron affinity increases from left to right in a period due to the increase in Z_{eff}; P has a lower electron affinity than expected due to its half-filled 3*p*shell, which requires the added electron to enter an already occupied 3*p* orbital.
16.

STRUCTURE AND REACTIVITY

1. The following table lists the valences, coordination numbers, and ionic radii for a series of cations. Which would you substitute for K^+ in a crystalline lattice? Explain your answer.

Metal	Charge	Coordination Number	Ionic Radius (pm)
Li	+1	4	76
Na	+1	6	102
K	+1	6	138
Mg	+2	6	72
Ca	+2	6	100
Sr	+2	6	118

ANSWER

1. Sr^{2+}; it is the ion with the radius closest to that of K^+.

[1] You may recall from Chapter 8 "Ionic versus Covalent Bonding" that the role of *d* orbitals in bonding in main group compounds with coordination numbers of 5 or higher remains somewhat controversial. In fact, theoretical descriptions of the bonding in molecules such as SF_6 have been published without mentioning the participation of *d* orbitals on sulfur. Arguments based on *d*-orbital availability and on the small size of the central atom, however, predict that coordination numbers greater than 4 are unusual for the elements of the second period, which is in agreement with experimental results.

21.2 The Chemistry of Hydrogen

LEARNING OBJECTIVE

1. To describe the physical and chemical properties of hydrogen and predict its reactivity.

We now turn from an overview of periodic trends to a discussion of the *s*-block elements, first by focusing on hydrogen, whose chemistry is sufficiently distinct and important to be discussed in a category of its own. Most versions of the periodic table place hydrogen in the upper left corner immediately above lithium, implying that hydrogen, with a $1s^1$ electron configuration, is a member of group 1. In fact, the chemistry of hydrogen does *not* greatly resemble that of the metals of group 1. Indeed, some versions of the periodic table place hydrogen above fluorine in group 17 because the addition of a single electron to a hydrogen atom completes its valence shell.

Note the Pattern

Although hydrogen has an ns^1 electron configuration, its chemistry does not resemble that of the metals of group 1.

Isotopes of Hydrogen

Hydrogen, the most abundant element in the universe, is the ultimate source of all other elements by the process of nuclear fusion. (For more information on nuclear fusion, seeChapter 20 "Nuclear Chemistry".) Table 21.2 "The Isotopes of Hydrogen" compares the three isotopes of hydrogen, all of which contain one proton and one electron per atom. The most common isotope is protium (^{1}H or H), followed by deuterium (^{2}H or D), which has an additional neutron. The rarest isotope of hydrogen is tritium (^{3}H or T), which is produced in the upper atmosphere by a nuclear reaction when cosmic rays strike nitrogen and other atoms; it is then washed into the oceans by rainfall. Tritium is radioactive, decaying to ^{3}He with a half-life of only 12.32 years. Consequently, the atmosphere and oceans contain only a very low, steady-state level of tritium. The term*hydrogen* and the symbol H normally refer to the naturally occurring mixture of the three isotopes.

Table 21.2 The Isotopes of Hydrogen

	Protium	Deuterium	Tritium
Symbol	$H11$	$H12$	$H13$
neutrons	0	1	2
mass (amu)	1.00783	2.0140	3.01605
abundance (%)	99.9885	0.0115	$\sim 10^{-17}$
half-life (years)	—	—	12.32
boiling point of X_2 (K)	20.28	23.67	25
melting point/boiling point of X_2O (°C)	0.0/100.0	3.8/101.4	4.5/?

The different masses of the three isotopes of hydrogen cause them to have different physical properties. Thus H_2, D_2, and T_2 differ in their melting points, boiling points, densities, and heats of fusion and vaporization. In 1931, Harold Urey and coworkers discovered deuterium by slowly evaporating several liters of liquid hydrogen until a volume of about 1 mL remained. When that remaining liquid was vaporized and its emission spectrum examined, they observed new absorption lines in addition to those previously identified as originating from hydrogen. The natural abundance of tritium, in contrast, is so low that it could not be detected by similar experiments; it was first prepared in 1934 by a nuclear reaction.

Harold Urey (1893–1981)

Urey won the Nobel Prize in Chemistry in 1934 for his discovery of deuterium (^2H). Urey was born and educated in rural Indiana. After earning a BS in zoology from the University of Montana in 1917, Urey changed career directions. He earned his PhD in chemistry at Berkeley with G. N. Lewis (of Lewis electron structure fame) and subsequently worked with Niels Bohr in Copenhagen. During World War II, Urey was the director of war research for the Atom Bomb Project at Columbia University. In later years, his research focused on the evolution of life. In 1953, he and his graduate student, Stanley Miller, showed that organic compounds, including amino acids, could be formed by passing an electric discharge through a mixture of compounds thought to be present in the atmosphere of primitive Earth.

Because the normal boiling point of D_2O is 101.4°C (compared to 100.0°C for H_2O), evaporation or fractional distillation can be used to increase the concentration of deuterium in a sample of water by the selective removal of the more volatile H_2O. Thus bodies of water that have no outlet, such as the Great Salt Lake and the Dead Sea, which maintain their level solely by evaporation, have significantly higher concentrations of deuterated water than does lake or seawater with at least one outlet. A more efficient way to obtain water highly enriched in deuterium is by prolonged electrolysis of an aqueous solution. Because a deuteron (D^+) has twice the mass of a proton (H^+), it diffuses more slowly toward the electrode surface. Consequently, the gas evolved at the cathode is enriched in H, the species that diffuses more rapidly, favoring the formation of H_2 over D_2 or HD. Meanwhile, the solution becomes enriched in deuterium. Deuterium-rich water is called *heavy water* because the density of D_2O (1.1044 g/cm^3 at 25°C) is greater than that of H_2O (0.99978 g/cm^3). Heavy water was an important constituent of early nuclear reactors. (For more information on nuclear reactors, see Chapter 20 "Nuclear Chemistry".)

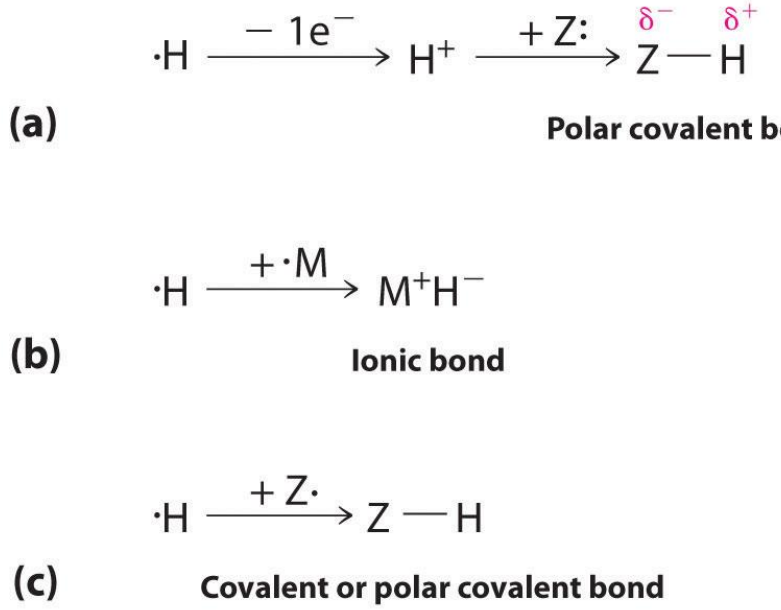
Because deuterons diffuse so much more slowly, D_2O will not support life and is actually toxic if administered to mammals in large amounts. The rate-limiting step in many important reactions catalyzed by enzymes involves proton transfer. The transfer of D^+ is so slow compared with that of H^+ because bonds to D break more slowly than those to H, so the delicate balance of reactions in the cell is disrupted. Nonetheless, deuterium and tritium are important research tools for biochemists. By incorporating these isotopes into specific positions in selected molecules, where they act as labels, or*tracers*, biochemists can follow the path of a molecule through an organism or a cell. Tracers can also be used to provide information about the mechanism of enzymatic reactions.

Bonding in Hydrogen and Hydrogen-Containing Compounds

The $1s^1$ electron configuration of hydrogen indicates a single valence electron. Because the 1*s* orbital has a maximum capacity of two electrons, hydrogen can form compounds with other elements in three ways (Figure 21.3 "Three Types of Bonding in Compounds of Hydrogen"):

1. **Losing its electron to form a proton (H^+) with an empty 1*s* orbital.** The proton is a Lewis acid that can accept a pair of electrons from another atom to form an electron-pair bond. In the acid–base reactions discussed in Chapter 16 "Aqueous Acid–Base Equilibriums", for example, the proton always binds to a lone pair of electrons on an atom in another molecule to form a polar covalent bond. If the lone pair of electrons belongs to an oxygen atom of a water molecule, the result is the hydronium ion (H_3O^+).
2. **Accepting an electron to form a** hydride ion**(H^-), which has a filled $1s^2$ orbital.** Hydrogen reacts with relatively electropositive metals, such as the alkali metals (group 1) and alkaline earth metals (group 2), to form *ionic hydrides*, which contain metal cations and H^- ions.
3. **Sharing its electron with an electron on another atom to form an electron-pair bond.** With a half-filled $1s^1$ orbital, the hydrogen atom can interact with singly occupied orbitals on other atoms to form either a covalent or a polar covalent electron-pair bond, depending on the electronegativity of the other atom.

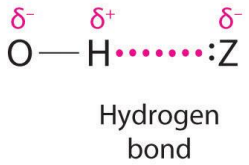
Figure 21.3 *Three Types of Bonding in Compounds of Hydrogen*



Because of its $1s^1$ electron configuration and the fact that the 1s orbital can accommodate no more than two electrons, hydrogen can (a) bond to other elements by losing an electron to form a proton, which can accept a pair of electrons from a more electronegative atom to form a polar covalent bond; (b) gain an electron from an electropositive metal to form a hydride ion, resulting in an ionic hydride; or (c) share its half-filled 1s orbital with a half-filled orbital on another atom to form a covalent or a polar covalent electron-pair bond.

Hydrogen can also act as a bridge between two atoms. One familiar example is thehydrogen bond, an electrostatic interaction between a hydrogen bonded to an electronegative atom and an atom that has one or more lone pairs of electrons (Figure 21.4 "The Hydrogen Bond"). An example of this kind of interaction is the hydrogen bonding network found in water (Figure 11.8 "The Hydrogen-Bonded Structure of Ice"). Hydrogen can also form a three-center bond (or electron-deficient bond), in which a hydride bridges two electropositive atoms. Compounds that contain hydrogen bonded to boron and similar elements often have this type of bonding. The B–H–B units found in boron hydrides cannot be described in terms of localized electron-pair bonds. Because the H atom in the middle of such a unit can accommodate a maximum of only two electrons in its 1*s* orbital, the B–H–B unit can be described as containing a hydride that interacts simultaneously with empty sp^3 orbitals on two boron atoms (Figure 21.5 "A Three-Center Bond Uses Two Electrons to Link Three Atoms"). In these bonds, only *two* bonding electrons are used to hold *three* atoms together, making them electron-deficient bonds. You encountered a similar phenomenon in the discussion of π bonding in ozone and the nitrite ion in Chapter 9 "Molecular Geometry and Covalent Bonding Models", Section 9.4 "Polyatomic Systems with Multiple Bonds". Recall that in both these cases, we used the presence of two electrons in a π molecular orbital extending over three atoms to explain the fact that the two O–O bond distances in ozone and the two N–O bond distances in nitrite are the same, which otherwise can be explained only by the use of resonance structures.

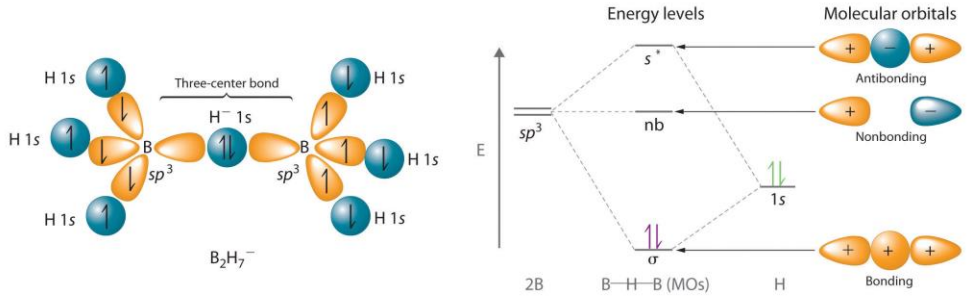
Figure 21.4 *The Hydrogen Bond*



The covalent bond between hydrogen and a very electronegative element, such as nitrogen, oxygen, or fluorine, is highly polar. The resulting partial positive charge on H allows it to interact

with a lone pair of electrons on another atom to form a hydrogen bond, which is typically a linear arrangement of the three atoms, with the hydrogen atom placed asymmetrically between the two heavier atoms.

Figure 21.5 *A Three-Center Bond Uses Two Electrons to Link Three Atoms*



In the B–H–B unit shown, a hydride, with a filled 1s orbital, interacts simultaneously with empty sp^3 hybrids on the boron atoms of two BH_3 units to give three molecular orbitals. The two bonding electrons occupy the lowest-energy (σ) bonding orbital, thereby holding all three atoms together.

Note the Pattern

Hydrogen can lose its electron to form H^+, accept an electron to form H^-, share its electron, hydrogen bond, or form a three-center bond.

Synthesis, Reactions, and Compounds of Hydrogen

The first known preparation of elemental hydrogen was in 1671, when Robert Boyle dissolved iron in dilute acid and obtained a colorless, odorless, gaseous product. Hydrogen was finally identified as an element in 1766, when Henry Cavendish showed that water was the sole product of the reaction of the gas with oxygen. The explosive properties of mixtures of hydrogen with air were not discovered until early in the 18th century; they partially caused the spectacular explosion of the hydrogen-filled dirigible*Hindenburg* in 1937 (Figure 21.6 "The Explosive Properties of Hydrogen"). Due to its extremely low molecular mass, hydrogen gas is difficult to condense to a liquid (boiling point = 20.3 K), and solid hydrogen has one of the lowest melting points known (13.8 K).

The most common way to produce small amounts of highly pure hydrogen gas in the laboratory was discovered by Boyle: reacting an active metal (M), such as iron, magnesium, or zinc, with dilute acid:

Equation 21.1

$$M(s) + 2H^+(aq) \rightarrow H_2(g) + M^{2+}(aq)$$

Hydrogen gas can also be generated by reacting metals such as aluminum or zinc with a strong base:

Equation 21.2

$$Al(s) + OH\text{-}(aq) + 3H2O(l) \rightarrow 32H2(g) + [Al(OH)4]\text{-}(aq)$$

Solid commercial drain cleaners such as Drano use this reaction to generate gas bubbles that help break up clogs in a drainpipe. (For more information on redox reactions like that of Drano, see Chapter 19 "Electrochemistry",Section 19.2 "Standard Potentials".) Hydrogen gas is also produced by reacting ionic hydrides with water. Because ionic hydrides are expensive, however, this reaction is generally used for only specialized purposes, such as producing HD gas by reacting a hydride with D_2O:

Equation 21.3

$$MH(s) + D_2O(l) \rightarrow HD(g) + M^+(aq) + OD^-(aq)$$

On an industrial scale, H_2 is produced from methane by means of *catalytic steam reforming*, a method used to convert hydrocarbons to a mixture of CO and H_2 known as*synthesis gas*, or *syngas*. (For more information on steam reforming, see Chapter 14 "Chemical Kinetics", Section 14.8 "Catalysis".) The process is carried out at elevated temperatures (800°C) in the presence of a nickel catalyst:

Equation 21.4

$$CH4(g) + H2O(g) \rightarrow NiCO(g) + 3H2(g)$$

Most of the elements in the periodic table form binary compounds with hydrogen, which are collectively referred to as *hydrides*. Binary hydrides in turn can be classified in one of three ways, each with its own characteristic properties. *Covalent hydrides*contain hydrogen bonded to another atom via a covalent bond or a polar covalent bond. Covalent hydrides are usually molecular substances that are relatively volatile and have low melting points. *Ionic hydrides* contain the hydride ion as the anion with cations derived from electropositive metals. Like most ionic compounds, they are typically nonvolatile solids that contain three-dimensional lattices of cations and anions. Unlike most ionic compounds, however, they often decompose to $H_2(g)$ and the parent metal after heating. *Metallic hydrides* are formed by hydrogen and less electropositive metals such as the transition metals. The properties of metallic hydrides are usually similar to those of the parent metal. Consequently, metallic hydrides are best viewed as metals that contain many hydrogen atoms present as interstitial impurities.

Note the Pattern

Covalent hydrides are relatively volatile and have low melting points; ionic hydrides are generally nonvolatile solids in a lattice framework.

Summary

The three isotopes of hydrogen—**protium (1H or H)**, **deuterium (2H or D)**, and **tritium (3H or T)**—have different physical properties. Deuterium and tritium can be used as *tracers*, substances that enable biochemists to follow the path of a molecule through an organism or a cell. Hydrogen can form compounds that contain a proton (H^+), a **hydride ion (H–)**, an electron-pair bond to H, a**hydrogen bond**, or a **three-center bond (or electron-deficient bond)**, in which two electrons are shared between three atoms. Hydrogen gas can be generated by reacting an active metal with dilute acid, reacting Al or Zn with a strong base, or industrially by *catalytic steam reforming*, which produces*synthesis gas*, or *syngas*.

KEY TAKEAWAY

- Hydrogen can lose an electron to form a proton, gain an electron to form a hydride ion, or form a covalent bond or polar covalent electron-pair bond.

CONCEPTUAL PROBLEMS

1. Some periodic tables include hydrogen as a group 1 element, whereas other periodic tables include it as a group 17 element. Refer to the properties of hydrogen to propose an explanation for its placement in each group. In each case, give one property of hydrogen that would exclude it from groups 1 and 17.
2. If there were a planet where the abundances of D_2O and H_2O were reversed and life had evolved to adjust to this difference, what would be the effects of consuming large amounts of H_2O?
3. Describe the bonding in a hydrogen bond and the central B–H bond in $B_2H_7^-$. Why are compounds containing isolated protons unknown?
4. With which elements does hydrogen form ionic hydrides? covalent hydrides? metallic hydrides? Which of these types of hydrides can behave like acids?
5. Indicate which elements are likely to form ionic, covalent, or metallic hydrides and explain your reasoning:

a. Sr

b. Si

c. O

d. Li

e. B

f. Be

g. Pd

h. Al

6. Which has the higher ionization energy—H or H^-? Why?

7. The electronegativities of hydrogen, fluorine, and iodine are 2.20, 3.98, and 2.66, respectively. Why, then, is HI a stronger acid than HF?

8. If H_2O were a linear molecule, would the density of ice be less than or greater than that of liquid water? Explain your answer.

9. In addition to ion–dipole attractions, hydrogen bonding is important in solid crystalline hydrates, such as $Na_4XeO_6 \cdot 8H_2O$. Based on this statement, explain why anhydrous Na_4XeO_6 does not exist.

ANSWERS

1. H has one electron in an *s* orbital, like the group 1 metals, but it is also one electron short of a filled principal shell, like the group 17 elements. Unlike the alkali metals, hydrogen is not a metal. Unlike the halogens, elemental hydrogen is not a potent oxidant.

2.

3.

4.

5.

a. ionic; it is an alkaline earth metal.

b. covalent; it is a semimetal.

c. covalent; it is a nonmetal.

d. ionic; it is an alkali metal.

e. covalent; it is a semimetal.

f. covalent; it is a period 2 alkaline earth metal.

g. metallic; it is a transition metal.

h. covalent; it is a group 13 metal.

6.

7.

8.

9. Hydrogen bonding with waters of hydration will partially neutralize the negative charge on the terminal oxygen atoms on the XeO_6^{4-} ion, which stabilizes the solid.

STRUCTURE AND REACTIVITY

1. One of the largest uses of methane is to produce syngas, which is a source of hydrogen for converting nitrogen to ammonia. Write a complete equation for formation of syngas from methane and carbon dioxide. Calculate $\Delta G°$ for this reaction at 298 K and determine the temperature at which the reaction becomes spontaneous.
2. An alternative method of producing hydrogen is the water–gas shift reaction:

   $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$

   Use Chapter 25 "Appendix A: Standard Thermodynamic Quantities for Chemical Substances at 25°C" to calculate $\Delta G°$ for this reaction at 298 K and determine the temperature at which the reaction changes from spontaneous to nonspontaneous (or vice versa).
3. Predict the products of each reaction at 25°C and then balance each chemical equation.

a. $CsH(s) + D_2O(l) \rightarrow$

b. $CH_3CO_2H(l) + D_2O(l) \rightarrow$

c. $H_3PO_4(aq) + D_2O(l) \rightarrow$

d. $NH_2CH_2CO_2H(s) + D_2O(l) \rightarrow$

e. $NH_4Cl(s) + D_2O(l) \rightarrow$

4. Using heavy water (D_2O) as the source of deuterium, how could you conveniently prepare

a. D_2SO_4?

b. LiD?

5. What are the products of reacting NaH with D_2O? Do you expect the same products from reacting NaD and H_2O? Explain your answer.
6. A 2.50 g sample of zinc metal reacts with 100.0 mL of 0.150 M HCl. What volume of H_2(in liters) is produced at 23°C and 729 mmHg?
7. A chemical reaction requires 16.8 L of H_2 gas at standard temperature and pressure. How many grams of magnesium metal are needed to produce this amount of hydrogen gas?

8. Seawater contains 3.5% dissolved salts by mass and has an average density of 1.026 g/mL. The volume of the ocean is estimated to be 1.35×10^{21} L. Using the data in Table 21.2 "The Isotopes of Hydrogen", calculate the total mass of deuterium in the ocean.
9. From the data in Table 21.2 "The Isotopes of Hydrogen", determine the molarity of DOH in water. Do you expect the molarity of D_2O in water to be similar? Why or why not?
10. From the data in Table 21.2 "The Isotopes of Hydrogen", calculate how many liters of water you would have to evaporate to obtain 1.0 mL of TOD (tritium-oxygen-deuterium). The density of TOD is 1.159 g/mL.

21.3 The Alkali Metals (Group 1)

LEARNING OBJECTIVES

1. To describe how the alkali metals are isolated.
2. To be familiar with the reactions, compounds, and complexes of the alkali metals.

The alkali metals are so reactive that they are never found in nature in elemental form. Although some of their ores are abundant, isolating them from their ores is somewhat difficult. For these reasons, the group 1 elements were unknown until the early 19th century, when Sir Humphry Davy first prepared sodium (Na) and potassium (K) by passing an electric current through molten alkalis. (The ashes produced by the combustion of wood are largely composed of potassium and sodium carbonate.) Lithium (Li) was discovered 10 years later when the Swedish chemist Johan Arfwedson was studying the composition of a new Brazilian mineral. Cesium (Cs) and rubidium (Rb) were not discovered until the 1860s, when Robert Bunsen conducted a systematic search for new elements. Known to chemistry students as the inventor of the Bunsen burner, Bunsen's spectroscopic studies of ores showed sky blue and deep red emission lines that he attributed to two new elements, Cs and Rb, respectively. Francium (Fr) is found in only trace amounts in nature, so our knowledge of its chemistry is limited. All the isotopes of Fr have very short half-lives, in contrast to the other elements in group 1.

Sir Humphry Davy (1778–1829)

Davy was born in Penzance, Cornwall, England. He was a bit of a wild man in the laboratory, often smelling and tasting the products of his experiments, which almost certainly shortened his life. He discovered the physiological effects that cause nitrous oxide to be called "laughing gas" (and became addicted to it!), and he almost lost his eyesight in an explosion of nitrogen trichloride (NCl_3), which he was the first to prepare. Davy was one of the first to recognize the utility of Alessandro Volta's "electric piles" (batteries). By connecting several "piles" in series and inserting electrodes into molten salts of the alkali

metals and alkaline earth metals, he was able to isolate six previously unknown elements as pure metals: sodium, potassium, calcium, strontium, barium, and magnesium. He also discovered boron and was the first to prepare phosphine (PH_3) and hydrogen telluride (H_2Te), both of which are highly toxic.

Robert Wilhelm Bunsen (1811–1899)

Bunsen was born and educated in Göttingen, Germany. His early work dealt with organic arsenic compounds, whose highly toxic nature and explosive tendencies almost killed him and did cost him an eye. He designed the Bunsen burner, a reliable gas burner, and used it and emission spectra to discover cesium (named for its blue line) and rubidium (named for its red line).

Preparation of the Alkali Metals

Because the alkali metals are among the most potent reductants known, obtaining them in pure form requires a considerable input of energy. Pure lithium and sodium for example, are typically prepared by the electrolytic reduction of molten chlorides:

Equation 21.5

$$LiCl(l) \rightarrow Li(l) + 12Cl2(g)$$

In practice, $CaCl_2$ is mixed with LiCl to lower the melting point of the lithium salt. The electrolysis is carried out in an argon atmosphere rather than the nitrogen atmosphere typically used for substances that are highly reactive with O_2 and water because Li reacts with nitrogen gas to form lithium nitride (Li_3N). Metallic sodium is produced by the electrolysis of a molten mixture of NaCl and $CaCl_2$. In contrast, potassium is produced commercially from the reduction of KCl by Na, followed by the fractional distillation of K(g). Although rubidium and cesium can also be produced by electrolysis, they are usually obtained by reacting their hydroxide salts with a reductant such as Mg:

Equation 21.6

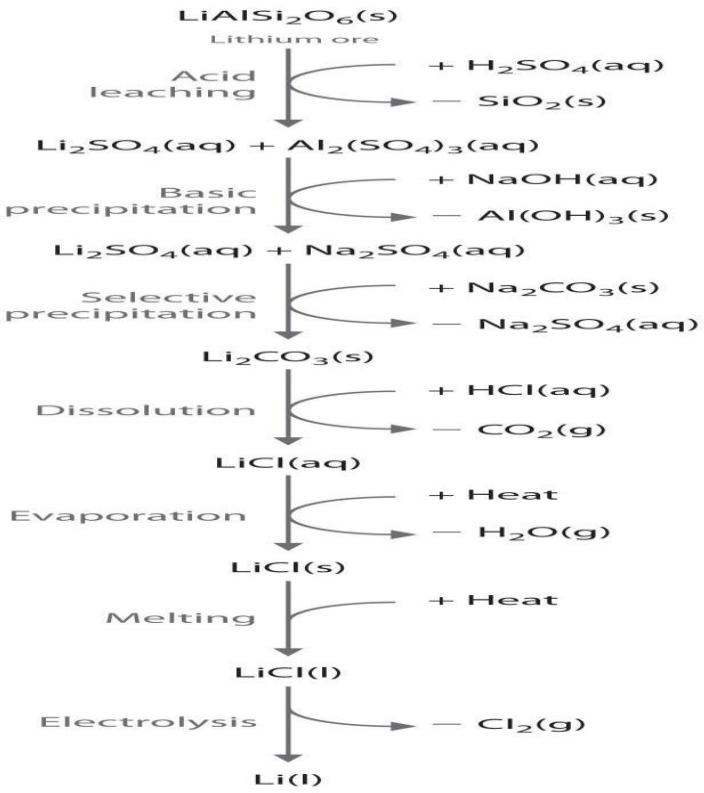
$$2RbOH(s) + Mg(s) \rightarrow 2Rb(l) + Mg(OH)_2(s)$$

Massive deposits of essentially pure NaCl and KCl are found in nature and are the major sources of sodium and potassium. The other alkali metals are found in low concentrations in a wide variety of minerals, but ores that contain high concentrations of these elements are relatively rare. No concentrated sources of rubidium are known, for example, even though it is the 16th most abundant element on Earth. Rubidium is obtained commercially by isolating the 2%–4% of Rb present as an impurity in micas, minerals that are composed of sheets of complex hydrated potassium–aluminum silicates.

Alkali metals are recovered from silicate ores in a multistep process that takes advantage of the pH-dependent solubility of selected salts of each metal ion. The steps in this process are *leaching*, which uses

sulfuric acid to dissolve the desired alkali metal ion and Al^{3+} from the ore; *basic precipitation* to remove Al^{3+} from the mixture as $Al(OH)_3$; *selective precipitation* of the insoluble alkali metal carbonate; *dissolution* of the salt again in hydrochloric acid; and isolation of the metal by *evaporation* and*electrolysis*. Figure 21.7 "Isolating Lithium from Spodumene, a Lithium Silicate Ore"illustrates the isolation of liquid lithium from a lithium silicate ore by this process.

Figure 21.7 *Isolating Lithium from Spodumene, a Lithium Silicate Ore*



The key steps are acid leaching, basic precipitation of aluminum hydroxide, selective precipitation of insoluble lithium carbonate, conversion to lithium chloride, evaporation, and electrolysis. The other alkali metals and the alkaline earth metals are recovered from their ores by similar processes.

General Properties of the Alkali Metals

Various properties of the group 1 elements are summarized in Table 21.3 "Selected Properties of the Group 1 Elements". In keeping with overall periodic trends, the atomic and ionic radii increase smoothly from Li to Cs, and the first ionization energies decrease as the atoms become larger. As a result of their low first ionization energies, the alkali metals have an overwhelming tendency to form ionic compounds

where they have a +1 charge. All the alkali metals have relatively high electron affinities because the addition of an electron produces an anion (M^-) with an ns^2 electron configuration. The densities of the elements generally increase from Li to Cs, reflecting another common trend: because the atomic masses of the elements increase more rapidly than the atomic volumes as you go down a group, the densest elements are near the bottom of the periodic table. An unusual trend in the group 1 elements is the smooth decrease in the melting and boiling points from Li to Cs. As a result, Cs (melting point = 28.5°C) is one of only three metals (the others are Ga and Hg) that are liquids at body temperature (37°C).

Table 21.3 Selected Properties of the Group 1 Elements

	Lithium	Sodium	Potassium	Rubidium	Cesium	Francium
atomic symbol	Li	Na	K	Rb	Cs	Fr
atomic number	3	11	19	37	55	87
atomic mass	6.94	22.99	39.10	85.47	132.91	223
valence electron configuration	$2s^1$	$3s^1$	$4s^1$	$5s^1$	$6s^1$	$7s^1$
melting point/boiling point (°C)	180.5/1342	97.8/883	63.5/759	39.3/688	28.5/671	27/—
density (g/cm^3) at 25°C	0.534	0.97	0.89	1.53	1.93	—
atomic radius (pm)	167	190	243	265	298	—
first ionization energy (kJ/mol)	520	496	419	403	376	393
most common oxidation state	+1	+1	+1	+1	+1	+1
ionic radius (pm)*	76	102	138	152	167	—
electron affinity (kJ/mol)	−60	−53	−48	−47	−46	—
electronegativity	1.0	0.9	0.8	0.8	0.8	0.7
standard electrode potential ($E°$, V)	−3.04	−2.71	−2.93	−2.98	−3.03	—
product of reaction with O_2	Li_2O	Na_2O_2	KO_2	RbO_2	CsO_2	—
type of oxide	basic	basic	basic	basic	basic	—
product of reaction with N_2	Li_3N	none	none	none	none	—
product of reaction with X_2	LiX	NaX	KX	RbX	CsX	—

	Lithium	Sodium	Potassium	Rubidium	Cesium	Francium
product of reaction with H_2	LiH	NaH	KH	RbH	CsH	—
***The values cited are for four-coordinate ions except for Rb^+ and Cs^+, whose values are given for the six-coordinate ion.**						

The standard reduction potentials ($E°$) of the alkali metals do not follow the trend based on ionization energies. (For more information on reduction potentials, see Chapter 19 "Electrochemistry"). Unexpectedly, lithium is the strongest reductant, and sodium is the weakest (Table 21.3 "Selected Properties of the Group 1 Elements"). Because Li^+ is much smaller than the other alkali metal cations, its hydration energy is the highest. The high hydration energy of Li^+ more than compensates for its higher ionization energy, making lithium metal the strongest reductant in aqueous solution. This apparent anomaly is an example of how the physical or the chemical behaviors of the elements in a group are often determined by the subtle interplay of opposing periodic trends.

Reactions and Compounds of the Alkali Metals

All alkali metals are electropositive elements with an ns^1 valence electron configuration, forming the monocation (M^+) by losing the single valence electron. Because removing a second electron would require breaking into the (n − 1) closed shell, which is energetically prohibitive, the chemistry of the alkali metals is largely that of ionic compounds that contain M^+ ions. However, as we discuss later, the lighter group 1 elements also form a series of organometallic compounds that contain polar covalent M–C bonds.

All the alkali metals react vigorously with the halogens (group 17) to form the corresponding ionic halides, where X is a halogen:

Equation 21.7

$$2M(s) + X_2(s, l, g) \rightarrow 2M^+X^-(s)$$

Similarly, the alkali metals react with the heavier chalcogens (sulfur, selenium, and tellurium in group 16) to produce metal chalcogenides, where Y is S, Se, or Te:

Equation 21.8

$$2M(s) + Y(s) \rightarrow M_2Y(s)$$

When excess chalcogen is used, however, a variety of products can be obtained that contain chains of chalcogen atoms, such as the sodium polysulfides (Na_2S_n, where n = 2–6). For example, Na_2S_3 contains the S_3^{2-} ion, which is V shaped with an S–S–S angle of about 103°. The one-electron oxidation product of the trisulfide ion (S_3^-) is responsible for the intense blue color of the gemstones lapis lazuli and blue

ultramarine (Figure 21.8 "The Trisulfide Anion Is Responsible for the Deep Blue Color of Some Gemstones").

Figure 21.8 *The Trisulfide Anion Is Responsible for the Deep Blue Color of Some Gemstones*

(a) The rich blue color of lapis lazuli is due to small amounts of the normally unstable S_3^- anion. (b) The aluminosilicate cages of the minerals (zeolites) that make up the matrix of blue ultramarine stabilize the reactive anion; excess Na^+ ions in the structure balance the negative charges on the zeolite framework and the S_3^- anion.

Reacting the alkali metals with oxygen, the lightest element in group 16, is more complex, and the stoichiometry of the product depends on both the metal:oxygen ratio and the size of the metal atom. For instance, when alkali metals burn in air, the observed products are Li_2O (white), Na_2O_2 (pale yellow), KO_2 (orange), RbO_2(brown), and CsO_2 (orange). Only Li_2O has the stoichiometry expected for a substance that contains two M^+ cations and one O^{2-} ion. In contrast, Na_2O_2 contains the O_2^{2-}(peroxide) anion plus two Na^+ cations. The other three salts, with stoichiometry MO_2, contain the M^+ cation and the O_2^- (superoxide) ion. Because O^{2-} is the smallest of the three oxygen anions, it forms a stable ionic lattice with the smallest alkali metal cation (Li^+). In contrast, the larger alkali metals—potassium, rubidium, and cesium—react with oxygen in air to give the metal superoxides. Because the Na^+ cation is intermediate in size, sodium reacts with oxygen to form a compound with an intermediate stoichiometry: sodium peroxide. Under specific reaction conditions, however, it is possible to prepare the oxide, peroxide, and superoxide salts of all five alkali metals, except for lithium superoxide (LiO_2).

Note the Pattern

The chemistry of the alkali metals is largely that of ionic compounds containing the M^+ ions.

The alkali metal peroxides and superoxides are potent oxidants that react, often vigorously, with a wide variety of reducing agents, such as charcoal or aluminum metal. For example, Na_2O_2 is used industrially for bleaching paper, wood pulp, and fabrics such as linen and cotton. In submarines, Na_2O_2 and KO_2 are used to purify and regenerate the air by removing the CO_2 produced by respiration and replacing it with O_2. Both compounds react with CO_2 in a redox reaction in which O_2^{2-} or O_2^- is simultaneously oxidized and reduced, producing the metal carbonate and O_2:

Equation 21.9

$$2Na_2O_2(s) + 2CO_2(g) \rightarrow 2Na_2CO_3(s) + O_2(g)$$

Equation 21.10

$4KO_2(s) + 2CO_2(g) \rightarrow 2K_2CO_3(s) + 3O_2(g)$

The presence of water vapor, the other product of respiration, makes KO_2 even more effective at removing CO_2 because potassium bicarbonate, rather than potassium carbonate, is formed:

Equation 21.11

$4KO_2(s) + 4CO_2(g) + 2H_2O(g) \rightarrow 4KHCO_3(s) + 3O_2(g)$

Notice that 4 mol of CO_2 are removed in this reaction, rather than 2 mol in Equation 21.10.

Lithium, the lightest alkali metal, is the only one that reacts with atmospheric nitrogen, forming lithium nitride (Li_3N). Lattice energies again explain why the larger alkali metals such as potassium do not form nitrides: packing three large K^+ cations around a single relatively small anion is energetically unfavorable. In contrast, all the alkali metals react with the larger group 15 elements phosphorus and arsenic to form metal phosphides and arsenides (where Z is P or As):

Equation 21.12

$12M(s) + Z_4(s) \rightarrow 4M_3Z(s)$

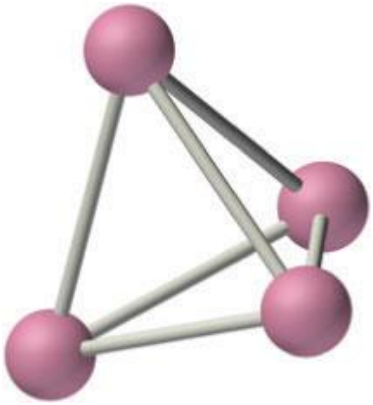
Note the Pattern

Because of lattice energies, only lithium forms a stable oxide and nitride.

The alkali metals react with all group 14 elements, but the compositions and properties of the products vary significantly. For example, reaction with the heavier group 14 elements gives materials that contain polyatomic anions and three-dimensional cage structures, such as K_4Si_4 whose structure is shown here. In contrast, lithium and sodium are oxidized by carbon to produce a compound with the stoichiometry M_2C_2(where M is Li or Na):

Equation 21.13

$2M(s) + 2C(s) \rightarrow M_2C_2(s)$



The three-dimensional cage structure of the Si_4^{4-} ion in the ionic compound K_4S_4. *The Si_4^{4-} ion is isoelectronic and isostructural with the P_4 molecule.*

The same compounds can be obtained by reacting the metal with acetylene (C_2H_2). In this reaction, the metal is again oxidized, and hydrogen is reduced:

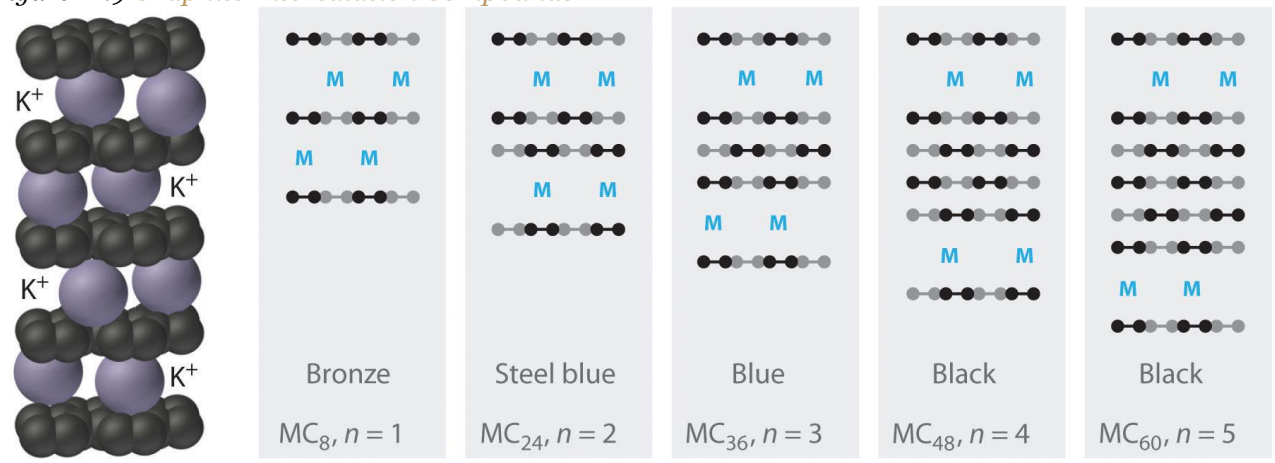
Equation 21.14

$$2M(s) + C_2H_2(g) \rightarrow M_2C_2(s) + H_2(g)$$

The acetylide ion (C_2^{2-}), formally derived from acetylene by the loss of both hydrogens as protons, is a very strong base. Reacting acetylide salts with water produces acetylene and MOH(aq).

The heavier alkali metals (K, Rb, and Cs) also react with carbon in the form of graphite. Instead of disrupting the hexagonal sheets of carbon atoms, however, the metals insert themselves *between* the sheets of carbon atoms to give new substances calledgraphite intercalation compounds (part (a) inFigure 21.9 "Graphite Intercalation Compounds"). The stoichiometries of these compounds include MC_{60} and MC_{48}, which are black/gray; MC_{36} and MC_{24}, which are blue; and MC_8, which is bronze (part (b) in Figure 21.9 "Graphite Intercalation Compounds"). The remarkably high electrical conductivity of these compounds (about 200 times greater than graphite) is attributed to a net transfer of the valence electron of the alkali metal to the graphite layers to produce, for example, $K^+C_8^-$.

Figure 21.9 Graphite Intercalation Compounds



(a) KC_8 **(b) Layer arrangements and stoichiometries**

Reacting graphite with alkali metals such as K, Rb, and Cs results in partial reduction of the graphite and insertion of layers of alkali metal cations between sets of n layers of carbon atoms. (a) In KC_8, layers of K^+ ions are inserted between every pair of carbon layers, giving n = 1. (b) The

stoichiometry and color of intercalation compounds depend on the number of layers of carbon atoms (n) between each layer of intercalated metal atoms. This schematic diagram illustrates the most common structures that have been observed.

All the alkali metals react directly with gaseous hydrogen at elevated temperatures to produce ionic hydrides (M^+H^-):

Equation 21.15

$$2M(s) + H_2(g) \rightarrow 2MH(s)$$

All are also capable of reducing water to produce hydrogen gas:

Equation 21.16

$$M(s) + H2O(l) \rightarrow 12H2(g) + MOH(aq)$$

Although lithium reacts rather slowly with water, sodium reacts quite vigorously (Figure 21.10 "Reacting Sodium with Water"), and the heavier alkali metals (K, Rb, and Cs) react so vigorously that they invariably explode. This trend, which is not consistent with the relative magnitudes of the reduction potentials of the elements, serves as another example of the complex interplay of different forces and phenomena—in this case, kinetics and thermodynamics. Although the driving force for the reaction is greatest for lithium, the heavier metals have lower melting points. The heat liberated by the reaction causes them to melt, and the larger surface area of the liquid metal in contact with water greatly accelerates the reaction rate.

Figure 21.10 *Reacting Sodium with Water*

Alkali metal cations are found in a wide variety of ionic compounds. In general, any alkali metal salt can be prepared by reacting the alkali metal hydroxide with an acid and then evaporating the water:

Equation 21.17

$$2MOH(aq) + H_2SO_4(aq) \rightarrow M_2SO_4(aq) + 2H_2O(l)$$

Equation 21.18

$$MOH(aq) + HNO_3(aq) \rightarrow MNO_3(aq) + H_2O(l)$$

Hydroxides of alkali metals also can react with organic compounds that contain an acidic hydrogen to produce a salt. An example is the preparation of sodium acetate (CH_3CO_2Na) by reacting sodium hydroxide and acetic acid:

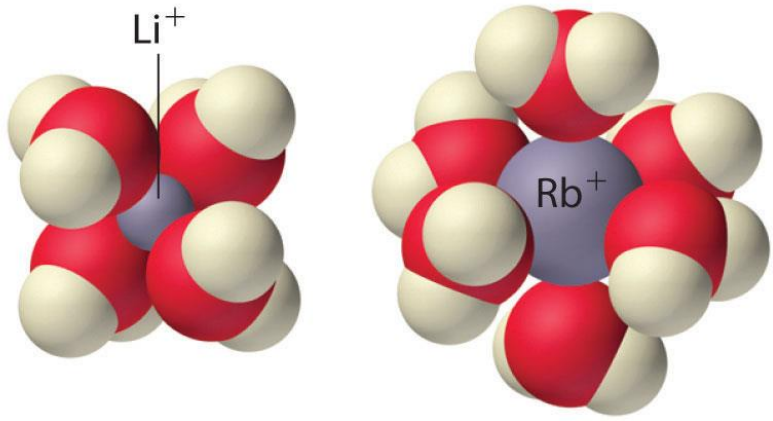
Equation 21.19

$$CH_3CO_2H(aq) + NaOH(s) \rightarrow CH_3CO_2Na(aq) + H_2O(l)$$

Soap is a mixture of the sodium and potassium salts of naturally occurring carboxylic acids, such as palmitic acid [$CH_3(CH_2)_{14}CO_2H$] and stearic acid [$CH_3(CH_2)_{16}CO_2H$]. Lithium salts, such as lithium stearate [$CH_3(CH_2)_{14}CO_2Li$], are used as additives in motor oils and greases.

Complexes of the Alkali Metals

Because of their low positive charge (+1) and relatively large ionic radii, alkali metal cations have only a weak tendency to react with simple Lewis bases to form metal complexes like those discussed in Chapter 17 "Solubility and Complexation Equilibriums". Complex formation is most significant for the smallest cation (Li^+) and decreases with increasing radius. In aqueous solution, for example, Li^+ forms the tetrahedral $[Li(H_2O)_4]^+$ complex. In contrast, the larger alkali metal cations form octahedral $[M(H_2O)_6]^+$ complexes. Complex formation is primarily due to the electrostatic interaction of the metal cation with polar water molecules. Because of their high affinity for water, anhydrous salts that contain Li^+ and Na^+ ions (such as Na_2SO_4) are often used as *drying agents*. These compounds absorb trace amounts of water from nonaqueous solutions to form hydrated salts, which are then easily removed from the solution by filtration.



The tetrahedral $[Li(H_2O)_4]^+$ and octahedral $[Rb(H_2O)6]^+$ complexes. *The Li^+ ion is so small that it can accommodate only four water molecules around it, but the larger alkali metal cations tend to bind six water molecules.*

Note the Pattern

Because of their low positive charge (+1) and relatively large ionic radii, alkali metal cations have only a weak tendency to form complexes with simple Lewis bases.

Electrostatic interactions also allow alkali metal ions to form complexes with certain cyclic polyethers and related compounds, such as crown ethers and cryptands. As discussed in Chapter 13

"Solutions", crown ethers are cyclic polyethers that contain four or more oxygen atoms separated by two or three carbon atoms. All crown ethers have a central cavity that can accommodate a metal ion coordinated to the ring of oxygen atoms, and crown ethers with rings of different sizes prefer to bind metal ions that fit into the cavity. For example, 14-crown-4, with the smallest cavity that can accommodate a metal ion, has the highest affinity for Li^+, whereas 18-crown-6 forms the strongest complexes with K^+ (part (a) in Figure 13.7 "Crown Ethers and Cryptands").

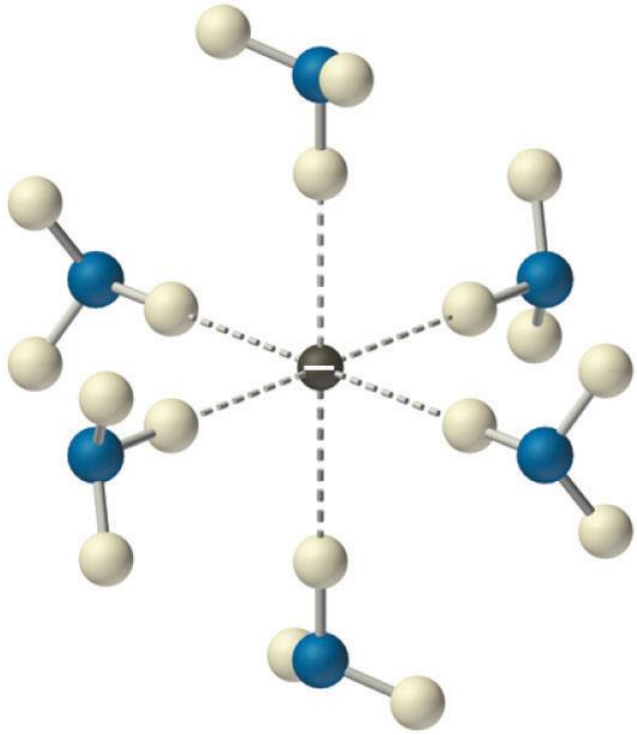
Cryptands are more nearly spherical analogues of crown ethers and are even more powerful and selective complexing agents. Cryptands consist of three chains containing oxygen that are connected by two nitrogen atoms (part (b) in Figure 13.7 "Crown Ethers and Cryptands"). They can completely surround (encapsulate) a metal ion of the appropriate size, coordinating to the metal by a lone pair of electrons on each O atom and the two N atoms. Like crown ethers, cryptands with different cavity sizes are highly selective for metal ions of particular sizes. Crown ethers and cryptands are often used to dissolve simple inorganic salts such as $KMnO_4$ in nonpolar organic solvents (Figure 13.8 "Effect of a Crown Ether on the Solubility of KMnO").

Liquid Ammonia Solutions

A remarkable feature of the alkali metals is their ability to dissolve reversibly in liquid ammonia. Just as in their reactions with water, reacting alkali metals with liquid ammonia eventually produces hydrogen gas and the metal salt of the conjugate base of the solvent—in this case, the *amide* ion (NH_2^-) rather than hydroxide:

Equation 21.20

$$follows: K(s) + CH3OH(l) \rightarrow 12H2(g) + CH3OK(soln).$$



Solvated electrons. *The presence of solvated electrons (e^-, NH_3) in solutions of alkali metals in liquid ammonia is indicated by the intense color of the solution and its electrical conductivity.*

where the (am) designation refers to an ammonia solution, analogous to (aq) used to indicate aqueous solutions. Without a catalyst, the reaction in Equation 21.20 tends to be rather slow. In many cases, the alkali metal amide salt (MNH_2) is not very soluble in liquid ammonia and precipitates, but when dissolved, very concentrated solutions of the alkali metal are produced. One mole of Cs metal, for example, will dissolve in as little as 53 mL (40 g) of liquid ammonia. The pure metal is easily recovered when the ammonia evaporates.

Solutions of alkali metals in liquid ammonia are intensely colored and good conductors of electricity due to the presence of *solvated electrons* (e^-, NH_3), which are not attached to single atoms. A solvated electron is loosely associated with a cavity in the ammonia solvent that is stabilized by hydrogen bonds. Alkali metal–liquid ammonia solutions of about 3 M or less are deep blue (Figure 21.11 "Alkali Metal–Liquid Ammonia Solutions") and conduct electricity about 10 times better than an aqueous NaCl solution because of the high mobility of the solvated electrons. As the concentration of the metal increases above 3 M, the color changes to metallic bronze or gold, and the conductivity increases to a value comparable with that of the pure liquid metals.

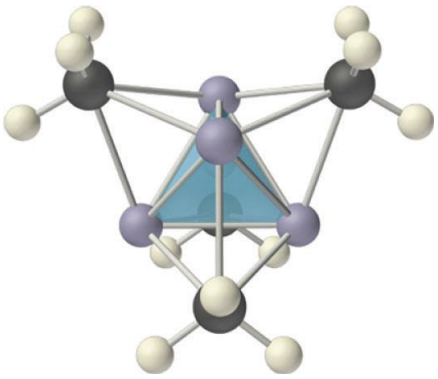
Figure 21.11 *Alkali Metal–Liquid Ammonia Solutions*

In addition to solvated electrons, solutions of alkali metals in liquid ammonia contain the metal cation (M^+), the neutral metal atom (M), metal dimers (M_2), and the metal anion (M^-). The anion is formed by adding an electron to the singly occupied *ns* valence orbital of the metal atom. Even in the absence of a catalyst, these solutions are not very stable and eventually decompose to the thermodynamically favored products: $M^+NH_2^-$ and hydrogen gas (Equation 21.20). Nonetheless, the solvated electron is a potent reductant that is often used in synthetic chemistry.

Organometallic Compounds of the Group 1 Elements

Compounds that contain a metal covalently bonded to a carbon atom of an organic species are calledorganometallic compounds. The properties and reactivities of organometallic compounds differ greatly from those of either the metallic or organic components. Because of its small size, lithium, for example, forms an extensive series of covalent organolithium compounds, such as methyllithium ($LiCH_3$), which are by far the most stable and best-known group 1 organometallic compounds. These volatile, low-melting-point solids or liquids can be sublimed or distilled at relatively low temperatures and are soluble in nonpolar solvents. Like organic compounds, the molten solids do not conduct electricity to any significant degree. Organolithium compounds have a tendency to form oligomers with the formula $(RLi)_n$, where R represents the organic component. For example, in both the solid state and solution, methyllithium exists as a tetramer with the structure shown in Figure 21.12 "The Tetrameric Structure of Methyllithium", where each triangular face of the Li_4 tetrahedron is bridged by the carbon atom of a methyl group. Effectively, the carbon atom of each CH_3 group is using a single pair of electrons in an sp^3 hybrid lobe to bridge *three* lithium atoms, making this an example of two-electron,*four-center* bonding. Clearly, such a structure, in which each carbon atom is apparently bonded to *six* other atoms, cannot be explained using any of the electron-pair bonding schemes discussed in Chapter 8 "Ionic versus Covalent Bonding" andChapter 9 "Molecular Geometry and Covalent Bonding Models". Molecular orbital theory can explain the bonding in methyllithium, but the description is beyond the scope of this text.

Figure 21.12 *The Tetrameric Structure of Methyllithium*



Methyllithium is not an ionic compound; it exists as tetrameric $(CH_3Li)_4$ molecules. The structure consists of a tetrahedral arrangement of four lithium atoms, with the carbon atom of a methyl group located above the middle of each triangular face of the tetrahedron. The carbon atoms thus bridge three lithium atoms to form four-center, two-electron bonds.

Note the Pattern

The properties and reactivities of organometallic compounds differ greatly from those of either the metallic or organic components.

Organosodium and organopotassium compounds are more ionic than organolithium compounds. They contain discrete M^+ and R^- ions and are insoluble or only sparingly soluble in nonpolar solvents.

Uses of the Alkali Metals

Because sodium remains liquid over a wide temperature range (97.8–883°C), it is used as a coolant in specialized high-temperature applications, such as nuclear reactors and the exhaust valves in high-performance sports car engines. Cesium, because of its low ionization energy, is used in photosensors in automatic doors, toilets, burglar alarms, and other electronic devices. In these devices, cesium is ionized by a beam of visible light, thereby producing a small electric current; blocking the light interrupts the electric current and triggers a response.

Compounds of sodium and potassium are produced on a huge scale in industry. Each year, the top 50 industrial compounds include NaOH, used in a wide variety of industrial processes; Na_2CO_3, used in the manufacture of glass; K_2O, used in porcelain glazes; and Na_4SiO_4, used in detergents.

Several other alkali metal compounds are also important. For example, Li_2CO_3 is one of the most effective treatments available for manic depression or bipolar disorder. It appears to modulate or dampen the effect on the brain of changes in the level of neurotransmitters, which are biochemical substances

responsible for transmitting nerve impulses between neurons. Consequently, patients who take "lithium" do not exhibit the extreme mood swings that characterize this disorder.

EXAMPLE 2

For each application, choose the more appropriate substance based on the properties and reactivities of the alkali metals and their compounds. Explain your choice in each case.

a. For a reaction that requires a strong base in a solution of tetrahydrofuran (THF), would you use LiOH or CsOH?

b. To extinguish a fire caused by burning lithium metal, would you use water, CO_2, N_2 gas, or sand (SiO_2)?

c. Both $LiNO_3$ and $CsNO_3$ are highly soluble in acetone (2-propanone). Which of these alkali metal salts would you use to precipitate I^- from an acetone solution?

Given: application and selected alkali metals

Asked for: appropriate metal for each application

Strategy:

Use the properties and reactivities discussed in this section to determine which alkali metal is most suitable for the indicated application.

Solution:

a. Both LiOH and CsOH are ionic compounds that contain the hydroxide anion. Li^+, however, is much smaller than Cs^+, so the Li^+ cation will be more effectively solvated by the oxygen of THF with its lone pairs of electrons. This difference will have two effects: (1) LiOH is likely to be much more soluble than CsOH in the nonpolar solvent, which could be a significant advantage, and (2) the solvated Li^+ions are less likely to form tight ion pairs with the OH^- ions in the relatively nonpolar solution, making the OH^- more basic and thus more reactive. Thus LiOH is the better choice.

b. Lithium is a potent reductant that reacts with water to form LiOH and H_2 gas, so adding a source of hydrogen such as water to a lithium fire is likely to produce an explosion. Lithium also reacts with oxygen and nitrogen in the air to form Li_2O and Li_3N, respectively, so we would not expect nitrogen to extinguish a lithium fire. Because CO_2 is a gaseous molecule that contains carbon in its highest accessible oxidation state (+4),

adding CO_2 to a strong reductant such as Li should result in a vigorous redox reaction. Thus water, N_2, and CO_2 are all unsuitable choices for extinguishing a lithium fire. In contrast, sand is primarily SiO_2, which is a network solid that is not readily reduced. Smothering a lithium fire with sand is therefore the best choice.

c. The salt with the smaller cation has the higher lattice energy, and high lattice energies tend to decrease the solubility of a salt. (For more information on lattice energies, see Chapter 8 "Ionic versus Covalent Bonding".) However, the solvation energy of the cation is also important in determining solubility, and small cations tend to have higher solvation energies. Recall from Chapter 13 "Solutions" that high solvation energies tend to increase the solubility of ionic substances. Thus CsI should be the least soluble of the alkali metal iodides, and LiI the most soluble. Consequently, $CsNO_3$ is the better choice.

Exercise

Indicate which of the alternative alkali metals or their compounds given is more appropriate for each application.

a. drying agent for an organic solvent—Li_2SO_4 or Rb_2SO_4

b. removing trace amounts of N_2 from highly purified Ar gas—Li, K, or Cs

c. reacting with an alkyl halide (formula RX) to prepare an organometallic compound (formula MR)—Li or K

Answer:

a. Li_2SO_4

b. Li

c. Li

EXAMPLE 3

Predict the products of each reaction and then balance each chemical equation.

a. $Na(s) + O_2(g) \rightarrow$

a. $Li_2O(s) + H_2O(l) \rightarrow$

b. $K(s) + CH_3OH(l) \rightarrow$

c. $Li(s) + CH_3Cl(l) \rightarrow$

d. $Li_3N(s) + KCl(s) \rightarrow$

Given: reactants

Asked for: products and balanced chemical equation

Strategy:

A Determine whether one of the reactants is an oxidant or a reductant or a strong acid or a strong base. If so, a redox reaction or an acid–base reaction is likely to occur. Identify the products of the reaction.

B If a reaction is predicted to occur, balance the chemical equation.

Solution:

a. **A** Sodium is a reductant, and oxygen is an oxidant, so a redox reaction is most likely. We expect an electron to be transferred from Na (thus forming Na^+) to O_2. We now need to determine whether the reduced product is a superoxide (O_2^-), peroxide (O_2^{2-}), or oxide (O^{2-}). Under normal reaction conditions, the product of the reaction of an alkali metal with oxygen depends on the identity of the metal. Because of differences in lattice energy, Li produces the oxide (Li_2O), the heavier metals (K, Rb, Cs) produce the superoxide (MO_2), and Na produces the peroxide (Na_2O_2).

B The balanced chemical equation is $2Na(s) + O_2(g) \rightarrow Na_2O_2(s)$.

a. **A** Li_2O is an ionic salt that contains the oxide ion (O^{2-}), which is the completely deprotonated form of water and thus is expected to be a strong base. The other reactant, water, is both a weak acid and a weak base, so we can predict that an acid–base reaction will occur.

b **B** The balanced chemical equation is $Li_2O(s) + H_2O(l) \rightarrow 2LiOH(aq)$.

c. **A** Potassium is a reductant, whereas methanol is both a weak acid and a weak base (similar to water). A weak acid produces H^+, which can act as an oxidant by
$accepting\ an\ electron\ to\ form\ 12H2.$
$This\ reaction,\ therefore,\ is\ an\ acid\ dissociation\ that$

d. is driven to completion by a reduction of the protons as they are released.

B The balanced chemical equation is as
$follows: K(s) + CH3OH(l) \rightarrow 12H2(g) + CH3OK(soln).$

e. **A** One of the reactants is an alkali metal, a potent reductant, and the other is an alkyl halide. Any compound that contains a carbon–halogen bond can, in principle, be reduced, releasing a halide ion and forming an organometallic compound. That outcome seems likely in this case because organolithium compounds are among the most stable organometallic compounds known.

B Two moles of lithium are required to balance the equation: $2Li(s) + CH_3Cl(l) \rightarrow LiCl(s) + CH_3Li(soln)$.

e. A Lithium nitride and potassium chloride are largely ionic compounds. The nitride ion (N^{3-}) is a very strong base because it is the fully deprotonated form of ammonia, a weak acid. An acid–base reaction requires an acid as well as a base, however, and KCl is not acidic. What about a redox reaction? Both substances contain ions that have closed-shell valence electron configurations. The nitride ion could act as a reductant by donating electrons to an oxidant and forming N_2. KCl is not an oxidant, however, and a redox reaction requires an oxidant as well as a reductant.

B We conclude that the two substances will not react with each other.

Exercise

Predict the products of each reaction and balance each chemical equation.

a. $K(s) + N_2(g) \rightarrow$

b. $Li_3N(s) + H_2O(l) \rightarrow$

c. $Na(s) + (CH_3)_2NH(soln) \rightarrow$

d. $C_6H_5Li(soln) + D_2O(l) \rightarrow C_6H_5D(l) + LiOD(soln)$

e. $CH_3CH_2Cl(soln) + 2Li \rightarrow$

Answer:

a. no reaction

b. $Li_3N(s) + 3H_2O(l) \rightarrow NH_3(aq) + 3LiOH(aq)$

c. $Na(s) + (CH3)2NH(soln) \rightarrow 12H2(g) + Na[(CH3)2N](soln)$

d. $C_6H_5Li(soln) + D_2O(l) \rightarrow C_6H_5D(l) + LiOD(soln)$

e. $CH_3CH_2Cl(soln) + 2Li \rightarrow CH_3CH_2Li(soln) + LiCl(soln)$

Summary

The first alkali metals to be isolated (Na and K) were obtained by passing an electric current through molten potassium and sodium carbonates. The alkali metals are among the most potent reductants known; most can be isolated by electrolysis of their molten salts or, in the case of rubidium and cesium, by reacting their hydroxide salts with a reductant. They can also be recovered from their silicate ores using a multistep process. Lithium, the strongest reductant, and sodium, the weakest, are examples of the physical and chemical effects of opposing periodic trends. The alkali metals react with halogens (group 17)

to form ionic halides; the heavier chalcogens (group 16) to produce metal chalcogenides; and oxygen to form compounds, whose stoichiometry depends on the size of the metal atom. The peroxides and superoxides are potent oxidants. The only alkali metal to react with atmospheric nitrogen is lithium. Heavier alkali metals react with graphite to form **graphite intercalation compounds**, substances in which metal atoms are inserted between the sheets of carbon atoms. With heavier group 14 elements, alkali metals react to give polyatomic anions with three-dimensional cage structures. All alkali metals react with hydrogen at high temperatures to produce the corresponding hydrides, and all reduce water to produce hydrogen gas. Alkali metal salts are prepared by reacting a metal hydroxide with an acid, followed by evaporation of the water. Both Li and Na salts are used as *drying agents*, compounds that are used to absorb water. Complexing agents such as**crown ethers** and **cryptands** can accommodate alkali metal ions of the appropriate size. Alkali metals can also react with liquid ammonia to form solutions that slowly decompose to give hydrogen gas and the metal salt of the*amide* ion (NH_2^-). These solutions, which contain unstable solvated electrons loosely associated with a cavity in the solvent, are intensely colored, good conductors of electricity, and excellent reductants. Alkali metals can react with organic compounds that contain an acidic proton to produce salts. They can also form **organometallic compounds**, which have properties that differ from those of their metallic and organic components.

KEY TAKEAWAYS

- The alkali metals are potent reductants whose chemistry is largely that of ionic compounds containing the M^+ ion.
- Alkali metals have only a weak tendency to form complexes with simple Lewis bases.

CONCEPTUAL PROBLEMS

1. Which of the group 1 elements reacts least readily with oxygen? Which is most likely to form a hydrated, crystalline salt? Explain your answers.
2. The alkali metals have a significant electron affinity, corresponding to the addition of an electron to give the M^- anion. Why, then, do they commonly lose the ns^1 electron to form the M^+ cation rather than gaining an electron to form M^-?
3. Lithium is a far stronger reductant than sodium; cesium is almost as strong as lithium, which does not agree with the expected periodic trend. What two opposing properties explain this apparent anomaly? Is the same anomaly found among the alkaline earth metals?

4. Explain why the ionic character of LiCl is less than that of NaCl. Based on periodic trends, would you expect the ionic character of $BeCl_2$ to be greater or less than that of LiCl? Why?
5. Alkali metals and carbon form intercalation compounds with extremely high electrical conductivity. Is this conductivity through the layers or along the layers? Explain your answer.
6. Electrolysis is often used to isolate the lighter alkali metals from their molten halides. Why are halides used rather than the oxides or carbonates, which are easier to isolate? With this in mind, what is the purpose of adding calcium chloride to the alkali metal halide?
7. The only alkali metal that reacts with oxygen to give a compound with the expected stoichiometry is lithium, which gives Li_2O. In contrast, sodium reacts with oxygen to give Na_2O_2, and the heavier alkali metals form superoxides. Explain the difference in the stoichiometries of these products.
8. Classify aqueous solutions of Li_2O, Na_2O, and CsO_2 as acidic, basic, or amphoteric.
9. Although methanol is relatively unreactive, it can be converted to a synthetically more useful form by reaction with LiH. Predict the products of reacting methanol with LiH. Describe the visual changes you would expect to see during this reaction.
10. Lithium reacts with atmospheric nitrogen to form lithium nitride (Li_3N). Why do the other alkali metals not form analogous nitrides? Explain why all the alkali metals react with arsenic to form the corresponding arsenides (M_3As).

STRUCTURE AND REACTIVITY

1. Write a balanced chemical equation to describe each reaction.

a. the electrolysis of fused (melted) sodium chloride

b. the thermal decomposition of $KClO_3$

c. the preparation of hydrogen fluoride from calcium fluoride and sulfuric acid

d. the oxidation of sodium metal by oxygen

2. What products are formed at the anode and the cathode during electrolysis of

a. molten lithium hydride?

b. molten lithium chloride?

c. aqueous sodium fluoride?

Write the corresponding half-reactions for each reaction.

3. Sodium metal is prepared by electrolysis of molten NaCl. If 25.0 g of chlorine gas are produced in the electrolysis of the molten salt using 9.6 A (C/s) of current, how many hours were required for the reaction? What mass of sodium was produced?
4. Sodium peroxide can remove CO_2 from the air and replace it with oxygen according to the following unbalanced chemical equation:

$Na_2O_2(s) + CO_2(g) \rightarrow Na_2CO_3(s) + O_2(g)$

a. Balance the chemical equation.
b. Identify each oxidation and reduction half-reaction.
c. Assuming complete reaction, what will be the pressure inside a sealed 1.50 L container after reacting excess sodium peroxide with carbon dioxide that was initially at 0.133 atm and 37°C?

5. Predict the products of each chemical reaction and then balance each chemical equation.

a. $K(s) + CH_3CH_2OH(l) \rightarrow$
b. $Na(s) + CH_3CO_2H(l) \rightarrow$
c. $NH_4Cl(s) + Li(s) \rightarrow$
d. $(CH_3)_2NH(l) + K(s) \rightarrow$

6. Predict the products of each reaction.

a. an alkyl chloride with lithium metal
b. rubidium with oxygen

7. A 655 mg sample of graphite was allowed to react with potassium metal, and 744 mg of product was isolated. What is the stoichiometry of the product?
8. Perchloric acid, which is used as a reagent in a number of chemical reactions, is typically neutralized before disposal. When a novice chemist accidentally used K_2CO_3 to neutralize perchloric acid, a large mass of $KClO_4$ ($K_{sp} = 1.05 \times 10^{-2}$) precipitated from solution. What mass of potassium ion is present in 1.00 L of a saturated solution of $KClO_4$?
9. A key step in the isolation of the alkali metals from their ores is selective precipitation. For example, lithium is separated from sodium and potassium by precipitation of Li_2CO_3($K_{sp} = 8.15 \times 10^{-4}$). If 500.0 mL of a 0.275 M solution of Na_2CO_3 are added to 500.0 mL of a 0.536 M lithium hydroxide solution, what mass of Li_2CO_3 will precipitate (assuming no further reactions occur)? What mass of lithium will remain in solution?

ANSWER

9. 5.54 g Li_2CO_3; 0.82 g Li^+

21.4 The Alkaline Earth Metals (Group 2)

LEARNING OBJECTIVES

1. To describe how to isolate the alkaline earth metals.
2. To be familiar with the reactions, compounds, and complexes of the alkaline earth metals.

Like the alkali metals, the alkaline earth metals are so reactive that they are never found in elemental form in nature. Because they form +2 ions that have very negative reduction potentials, large amounts of energy are needed to isolate them from their ores. Four of the six group 2 elements—magnesium (Mg), calcium (Ca), strontium (Sr), and barium (Ba)—were first isolated in the early 19th century by Sir Humphry Davy, using a technique similar to the one he used to obtain the first alkali metals. In contrast to the alkali metals, however, compounds of the alkaline earth metals had been recognized as unique for many centuries. In fact, the name *alkali* comes from the Arabic *al-qili*, meaning "ashes," which were known to neutralize acids. Medieval alchemists found that a portion of the ashes would melt on heating, and these substances were later identified as the carbonates of sodium and potassium (M_2CO_3). The ashes that did not melt (but did dissolve in acid), originally called alkaline earths, were subsequently identified as the alkaline earth oxides (MO). In 1808, Davy was able to obtain pure samples of Mg, Ca, Sr, and Ba by electrolysis of their chlorides or oxides.

Beryllium (Be), the lightest alkaline earth metal, was first obtained in 1828 by Friedrich Wöhler in Germany and simultaneously by Antoine Bussy in France. The method used by both men was reduction of the chloride by the potent "new" reductant, potassium:

Equation 21.21

$$BeCl2(s) + 2K(s) \rightarrow \text{D}Be(s) + 2KCl(s)$$

Radium was discovered in 1898 by Pierre and Marie Curie, who processed tons of residue from uranium mines to obtain about 120 mg of almost pure $RaCl_2$. Marie Curie was awarded the Nobel Prize in Chemistry in 1911 for its discovery. Because of its low abundance and high radioactivity however, radium has few uses and will not be discussed further.

Preparation of the Alkaline Earth Metals

The alkaline earth metals are produced for industrial use by electrolytic reduction of their molten chlorides, as indicated in this equation for calcium:

Equation 21.22

$CaCl_2(l) \rightarrow Ca(l) + Cl_2(g)$

The group 2 metal chlorides are obtained from a variety of sources. For example, $BeCl_2$is produced by reacting HCl with beryllia (BeO), which is obtained from the semiprecious stone *beryl* [$Be_3Al_2(SiO_3)_6$]. Chemical reductants can also be used to obtain the group 2 elements. For example, magnesium is produced on a large scale by heating a form of limestone called *dolomite*($CaCO_3 \cdot MgCO_3$) with an inexpensive iron/silicon alloy at 1150°C. Initially CO_2 is released, leaving behind a mixture of CaO and MgO; Mg^{2+} is then reduced:

Equation 21.23

$2CaO \cdot MgO(s) + Fe/Si(s) \rightarrow 2Mg(l) + Ca_2SiO_4(s) + Fe(s)$

An early source of magnesium was an ore called *magnesite* ($MgCO_3$) from the district of northern Greece called Magnesia. Strontium was obtained from *strontianite* ($SrCO_3$) found in a lead mine in the town of Strontian in Scotland. The alkaline earth metals are somewhat easier to isolate from their ores, as compared to the alkali metals, because their carbonate and some sulfate and hydroxide salts are insoluble.

General Properties of the Alkaline Earth Metals

Several important properties of the alkaline earth metals are summarized in Table 21.4 "Selected Properties of the Group 2 Elements". Although many of these properties are similar to those of the alkali metals (Table 21.3 "Selected Properties of the Group 1 Elements"), certain key differences are attributable to the differences in the valence electron configurations of the two groups (ns^2 for the alkaline earth metals versus ns^1 for the alkali metals).

Table 21.4 Selected Properties of the Group 2 Elements

	Beryllium	Magnesium	Calcium	Strontium	Barium	Radium
atomic symbol	Be	Mg	Ca	Sr	Ba	Ra
atomic number	4	12	20	38	56	88
atomic mass	9.01	24.31	40.08	87.62	137.33	226
valence electron configuration	$2s^2$	$3s^2$	$4s^2$	$5s^2$	$6s^2$	$7s^2$
melting point/boiling point (°C)	1287/2471	650/1090	842/1484	777/1382	727/1897	700/—

	Beryllium	Magnesium	Calcium	Strontium	Barium	Radium
density (g/cm^3) at 25°C	1.85	1.74	1.54	2.64	3.62	~5
atomic radius (pm)	112	145	194	219	253	—
first ionization energy (kJ/mol)	900	738	590	549	503	—
most common oxidation state	+2	+2	+2	+2	+2	+2
ionic radius (pm)*	45	72	100	118	135	—
electron affinity (kJ/mol)	≥ 0	≥ 0	−2	−5	−14	—
electronegativity	1.6	1.3	1.0	1.0	0.9	0.9
standard electrode potential ($E°$, V)	−1.85	−2.37	−2.87	−2.90	−2.91	−2.8
product of reaction with O_2	BeO	MgO	CaO	SrO	BaO_2	—
type of oxide	amphoteric	weakly basic	basic	basic	basic	—
product of reaction with N_2	none	Mg_3N_2	Ca_3N_2	Sr_3N_2	Ba_3N_2	—
product of reaction with X_2	BeX_2	MgX_2	CaX_2	SrX_2	BaX_2	—
product of reaction with H_2	none	MgH_2	CaH_2	SrH_2	BaH_2	—
***The values cited are for six-coordinate ions except for Be^{2+}, for which the value for the four-coordinate ion is given.**						

As with the alkali metals, the atomic and ionic radii of the alkaline earth metals increase smoothly from Be to Ba, and the ionization energies decrease. As we would expect, the first ionization energy of an alkaline earth metal, with an ns^2 valence electron configuration, is always significantly greater than that of the alkali metal immediately preceding it. The group 2 elements do exhibit some anomalies, however. For example, the density of Ca is less than that of Be and Mg, the two lightest members of the group, and Mg has the lowest melting and boiling points. In contrast to the alkali metals, the heaviest alkaline earth metal (Ba) is the strongest reductant, and the lightest (Be) is the weakest. The standard electrode potentials of Ca and Sr are not very different from that of Ba, indicating that the opposing trends in ionization energies and hydration energies are of roughly equal importance.

One major difference between the group 1 and group 2 elements is their electron affinities. With their half-filled *ns* orbitals, the alkali metals have a significant affinity for an additional electron. In contrast, the alkaline earth metals generally have little or no tendency to accept an additional electron because their *ns* valence orbitals are already full; an added electron would have to occupy one of the vacant *np* orbitals, which are much higher in energy.

Reactions and Compounds of the Alkaline Earth Metals

With their low first and second ionization energies, the group 2 elements almost exclusively form ionic compounds that contain M^{2+} ions. As expected, however, the lightest element (Be), with its higher ionization energy and small size, forms compounds that are largely covalent, as discussed in Section 21.1 "Overview of Periodic Trends". Some compounds of Mg^{2+} also have significant covalent character. Hence organometallic compounds like those discussed for Li in group 1 are also important for Be and Mg in group 2.

Note the Pattern

The group 2 elements almost exclusively form ionic compounds containing M^{2+}ions.

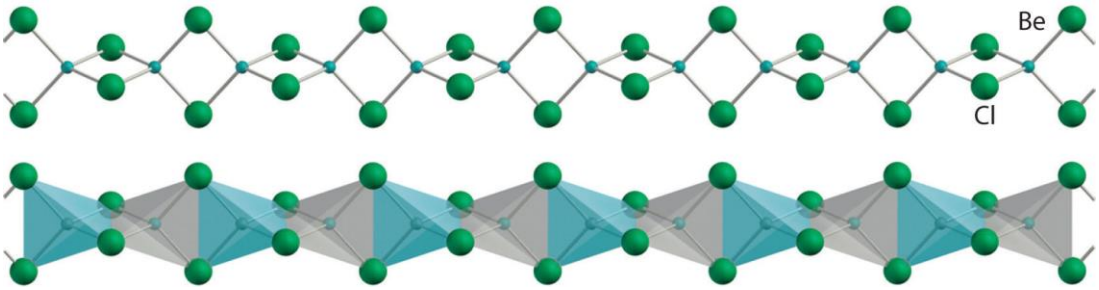
Note the Pattern

Because of their higher ionization energy and small size, both Be and Mg form organometallic compounds.

All alkaline earth metals react vigorously with the halogens (group 17) to form the corresponding halides (MX_2). Except for the beryllium halides, these compounds are all primarily ionic in nature, containing the M^{2+} cation and two X^- anions. The beryllium halides, with properties more typical of covalent compounds, have a polymeric halide-bridged structure in the solid state, as shown for $BeCl_2$. These compounds are volatile, producing vapors that contain the linear X–Be–X molecules predicted by the valence-shell electron-pair repulsion (VSEPR) model. (For more information on the VSEPR model, see Chapter 9 "Molecular Geometry and Covalent Bonding Models".) As expected for compounds with only four valence electrons around the central atom, the beryllium halides are potent Lewis acids. They react readily with Lewis bases, such as ethers, to form tetrahedral adducts in which the central beryllium is surrounded by an octet of electrons:

Equation 21.24

$$BeCl_2(s) + 2(CH_3CH_2)_2O(l) \rightarrow BeCl_2[O(CH_2CH_3)_2]_2(soln)$$



Solid beryllium chloride ($BeCl_2$). *The solid has a polymeric, halide-bridged structure.*

The reactions of the alkaline earth metals with oxygen are less complex than those of the alkali metals. All group 2 elements except barium react directly with oxygen to form the simple oxide MO. Barium forms barium peroxide (BaO_2) because the larger O_2^{2-} ion is better able to separate the large Ba^{2+} ions in the crystal lattice. In practice, only BeO is prepared by direct reaction with oxygen, and this reaction requires finely divided Be and high temperatures because Be is relatively inert. The other alkaline earth oxides are usually prepared by the thermal decomposition of carbonate salts:

Equation 21.25

$$MCO3(s) \rightarrow \mathrm{D}MO(s) + CO2(g)$$

The reactions of the alkaline earth metals with the heavier chalcogens (Y) are similar to those of the alkali metals. When the reactants are present in a 1:1 ratio, the binary chalcogenides (MY) are formed; at lower M:Y ratios, salts containing polychalcogenide ions (Y_n^{2-}) are formed.

In the reverse of Equation 21.25, the oxides of Ca, Sr, and Ba react with CO_2 to regenerate the carbonate. Except for BeO, which has significant covalent character and is therefore amphoteric, all the alkaline earth oxides are basic. Thus they react with water to form the hydroxides—$M(OH)_2$:

Equation 21.26

$$MO(s) + H_2O(l) \rightarrow M^{2+}(aq) + 2OH^-(aq)$$

and they dissolve in aqueous acid. Hydroxides of the lighter alkaline earth metals are insoluble in water, but their solubility increases as the atomic number of the metal increases. Because BeO and MgO are much more inert than the other group 2 oxides, they are used as refractory materials in applications involving high temperatures and mechanical stress. For example, MgO (melting point = 2825°C) is used to coat the heating elements in electric ranges.

The carbonates of the alkaline earth metals also react with aqueous acid to give CO_2 and H_2O:

Equation 21.27

$$MCO_3(s) + 2H^+(aq) \rightarrow M^{2+}(aq) + CO_2(g) + H_2O(l)$$

The reaction in Equation 21.27 is the basis of antacids that contain MCO_3, which is used to neutralize excess stomach acid.

The trend in the reactivities of the alkaline earth metals with nitrogen is the opposite of that observed for the alkali metals. Only the lightest element (Be) does *not* react readily with N_2 to form the nitride (M_3N_2), although finely divided Be will react at high temperatures. The higher lattice energy due to the highly charged M^{2+} and N^{3-} ions is apparently sufficient to overcome the chemical inertness of the N_2 molecule, with its N≡N bond. Similarly, all the alkaline earth metals react with the heavier group 15 elements to form binary compounds such as phosphides and arsenides with the general formula M_3Z_2.

Note the Pattern

Higher lattice energies cause the alkaline earth metals to be more reactive than the alkali metals toward group 15 elements.

When heated, all alkaline earth metals, except for beryllium, react directly with carbon to form ionic carbides with the general formula MC_2. The most important alkaline earth carbide is calcium carbide (CaC_2), which reacts readily with water to produce acetylene. For many years, this reaction was the primary source of acetylene for welding and lamps on miners' helmets. In contrast, beryllium reacts with elemental carbon to form Be_2C, which formally contains the C^{4-} ion (although the compound is covalent). Consistent with this formulation, reaction of Be_2C with water or aqueous acid produces methane:

Equation 21.28

$$Be_2C(s) + 4H_2O(l) \rightarrow 2Be(OH)_2(s) + CH_4(g)$$

Beryllium does not react with hydrogen except at high temperatures (1500°C), although BeH_2 can be prepared at lower temperatures by an indirect route. All the heavier alkaline earth metals (Mg through Ba) react directly with hydrogen to produce the binary hydrides (MH_2). The hydrides of the heavier alkaline earth metals are ionic, but both BeH_2 and MgH_2 have polymeric structures that reflect significant covalent character. All alkaline earth hydrides are good reducing agents that react rapidly with water or aqueous acid to produce hydrogen gas:

Equation 21.29

$$CaH_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + 2H_2(g)$$

Like the alkali metals, the heavier alkaline earth metals are sufficiently electropositive to dissolve in liquid ammonia. In this case, however, two solvated electrons are formed per metal atom, and no equilibriums involving metal dimers or metal anions are known. Also, like the alkali metals, the alkaline earth metals

form a wide variety of simple ionic salts with oxoanions, such as carbonate, sulfate, and nitrate. The nitrate salts tend to be soluble, but the carbonates and sulfates of the heavier alkaline earth metals are quite insoluble because of the higher lattice energy due to the doubly charged cation and anion. The solubility of the carbonates and the sulfates decreases rapidly down the group because hydration energies decrease with increasing cation size.

Note the Pattern

The solubility of alkaline earth carbonate and sulfates decrease down the group because the hydration energies decrease.

Complexes of the Alkaline Earth Metals

Because of their higher positive charge (+2) and smaller ionic radii, the alkaline earth metals have a much greater tendency to form complexes with Lewis bases than do the alkali metals. This tendency is most important for the lightest cation (Be^{2+}) and decreases rapidly with the increasing radius of the metal ion.

Note the Pattern

The alkaline earth metals have a substantially greater tendency to form complexes with Lewis bases than do the alkali metals.

The chemistry of Be^{2+} is dominated by its behavior as a Lewis acid, forming complexes with Lewis bases that produce an octet of electrons around beryllium. For example, Be^{2+} salts dissolve in water to form acidic solutions that contain the tetrahedral $[Be(H_2O)_4]^{2+}$ ion. Because of its high charge-to-radius ratio, the Be^{2+} ion polarizes coordinated water molecules, thereby increasing their acidity:

Equation 21.30

$$[Be(H_2O)_4]^{2+}(aq) \rightarrow [Be(H_2O)_3(OH)]^{+}(aq) + H^{+}(aq)$$

Similarly, in the presence of a strong base, beryllium and its salts form the tetrahedral hydroxo complex: $[Be(OH)_4]^{2-}$. Hence beryllium oxide is amphoteric. Beryllium also forms a very stable tetrahedral fluoride complex: $[BeF_4]^{2-}$. Recall that beryllium halides behave like Lewis acids by forming adducts with Lewis bases (Equation 21.24).

The heavier alkaline earth metals also form complexes, but usually with a coordination number of 6 or higher. Complex formation is most important for the smaller cations (Mg^{2+} and Ca^{2+}). Thus aqueous solutions of Mg^{2+} contain the octahedral $[Mg(H_2O)_6]^{2+}$ ion. Like the alkali metals, the alkaline earth metals form complexes with neutral cyclic ligands like the crown ethers and cryptands discussed in Section 21.3 "The Alkali Metals (Group 1)".

Organometallic Compounds Containing Group 2 Elements

Like the alkali metals, the lightest alkaline earth metals (Be and Mg) form the most covalent-like bonds with carbon, and they form the most stable organometallic compounds. Organometallic compounds of magnesium with the formula RMgX, where R is an alkyl or aryl group and X is a halogen, are universally called *Grignard reagents*, after Victor Grignard (1871–1935), the French chemist who discovered them. (For more information on the Grignard reagents, see Chapter 24 "Organic Compounds", Section 24.5 "Common Classes of Organic Compounds".) Grignard reagents can be used to synthesize various organic compounds, such as alcohols, aldehydes, ketones, carboxylic acids, esters, thiols, and amines.

Uses of the Alkaline Earth Metals

Elemental magnesium is the only alkaline earth metal that is produced on a large scale (about 5×10^5 tn per year). Its low density (1.74 g/cm^3 compared with 7.87 g/cm^3 for iron and 2.70 g/cm^3 for aluminum) makes it an important component of the lightweight metal alloys used in aircraft frames and aircraft and automobile engine parts (Figure 21.13 "Magnesium Alloys Are Lightweight and Corrosion Resistant"). Most commercial aluminum actually contains about 5% magnesium to improve its corrosion resistance and mechanical properties. Elemental magnesium also serves as an inexpensive and powerful reductant for the production of a number of metals, including titanium, zirconium, uranium, and even beryllium, as shown in the following equation:

Equation 21.31

$$TiCl_4(l) + 2Mg(s) \rightarrow Ti(s) + 2MgCl_2(s)$$

The only other alkaline earth that is widely used as the metal is beryllium, which is extremely toxic. Ingestion of beryllium or exposure to beryllium-containing dust causes a syndrome called *berylliosis*, characterized by severe inflammation of the respiratory tract or other tissues. A small percentage of beryllium dramatically increases the strength of copper or nickel alloys, which are used in nonmagnetic, nonsparking tools (such as wrenches and screwdrivers), camera springs, and electrical contacts. The low atomic number of beryllium gives it a very low tendency to absorb x-rays and makes it uniquely suited for applications involving radioactivity. Both elemental Be and BeO, which is a high-temperature ceramic, are used in nuclear reactors, and the windows on all x-ray tubes and sources are made of beryllium foil. Millions of tons of calcium compounds are used every year. As discussed in earlier chapters, $CaCl_2$ is used as “road salt” to lower the freezing point of water on roads in cold temperatures. In addition, $CaCO_3$ is a

major component of cement and an ingredient in many commercial antacids. “Quicklime” (CaO), produced by heating $CaCO_3$ (Equation 21.25), is used in the steel industry to remove oxide impurities, make many kinds of glass, and neutralize acidic soil. Other applications of group 2 compounds described in earlier chapters include the medical use of $BaSO_4$ in “barium milkshakes” for identifying digestive problems by x-rays and the use of various alkaline earth compounds to produce the brilliant colors seen in fireworks.

EXAMPLE 4

For each application, choose the most appropriate substance based on the properties and reactivities of the alkaline earth metals and their compounds. Explain your choice in each case. Use any tables you need in making your decision, such as K_{sp} values (Table 17.1 "Solubility Products for Selected Ionic Substances at 25°C"), lattice energies (Table 8.1 "Representative Calculated Lattice Energies"), and band-gap energies (Chapter 12 "Solids", Section 12.6 "Bonding in Metals and Semiconductors").

a. To neutralize excess stomach acid that causes indigestion, would you use $BeCO_3$, $CaCO_3$, or $BaCO_3$?

b. To remove CO_2 from the atmosphere in a space capsule, would you use MgO, CaO, or BaO?

c. As a component of the alloy in an automotive spark plug electrode, would you use Be, Ca, or Ba?

Given: application and selected alkaline earth metals

Asked for: most appropriate substance for each application

Strategy:

Based on the discussion in this section and any relevant information elsewhere in this book, determine which substance is most appropriate for the indicated use.

Solution:

a. All the alkaline earth carbonates will neutralize an acidic solution by Equation 21.27. Because beryllium and its salts are toxic, however, $BeCO_3$ cannot be used as an antacid. Of the remaining choices, $CaCO_3$ is somewhat more soluble than $BaCO_3$ (according to the K_{sp} values in Table 17.1 "Solubility Products for Selected Ionic Substances at 25°C"), suggesting that it will act more rapidly. Moreover, the formula mass of $CaCO_3$ is 100.1 amu,

whereas that of $BaCO_3$ is almost twice as large. Therefore, neutralizing a given amount of acid would require twice the mass of $BaCO_3$ compared with $CaCO_3$. Furthermore, reaction of $BaCO_3$ with acid produces a solution containing Ba^{2+} ions, which are toxic. (Ba^{2+} is a stimulant that can cause ventricular fibrillation of the heart.) Finally, $CaCO_3$ is produced on a vast scale, so $CaCO_3$ is likely to be significantly less expensive than any barium compound. Consequently, $CaCO_3$ is the best choice for an antacid.

b. This application involves reacting CO_2 with an alkaline earth oxide to form the carbonate, which is the reverse of the thermal decomposition reaction in which MCO_3 decomposes to CO_2 and the metal oxide MO (Equation 21.25). Owing to their higher lattice energies, the smallest alkaline earth metals should form the most stable oxides. (For more information on lattice energies, see Chapter 8 "Ionic versus Covalent Bonding".) Hence their carbonates should decompose at the lowest temperatures, as is observed ($BeCO_3$ decomposes at 100°C; $BaCO_3$ at 1360°C). If the carbonate with the smallest alkaline earth metal decomposes most readily, we would expect the reverse reaction (formation of a carbonate) to occur most readily with the largest metal cation (Ba^{2+}). Hence BaO is the best choice.

c. The alloy in a spark plug electrode must release electrons and promote their flow across the gap between the electrodes at high temperatures. (For more information on solid electrolytes, see Chapter 12 "Solids", Section 12.5 "Correlation between Bonding and the Properties of Solids".) Of the three metals listed, Ba has the lowest ionization energy and thus releases electrons most readily. Heating a barium-containing alloy to high temperatures will cause some ionization to occur, providing the initial step in forming a spark.

Exercise

Which of the indicated alkaline earth metals or their compounds is most appropriate for each application?

a. drying agent for removing water from the atmosphere—$CaCl_2$, $MgSO_4$, or BaF_2

b. removal of scale deposits (largely $CaCO_3$) in water pipes—HCl(aq) or H_2SO_4(aq)

c. removal of traces of N_2 from purified argon gas—Be, Ca, or Ba

Answer:

a. $MgSO_4$

b. HCl

c. Ba

EXAMPLE 5

Predict the products of each reaction and then balance each chemical equation.

a. $CaO(s) + HCl(g) \rightarrow$

b. $MgO(s) + \text{excess } OH^-(aq) \rightarrow$

$$CaH2(s) + TiO2(s)- \rightarrow \text{D}\, CaH2(s) + TiO2(s)- \rightarrow \text{D}$$

Given: reactants

Asked for: products and balanced chemical equation

Strategy:

Follow the procedure given in Example 3 to predict the products of each reaction and then balance each chemical equation.

Solution:

a. **A** Gaseous HCl is an acid, and CaO is a basic oxide that contains the O^{2-}ion. This is therefore an acid–base reaction that produces $CaCl_2$ and H_2O.

B The balanced chemical equation is $CaO(s) + 2HCl(g) \rightarrow CaCl_2(aq) + H_2O(l)$.

b. **A** Magnesium oxide is a basic oxide, so it can either react with water to give a basic solution or dissolve in an acidic solution. Hydroxide ion is also a base. Because we have two bases but no acid, an acid–base reaction is impossible. A redox reaction is not likely because MgO is neither a good oxidant nor a good reductant.

B We conclude that no reaction occurs.

c. **A** Because CaH_2 contains the hydride ion (H^-), it is a good reductant. It is also a strong base because H^- ions can react with H^+ ions to form H_2. Titanium oxide (TiO_2) is a metal oxide that contains the metal in its highest oxidation state (+4 for a group 4 metal); it can act as an oxidant by accepting electrons. We therefore predict that a redox reaction will occur, in which H^- is oxidized and Ti^{4+} is reduced. The most probable reduction product is metallic titanium, but what is the oxidation product? Oxygen

must appear in the products, and both CaO and H_2O are stable compounds. The +1 oxidation state of hydrogen in H_2O is a sign that an oxidation has occurred ($2H^- \rightarrow 2H^+ + 4e^-$).

B The balanced chemical equation $a.\quad BeCl2(s) + Mg(s) - \rightarrow D$ also write the products as $Ti(s) + Ca(OH)_2(s)$.

Exercise

Predict the products of each reaction and then balance each chemical equation.

a. $a.\quad BeCl2(s) + Mg(s) - \rightarrow D_{BaCl_2(aq)} + Na_2SO_4(aq) \rightarrow$

b. $BeO(s) + OH^-(aq) + H_2O(l) \rightarrow$

Answer:

a. $a.\quad BeCl2(s) + Mg(s) - \rightarrow DBe(s) + MgCl2(s)_{BaCl_2(aq)} + Na_2SO_4(aq) \rightarrow$

$BaSO_4(s) + 2NaCl(aq)$

b. $BeO(s) + 2OH^-(aq) + H_2O(l) \rightarrow [Be(OH)_4]^{2-}(aq)$

Summary

Pure samples of most of the alkaline earth metals can be obtained by electrolysis of the chlorides or oxides. Beryllium was first obtained by the reduction of its chloride; radium chloride, which is radioactive, was obtained through a series of reactions and separations. In contrast to the alkali metals, the alkaline earth metals generally have little or no affinity for an added electron. All alkaline earth metals react with the halogens to produce the corresponding halides, with oxygen to form the oxide (except for barium, which forms the peroxide), and with the heavier chalcogens to form chalcogenides or polychalcogenide ions. All oxides except BeO react with CO_2 to form carbonates, which in turn react with acid to produce CO_2 and H_2O. Except for Be, all the alkaline earth metals react with N_2 to form nitrides, and all react with carbon and hydrogen to form carbides and hydrides. Alkaline earth metals dissolve in liquid ammonia to give solutions that contain two solvated electrons per metal atom. The alkaline earth metals have a greater tendency than the alkali metals to form complexes with crown ethers, cryptands, and other Lewis bases. The most important alkaline earth organometallic compounds are *Grignard reagents* (RMgX), which are used to synthesize organic compounds.

KEY TAKEAWAY

- Group 2 elements almost exclusively form ionic compounds containing the M^{2+} ion, they are more reactive toward group 15 elements, and they have a greater tendency to form complexes with Lewis bases than do the alkali metals.

CONCEPTUAL PROBLEMS

1. The electronegativities of Li and Sr are nearly identical (0.98 versus 0.95, respectively). Given their positions in the periodic table, how do you account for this?
2. Arrange Na, Ba, Cs, and Li in order of increasing Z_{eff}.
3. Do you expect the melting point of NaCl to be greater than, equal to, or less than that of $MgCl_2$? Why?
4. Which of the group 2 elements would you expect to form primarily ionic rather than covalent organometallic compounds? Explain your reasoning.
5. Explain why beryllium forms compounds that are best regarded as covalent in nature, whereas the other elements in group 2 generally form ionic compounds.
6. Why is the trend in the reactions of the alkaline earth metals with nitrogen the reverse of the trend seen for the alkali metals?
7. Is the bonding in the alkaline earth hydrides primarily ionic or covalent in nature? Explain your answer. Given the type of bonding, do you expect the lighter or heavier alkaline earth metals to be better reducing agents?
8. Using arguments based on ionic size, charge, and chemical reactivity, explain why beryllium oxide is amphoteric. What element do you expect to be most similar to beryllium in its reactivity? Why?
9. Explain why the solubility of the carbonates and sulfates of the alkaline earth metals decreases with increasing cation size.
10. Beryllium oxide is amphoteric, magnesium oxide is weakly basic, and calcium oxide is very basic. Explain how this trend is related to the ionic character of the oxides.
11. *Do you expect the* ΔH_f *of* CaH_2 *to be greater than, the same as, or less than that of* BaH_2*? Why or* why not?
12. Which of the *s*-block elements would you select to carry out a chemical reduction on a small scale? Consider cost, reactivity, and stability in making your choice. How would your choice differ if the reduction were carried out on an industrial scale?

STRUCTURE AND REACTIVITY

1. Beryllium iodide reacts vigorously with water to produce HI. Write a balanced chemical equation for this reaction and explain why it is violent.
2. Predict the products of each reaction and then balance each chemical equation.

a. $Mg(OH)_2(aq) + (NH_4)_3PO_4(aq) \rightarrow$

b. calcium carbonate and sulfuric acid →

c. $CaCl_2(aq) + Na_3PO_4(aq) \rightarrow$

d. the thermal decomposition of $SrCO_3$

3. Predict the products of each reaction and then balance each chemical equation.

a. $Sr(s) + O_2(g) \rightarrow$

b. the thermal decomposition of $CaCO_3(s)$

c. $CaC_2(s) + H_2O(l) \rightarrow$

d. $RbHCO_3(s) + H_2SO_4(aq) \rightarrow$

4. Indicate whether each pair of substances will react and, if so, write a balanced chemical equation for the reaction.

a. an alkyl chloride and magnesium metal

b. strontium metal and nitrogen

c. magnesium metal and cold water

d. beryllium and nitrogen

5. Using a thermodynamic cycle and information presented in Chapter 7 "The Periodic Table and Periodic Trends" and Chapter 8 "Ionic versus Covalent Bonding", calculate the lattice energy of $magnesium\ nitride\ (Mg_3N_2).\ (\Delta H\square f\ for\ Mg_3N_2\ is\ -463\ kJ/mol,\ and\ \Delta H°\ for$

6. $N(g) + 3e^- \rightarrow N^{3-}$ is +1736 kJ.) How does the lattice energy of Mg_3N_2 compare with that of $MgCl_2$ and MgO? (See Chapter 25 "Appendix A: Standard Thermodynamic Quantities for Chemical Substances at 25°C" for the enthalpy of formation values.)
7. The solubility products of the carbonate salts of magnesium, calcium, and strontium are 6.82×10^{-6}, 3.36×10^{-9}, and 5.60×10^{-10}, respectively. How many milligrams of each compound would be present in 200.0 mL of a saturated solution of each? How would the solubility depend on the pH of the solution? Why?
8. The solubility products of $BaSO_4$ and $CaSO_4$ are 1.08×10^{-10} and 4.93×10^{-5}, respectively. What accounts for this difference? When 500.0 mL of a solution that contains 1.00 M $Ba(NO_3)_2$ and 3.00 M $Ca(NO_3)_2$ is mixed

with a 2.00 M solution of Na_2SO_4, a precipitate forms. What is the identity of the precipitate? How much of it will form before the second salt precipitates?

9. Electrolytic reduction is used to produce magnesium metal from $MgCl_2$. The goal is to produce 200.0 kg of Mg by this method.

a. How many kilograms of $MgCl_2$ are required?

b. How many liters of chlorine gas will be released at standard temperature and pressure?

c. How many hours will it take to process the magnesium metal if a total current of 1.00×10^4 A is used?

10. A sample consisting of 20.35 g of finely divided calcium metal is allowed to react completely with nitrogen. What is the mass of the product?

11. What mass of magnesium hydride will react with water to produce 1.51 L of hydrogen gas at standard temperature and pressure?

ANSWERS

1.

2.

3.

a. $2Sr(s) + O_2(g) \rightarrow 2SrO(s)$

b. $a.\quad CaCO3(s)- \rightarrow DCaO(s)+ CO2(g)$

c. $CaC_2(s) + 2H_2O(l) \rightarrow C_2H_2(g) + Ca(OH)_2(aq)$

d. $2RbHCO_3(s) + H_2SO_4(aq) \rightarrow Rb_2SO_4(aq) + 2CO_2(g) + 2H_2O(l)$

4.

5.

6.

7. The Ba^{2+} ion is larger and has a lower hydration energy than the Ca^{2+} ion. The precipitate is $BaSO_4$; 117 g of $BaSO_4$.

8.

9. 25.09 g of Ca_3N_2

21.5 The *s*-Block Elements in Biology

LEARNING OBJECTIVE

1. To be familiar with the roles of the *s*-block elements in biology.

The *s*-block elements play important roles in biological systems. Covalent hydrides, for example, are the building blocks of organic compounds, and other compounds and ions containing *s*-block elements are found in tissues and cellular fluids. In this section, we describe some ways in which biology depends on the properties of the group 1 and group 2 elements.

Covalent Hydrides

There are three major classes of hydrides—covalent, ionic, and metallic—but only covalent hydrides occur in living cells and have any biochemical significance. As you learned in Chapter 7 "The Periodic Table and Periodic Trends", carbon and hydrogen have similar electronegativities, and the C–H bonds in organic molecules are strong and essentially nonpolar. Little acid–base chemistry is involved in the cleavage or formation of these bonds. In contrast, because hydrogen is less electronegative than oxygen and nitrogen (symbolized by Z), the H–Z bond in the hydrides of these elements is polarized ($H^{\delta+}$–$Z^{\delta-}$). Consequently, the hydrogen atoms in these H–Z bonds are relatively acidic. Moreover, S–H bonds are relatively weak due to poor *s* orbital overlap, so they are readily cleaved to give a proton. Hydrides in which H is bonded to O, N, or S atoms are therefore polar, hydrophilic molecules that form hydrogen bonds. They also undergo acid–base reactions by transferring a proton.

Note the Pattern

Covalent hydrides in which H is bonded to O, N, or S atoms are polar and hydrophilic, form hydrogen bonds, and transfer a proton in their acid-base reactions.

Hydrogen bonds are crucial in biochemistry, in part because they help hold proteins in their biologically active folded structures. Hydrogen bonds also connect the two intertwining strands of DNA (deoxyribonucleic acid), the substance that contains the genetic code for all organisms. (For more information on DNA, see Chapter 24 "Organic Compounds", Section 24.6 "The Molecules of Life".) Because hydrogen bonds are easier to break than the covalent bonds that form the individual DNA strands, the two intertwined strands can be separated to give intact single strands, which is essential for the duplication of genetic information.

In addition to the importance of hydrogen bonds in biochemical molecules, the extensive hydrogen-bonding network in water is one of the keys to the existence of life on our planet. Based on its molecular

mass, water should be a gas at room temperature (20°C), but the strong intermolecular interactions in liquid water greatly increase its boiling point. Hydrogen bonding also produces the relatively open molecular arrangement found in ice, which causes ice to be less dense than water. Because ice floats on the surface of water, it creates an insulating layer that allows aquatic organisms to survive during cold winter months.

These same strong intermolecular hydrogen-bonding interactions are also responsible for the high heat capacity of water and its high heat of fusion. A great deal of energy must be removed from water for it to freeze. Consequently, as noted in Chapter 5 "Energy Changes in Chemical Reactions", large bodies of water act as “thermal buffers” that have a stabilizing effect on the climate of adjacent land areas. Perhaps the most striking example of this effect is the fact that humans can live comfortably at very high latitudes. For example, palm trees grow in southern England at the same latitude (51°N) as the southern end of frigid Hudson Bay and northern Newfoundland in North America, areas known more for their moose populations than for their tropical vegetation. Warm water from the Gulf Stream current in the Atlantic Ocean flows clockwise from the tropical climate at the equator past the eastern coast of the United States and then turns toward England, where heat stored in the water is released. The temperate climate of Europe is largely attributable to the thermal properties of water.

Note the Pattern

Strong intermolecular hydrogen-bonding interactions are responsible for the high heat capacity of water and its high heat of fusion.

Macrominerals

The members of group 1 and group 2 that are present in the largest amounts in organisms are sodium, potassium, magnesium, and calcium, all of which form monatomic cations with a charge of +1 (group 1, M^{+}) or +2 (group 2, M^{2+}). Biologically, these elements can be classified as *macrominerals* (Table 1.6 "Approximate Elemental Composition of a Typical 70 kg Human").

For example, calcium is found in the form of relatively insoluble calcium salts that are used as structural materials in many organisms. Hydroxyapatite [$Ca_5(PO_4)_3OH$] is the major component of bones, calcium carbonate ($CaCO_3$) is the major component of the shells of mollusks and the eggs of birds and reptiles, and calcium oxalate (CaO_2CCO_2) is found in many plants. Because calcium and strontium have similar sizes and charge-to-radius ratios, small quantities of strontium are always found in bone and other calcium-

containing structural materials. Normally this is not a problem because the Sr^{2+} ions occupy sites that would otherwise be occupied by Ca^{2+} ions. When trace amounts of radioactive ^{90}Sr are released into the atmosphere from nuclear weapons tests or a nuclear accident, however, the radioactive strontium eventually reaches the ground, where it is taken up by plants that are consumed by dairy cattle. The isotope then becomes concentrated in cow's milk, along with calcium. Because radioactive strontium coprecipitates with calcium in the hydroxyapatite that surrounds the bone marrow (where white blood cells are produced), children, who typically ingest more cow's milk than adults, are at substantially increased risk for leukemia, a type of cancer characterized by the overproduction of white blood cells.

Ion Transport

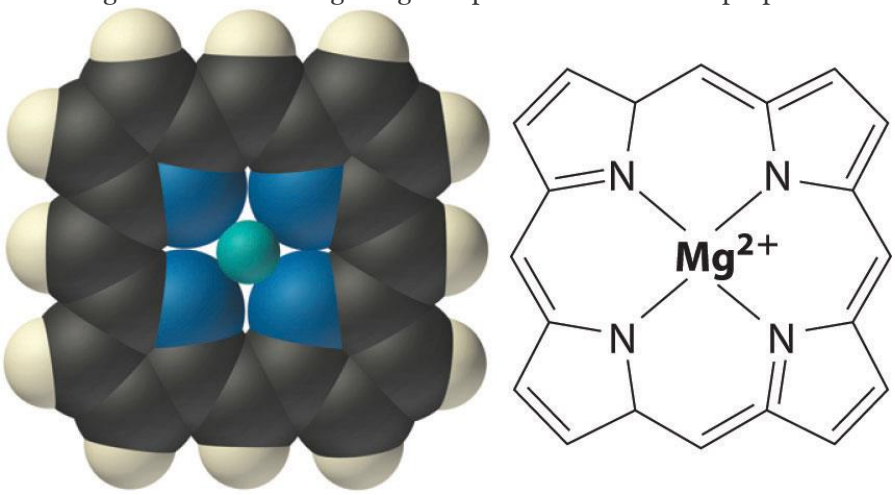
The Na^+, K^+, Mg^{2+}, and Ca^{2+} ions are important components of intracellular and extracellular fluids. Both Na^+ and Ca^{2+} are found primarily in *extra*cellular fluids, such as blood plasma, whereas K^+ and Mg^{2+} are found primarily in *intra*cellular fluids. Substantial inputs of energy are required to establish and maintain these concentration gradients and prevent the system from reaching equilibrium. Thus energy is needed to transport each ion across the cell membrane toward the side with the higher concentration. The biological machines that are responsible for the selective transport of these metal ions are complex assemblies of proteins called ion pumps. Ion pumps recognize and discriminate between metal ions in the same way that crown ethers and cryptands do, with a high affinity for ions of a certain charge and radius. Defects in the ion pumps or their control mechanisms can result in major health problems. For example, *cystic fibrosis*, the most common inherited disease in the United States, is caused by a defect in the transport system (in this case, chloride ions). Similarly, in many cases, *hypertension*, or high blood pressure, is thought to be due to defective Na^+ uptake and/or excretion. If too much Na^+ is absorbed from the diet (or if too little is excreted), water diffuses from tissues into the blood to dilute the solution, thereby decreasing the osmotic pressure in the circulatory system. The increased volume increases the blood pressure, and ruptured arteries called *aneurysms* can result, often in the brain. Because high blood pressure causes other medical problems as well, it is one of the most important biomedical disorders in modern society.

For patients who suffer from hypertension, low-sodium diets that use NaCl substitutes, such as KCl, are often prescribed. Although KCl and NaCl give similar flavors to foods, the K^+ is not readily taken up by the highly specific Na^+-uptake system. This approach to controlling hypertension is controversial, however,

because direct correlations between dietary Na^+ content and blood pressure are difficult to demonstrate in the general population. More important, recent observations indicate that high blood pressure may correlate more closely with inadequate intake of calcium in the diet than with excessive sodium levels. This finding is important because the typical “low-sodium” diet is also low in good sources of calcium, such as dairy products.

Some of the most important biological functions of the group 1 and group 2 metals are due to small changes in the cellular concentrations of the metal ion. The transmission of nerve impulses, for example, is accompanied by an increased flux of Na^+ ions into a nerve cell. Similarly, the binding of various hormones to specific receptors on the surface of a cell leads to a rapid influx of Ca^{2+} ions; the resulting sudden rise in the intracellular Ca^{2+} concentration triggers other events, such as muscle contraction, the release of neurotransmitters, enzyme activation, or the secretion of other hormones.

Within cells, K^+ and Mg^{2+} often activate particular enzymes by binding to specific, negatively charged sites in the enzyme structure. *Chlorophyll*, the green pigment used by all plants to absorb light and drive the process of *photosynthesis*, contains magnesium. During photosynthesis, CO_2 is reduced to form sugars such as glucose. The structure of the central portion of a chlorophyll molecule resembles a crown ether (part (a) in Figure 13.7 "Crown Ethers and Cryptands") with four five-member nitrogen-containing rings linked together to form a large ring that provides a “hole” the proper size to tightly bind Mg^{2+}.

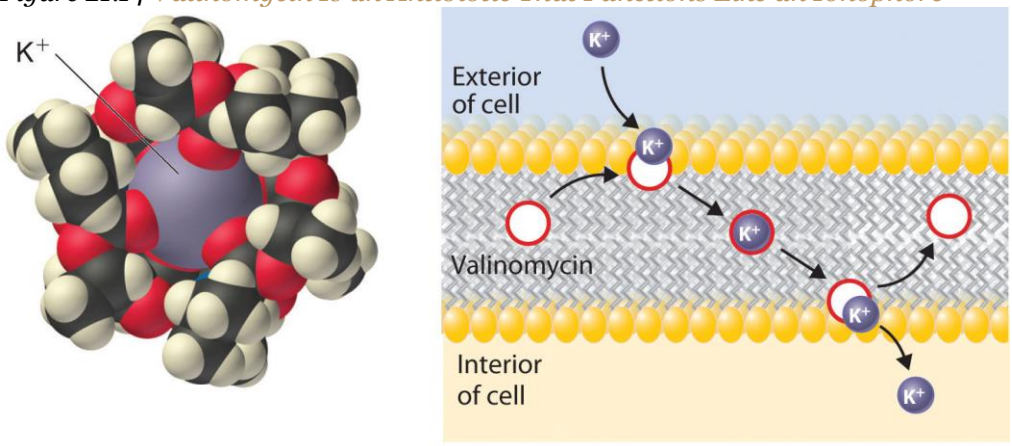


The structure of the central core of chlorophyll, a magnesium complex present in all photosynthetic tissues.*Note the resemblance to the crown ether complexes discussed in Chapter 13 "Solutions".*

Ionophores

Because the health of cells depends on maintaining the proper levels of cations in intracellular fluids, any change that affects the normal flux of metal ions across cell membranes could well cause an organism to die. Molecules that facilitate the transport of metal ions across membranes are generally called ionophores (*ion*plus *phore* from the Greek *phorein*, meaning “to carry”). Many ionophores are potent antibiotics that can kill or inhibit the growth of bacteria. An example is*valinomycin*, a cyclic molecule with a central cavity lined with oxygen atoms (part (a) in Figure 21.14 "Valinomycin Is an Antibiotic That Functions Like an Ionophore") that is similar to the cavity of a crown ether (part (a) in Figure 13.7 "Crown Ethers and Cryptands"). Like a crown ether, valinomycin is highly selective: its affinity for K^+ is about 1000 times greater than that for Na^+. By increasing the flux of K^+ ions into cells, valinomycin disrupts the normal K^+ gradient across a cell membrane, thereby killing the cell (part (b) in Figure 21.14 "Valinomycin Is an Antibiotic That Functions Like an Ionophore").

Figure 21.14 *Valinomycin Is an Antibiotic That Functions Like an Ionophore*



(a) K^+–valinomycin complex **(b) Transport of K^+ across a membrane**

(a) This model of the structure of the K^+–valinomycin complex, determined by x-ray diffraction, shows how the valinomycin molecule wraps itself around the K^+ ion, shielding it from the environment, in a manner reminiscent of a crown ether complex. (For more information on the crown ethers, see Chapter 13 "Solutions",Section 13.2 "Solubility and Molecular Structure".) (b) Valinomycin kills bacteria by facilitating the transport of K^+ ions across the cell membrane, thereby disrupting the normal distribution of ions in the bacterium. At the surface of the membrane, valinomycin binds a K^+ ion. Because the hydrophobic exterior of the valinomycin molecule forms a “doughnut” that shields the positive charge of the metal ion, the K^+–valinomycin complex is highly soluble in the nonpolar interior of the membrane. After the K^+–valinomycin complex diffuses across

the membrane to the interior of the cell, the K^+ ion is released, and the valinomycin is free to diffuse back to the other side of the membrane to bind another K^+ ion. Valinomycin thereby destroys the normal K^+ gradient across the membrane, killing the cell.

EXAMPLE 6

A common way to study the function of a metal ion in biology is to replace the naturally occurring metal with one whose reactivity can be traced by spectroscopic methods. The substitute metal ion must bind to the same site as the naturally occurring ion, and it must have a similar (or greater) affinity for that site, as indicated by its charge density. Arrange the following ions in order of increasing effectiveness as a replacement for Ca^{2+}, which has an ionic radius of 100 pm (numbers in parentheses are ionic radii): Na^+ (102 pm), Eu^{2+} (117 pm), Sr^{2+} (118 pm), F^- (133 pm), Pb^{2+} (119 pm), and La^{3+} (103 pm). Explain your reasoning.

Given: ions and ionic radii

Asked for: suitability as replacement for Ca^{2+}

Strategy:

Use periodic trends to arrange the ions from least effective to most effective as a replacement for Ca^{2+}.

Solution:

The most important properties in determining the affinity of a biological molecule for a metal ion are the size and charge-to-radius ratio of the metal ion. Of the possible Ca^{2+} replacements listed, the F^- ion has the opposite charge, so it should have no affinity for a Ca^{2+}-binding site. Na^+ is approximately the right size, but with a +1 charge it will bind much more weakly than Ca^{2+}. Although Eu^{2+}, Sr^{2+}, and Pb^{2+} are all a little larger than Ca^{2+}, they are probably similar enough in size and charge to bind. Based on its ionic radius, Eu^{2+} should bind most tightly of the three. La^{3+} is nearly the same size as Ca^{2+} and more highly charged. With a higher charge-to-radius ratio and a similar size, La^{3+} should bind tightly to a Ca^{2+} site and be the most effective replacement for Ca^{2+}. The order is $F^- << Na^+ << Pb^{2+} \sim Sr^{2+} \sim Eu^{2+} < La^{3+}$.

Exercise

The ionic radius of K^+ is 138 pm. Arrange the following ions in order of increasing affinity for a K^+-binding site in an enzyme (numbers in parentheses are ionic radii): Na^+ (102 pm), Rb^+ (152 pm), Ba^{2+} (135 pm), Cl^- (181 pm), and Tl^+ (150 pm).

Answer: $Cl^- << Na^+ < Tl^+ \sim Rb^+ < Ba^{2+}$

Summary

Covalent hydrides in which hydrogen is bonded to oxygen, nitrogen, or sulfur are polar, hydrophilic molecules that form hydrogen bonds and undergo acid–base reactions. Hydrogen-bonding interactions are crucial in stabilizing the structure of proteins and DNA and allow genetic information to be duplicated. The hydrogen-bonding interactions in water and ice also allow life to exist on our planet. The group 1 and group 2 metals present in organisms are *macrominerals*, which are important components of intracellular and extracellular fluids. Small changes in the cellular concentration of a metal ion can have a significant impact on biological functions. Metal ions are selectively transported across cell membranes by **ion pumps**, which bind ions based on their charge and radius. **Ionophores**, many of which are potent antibiotics, facilitate the transport of metal ions across membranes.

KEY TAKEAWAY

- Among their many roles in biology, the *s*-block elements allow genetic information to be duplicated and are important components of intracellular and extracellular fluids.

CONCEPTUAL PROBLEMS

1. Explain the thermochemical properties of water in terms of its intermolecular bonding interactions. How does this affect global climate patterns?
2. Of the three classes of hydrides, which is (are) biochemically significant? How do you account for this?
3. Many proteins are degraded and become nonfunctional when heated higher than a certain temperature, even though the individual protein molecules do not undergo a distinct chemical change. Propose an explanation for this observation.
4. Los Angeles has moderate weather throughout the year, with average temperatures between 57°F and 70°F. In contrast, Palm Springs, which is just 100 miles inland, has average temperatures between 55°F and 95°F. Explain the difference in the average temperature ranges between the two cities.
5. Although all group 1 ions have the same charge (+1), Na^+ and K^+ ions are selectively transported across cell membranes. What strategy do organisms employ to discriminate between these two cations?

STRUCTURE AND REACTIVITY

1. A 0.156 g sample of a chloride salt of an alkaline earth metal is dissolved in enough water to make 20.5 mL of solution. If this solution has an osmotic pressure of 2.68 atm at 25°C, what is the identity of the alkaline earth metal?

2. The thermal buffering capacity of water is one of the reasons the human body is capable of withstanding a wide range of temperatures. How much heat (in kilojoules) is required to raise the temperature of a 70.0 kg human from 37.0°C to 38.0°C? Assume that 70% of the mass of the body is water and that body fluids have the same specific heat as water.
3. During illness, body temperature can increase by more than 2°C. One piece of folklore is that you should "feed a fever." Using the data in Table 5.5 "Approximate Compositions and Fuel Values of Some Common Foods", how many fried chicken drumsticks would a 70.0 kg person need to eat to generate a 2.0°C change in body temperature? Assume the following: there is complete conversion of the caloric content of the chicken to thermal energy, 70% of the mass of the body is solely due to water, and body fluids have the same specific heat as water.
4. Hydrogen bonding is partly responsible for the high enthalpy of vaporization of water (ΔH_{vap} = 43.99 kJ/mol at 25°C), which contributes to cooling the body during exercise. Assume that a 50.0 kg runner produces 20.0 g of perspiration during a race, and all the perspiration is converted to water vapor at 37.0°C. What amount of heat (in joules) is removed from the runner's skin if the perspiration consists of only water?

ANSWER

1. Ba

21.6 End-of-Chapter Material

APPLICATION PROBLEMS

1. For each application, which of the indicated substances would you select and why? Base your selections on the properties and reactivities of the alkaline earth metals and their compounds.

a. source of CO_2 at low temperature—$BeCO_3$ or $CaCO_3$
b. window material for x-ray tubes—beryllium or strontium
c. source of iodide ions in aqueous solution—BaI_2 or BeI_2
d. formation of a stable organometallic compound by reacting a metal with an alkyl halide—calcium or magnesium
e. synthesis of refractory materials—magnesium oxide or barium oxide

2. Ultrahigh-purity tritium, which is needed in the nuclear weapons industry, is obtained by allowing a mixture of tritium and its nuclear decay product, helium-3, to diffuse through a thin block of palladium metal. Explain why this is an effective method for separating the two substances.
3. In one technique for harnessing solar energy, the blue-green algae *Anabaena cylindrica*is used to produce H_2 and O_2 photosynthetically. The resulting gases are collected, passed through palladium metal, and then recombined in a fuel cell to produce electricity. Draw a diagram showing how this process might work.
4. Scientists speculate that sodium atoms react with atmospheric ozone to produce a high-energy species, which is then reduced by atomic oxygen. This process is believed to occur as meteors enter Earth's atmosphere. Write equations for these reactions. Is sodium regenerated in this process?
5. Propose an effective compound for purifying and regenerating air for breathing in a submarine and justify your choice.
6. Explain why administering cryptands to a person suffering from iron toxicity could be an effective clinical treatment.
7. Calcium magnesium carbonate [$CaMg(CO_3)_2$], also known as dolomite, is a primary constituent of soils. It is formed when water containing magnesium ions comes in contact with calcium carbonate. Do you expect dolomite to be more or less resistant to acid rain than calcium carbonate? Why?
8. Few classes of reagents have proved to be as useful for organic syntheses as the Grignard reagents (RMgX), which are produced by reacting an organohalogen compound (RX) with magnesium in an ether solvent. The ease of formation of a Grignard reagent depends on the structure of the organohalogen compound.

a. For a given R group, arrange the alkyl halides (RX) in order of decreasing reactivity with Mg and justify your reasoning.

b. Is it possible to make a Grignard reagent using an organosodium compound and $MgCl_2$? Why or why not?

c. Is $MgCl_2$ or MgI_2 preferable for the reaction described in part (b)?

9. The percentage of the population that developed leukemia in the vicinity of the Chernobyl nuclear reactor rose substantially after the nuclear accident in 1986. Why? Based on information in this chapter, what might have been done to reduce the incidence of leukemia in children who lived in the affected region?
10. Explain how ingesting large amounts of NaCl could induce a heart attack.

11. The general mechanism by which valinomycin functions is described in the text. If you were asked to develop a new antibiotic that functions like valinomycin, what type of structural features would you want to incorporate into it?
12. You have been asked to determine the concentrations of both Mg^{2+} and Ca^{2+} in a sample of hard water using EDTA (ethylenediaminetetraacetic acid), which forms stable complexes with both metal ions. The procedure requires two titrations. In the first, you adjust the pH of the water to about 10 by adding a solution of KOH. You then add a small amount of an indicator that, by itself, is blue at pH 10 but which forms a red complex with either Mg^{2+} or Ca^{2+}. Titrating the sample with a solution of EDTA will cause the solution to turn from red to blue when all the metal ions have reacted with the EDTA. The second titration is identical to the first, *except* that it is carried out at pH 13, and the volume of EDTA solution needed to reach the endpoint is *less* than in the first titration. What is the difference between what is being measured in these two titrations? Which titration measures the concentration of only a single metal ion? Identify that metal ion and explain how the procedure described allows you to determine the concentrations of*both* Mg^{2+} and Ca^{2+}.
13. The primary component of ordinary glass is SiO_2, which is difficult to work with due to its high melting point (1700°C). Adding metal oxides lowers the melting temperature to a workable level (700–900°C) and causes the liquid to flow more easily. Both Na_2O and K_2O are commonly used for this purpose. Which of these oxides produces a glass that hardens more rapidly and at a higher temperature? Why is there a difference?
14. Lead poisoning can be treated by administering EDTA, an organic compound that binds to Pb^{2+} (ETDA is described in Problem 12), thereby removing lead from the system. If you are thinking of administering EDTA as a clinical treatment for Ni^{2+} poisoning because of its effectiveness in removing Pb^{2+}, what additional factors do you need to consider?
15. Silicon, aluminum, and oxygen, the most abundant constituents of Earth's crust, are found in many minerals. For example, two feldspars, which are typical components of granites, are albite and anorthite. Albite has the composition $Na[AlSi_3O_8]$; in anorthite, Al^{3+} replaces one of the Si^{4+} ions. Suggest a plausible cation in anorthite in place of Na^+.
16. When a plant root is immersed in an aqueous environment, its uptake of metal ions is dictated by equilibrium considerations. Metal ions can be captured by reaction with various types of carrier molecules. The resulting complexes can pass through the cell membrane and dissociate, thereby transporting the metal ions into the

cell. The Na^+, K^+, Mg^{2+}, and Ca^{2+} ions are all transported using this mechanism. Which of these ions would be captured by

a. oxygen donors with a neutral or low (−1) charge?

b. carboxylates, phosphates, and some neutral oxygen donors?

c. polyphosphates with a total negative charge greater than −2?

d. nitrogen donors?

17. Sodium carbonate has long been used in the glass industry, for making water softeners, and in the wood pulp and paper industries. Recently, sodium carbonate has proved useful for removing SO_2 and H_2SO_4 from the flue gases of coal- and oil-fired power stations. Write balanced chemical equations showing the reactions that occur when flue gases are passed through solid sodium carbonate.

18. Hard water contains high concentrations of Ca^{2+} and Mg^{2+}. These ions react with soaps (sodium and potassium salts of naturally occurring carboxylic acids) to form an insoluble scum. Explain how adding Na_2CO_3 to hard water can soften the water and improve the ability of soaps to remove dirt and grime.

19. Do you expect $MgCO_3$ or $Mg(OH)_2$ to be more soluble in water? Based on your answer, explain how adding $Ca(OH)_2$ softens water by removing Mg^{2+}. Be sure to show a balanced chemical equation for the reaction.

20. How does a low-sodium diet help lower blood pressure? Do you think a diet high in KCl would also be effective at lowering blood pressure? Explain your answer.

ANSWERS

1.

a. $BeCO_3$; less stable to decomposition due to small size of Be^{2+}

b. Be; low *Z* results in little absorption of x-rays

c. BaI_2; has greater ionic character

d. Mg; smaller size results in stronger polar covalent bonds to carbon

e. MgO; higher lattice energy and melting point

2.

3.

4.

5. KO_2; the reaction is $4KO_2(s) + 4CO_2(g) + 2H_2O(g) \rightarrow 4KHCO_3(s) + 3O_2(g)$.

6.

7. Dolomite will be less resistant to acid rain because $MgCO_3$ is more soluble than $CaCO_3$.
8.
9. Restrict milk consumption and supplement diet with calcium to minimize the uptake of strontium.
10.
11.
12.
13. The glass containing sodium will have a higher softening or melting temperature because the smaller sodium ions will link the silicate chains more strongly.
14.
15. Ca^{2+}
16.
17. $Na_2CO_3(s) + SO_2(g) \rightarrow Na_2SO_3(s) + CO_2(g)$; $Na_2CO_3(s) + H_2SO_4(g) \rightarrow Na_2SO_4(s) + CO_2(g) + H_2O(g)$

Chapter 22

The *p*-Block Elements

We continue our discussion of the chemistry of the main group elements with the *p*block of the periodic table. We will use the systematic approach developed in Chapter 21 "Periodic Trends and the ", which is based on valence electron configurations and periodic trends in atomic properties, while applying the unifying principles of chemical bonding, thermodynamics, and kinetics. The line that divides metals from nonmetals in the periodic table crosses the *p* block diagonally. As a result, the differences between metallic and nonmetallic properties are evident within each group, even though all members of each group have the same valence electron configuration. The *p* block is the only portion of the periodic table where we encounter the inert-pair effect. Moreover, as with the *s*-block elements, the chemistry of the lightest member of each group in the *p* block differs sharply from that of its heavier congeners but is similar to that of the element immediately below and to the right of it in the next group. Thus diagonal similarities in chemistry are seen across the *p* block.

22.1 The Elements of Group 13

LEARNING OBJECTIVE

1. To understand the trends in properties and the reactivity of the group 13 elements.

Group 13 is the first group to span the dividing line between metals and nonmetals, so its chemistry is more diverse than that of groups 1 and 2, which include only metallic elements. Except for the lightest element (boron), the group 13 elements are all relatively electropositive; that is, they tend to lose electrons in chemical reactions rather than gain them. Although group 13 includes aluminum, the most abundant metal on Earth, none of these elements was known until the early 19th century because they are never found in nature in their free state. Elemental boron and aluminum, which were first prepared by reducing B_2O_3 and $AlCl_3$, respectively, with potassium, could not be prepared until potassium had been isolated and shown to be a potent reductant. Indium (In) and thallium (Tl) were discovered in the 1860s by using spectroscopic techniques, long before methods were available for isolating them. Indium, named for its indigo (deep blue-violet) emission line, was first observed in the spectrum of zinc ores, while thallium (from the Greek *thallos*, meaning "a young, green shoot of a plant") was named for its brilliant green emission line. Gallium (Ga; Mendeleev's *eka*-aluminum) was discovered in 1875 by the French chemist Paul Émile Lecoq de Boisbaudran during a systematic search for Mendeleev's "missing" element in group 13.

Note the Pattern

Group 13 elements are never found in nature in their free state.

Preparation and General Properties of the Group 13 Elements

As reductants, the group 13 elements are less powerful than the alkali metals and alkaline earth metals. Nevertheless, their compounds with oxygen are thermodynamically stable, and large amounts of energy are needed to isolate even the two most accessible elements—boron and aluminum—from their oxide ores. Although boron is relatively rare (it is about 10,000 times less abundant than aluminum), concentrated deposits of borax [$Na_2B_4O_5(OH)_4 \cdot 8H_2O$] are found in ancient lake beds (Figure 22.1 "Borax Deposits") and were used in ancient times for making glass and glazing pottery. Boron is produced on a large scale by reacting borax with acid to produce boric acid [$B(OH)_3$], which is then dehydrated to the oxide (B_2O_3). Reduction of the oxide with magnesium or sodium gives amorphous boron that is only about 95% pure:

Equation 22.1

$$Na2B4O5(OH)4 \cdot 8H2O(s) \rightarrow acidB(OH)3(s) \rightarrow DB2O3(s)$$

Equation 22.2

$$B2O3(s) + 3Mg(s) \rightarrow D2B(s) + 3MgO(s)$$

(a) Concentrated deposits of crystalline borax [$Na_2B_4O_5(OH)_4 \cdot 8H_2O$] are found in ancient lake beds, such as the Mojave Desert and Death Valley in the western United States. (b) Borax is used in various cleaning products, including 20 Mule Team Borax, a laundry detergent named for the teams of 20 mules that hauled wagons full of borax from desert deposits to railroad terminals in the 1880s.

Pure, crystalline boron, however, is extremely difficult to obtain because of its high melting point (2300°C) and the highly corrosive nature of liquid boron. It is usually prepared by reducing pure BCl_3 with hydrogen gas at high temperatures or by the thermal decomposition of boron hydrides such as diborane (B_2H_6):

Equation 22.3

$$BCl3(g) + 32H2(g) \rightarrow B(s) + 3HCl(g)$$

Equation 22.4

$$B_2H_6(g) \rightarrow 2B(s) + 3H_2(g)$$

The reaction shown in Equation 22.3 is used to prepare boron fibers, which are stiff and light. Hence they are used as structural reinforcing materials in objects as diverse as the US space shuttle and the frames of lightweight bicycles that are used in races such as the Tour de France. Boron is also an important component of many ceramics and heat-resistant borosilicate glasses, such as Pyrex, which is used for ovenware and laboratory glassware.

In contrast to boron, deposits of aluminum ores such as *bauxite*, a hydrated form of Al_2O_3, are abundant. With an electrical conductivity about twice that of copper on a weight for weight basis, aluminum is used in more than 90% of the overhead electric power lines in the United States. However, because aluminum–oxygen compounds are stable, obtaining aluminum metal from bauxite is an expensive process.

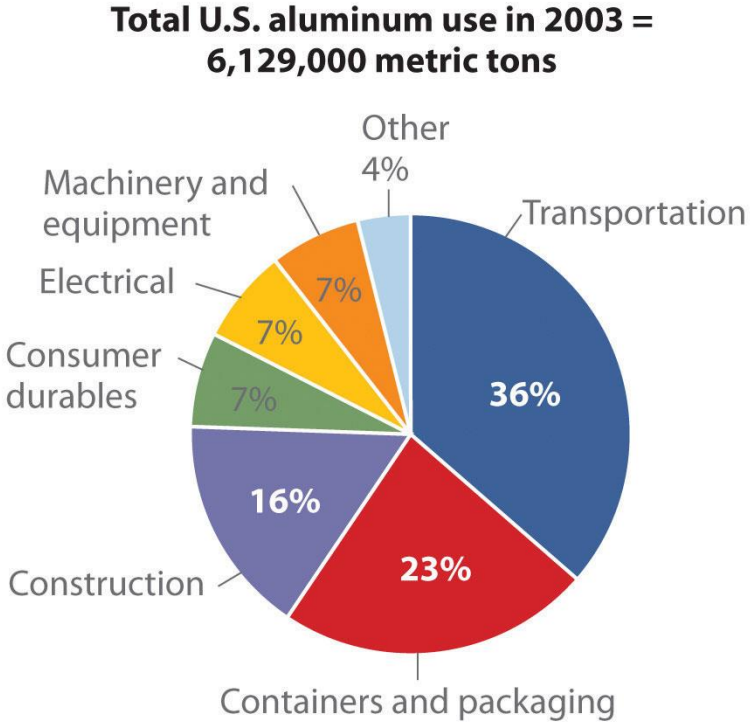
Aluminum is extracted from oxide ores by treatment with a strong base, which produces the soluble hydroxide complex $[Al(OH)_4]^-$. Neutralization of the resulting solution with gaseous CO_2 results in the precipitation of $Al(OH)_3$:

Equation 22.5

$$2[Al(OH)_4]^-(aq) + CO_2(g) \rightarrow 2Al(OH)_3(s) + CO_3^{2-}(aq) + H_2O(l)$$

Thermal dehydration of $Al(OH)_3$ produces Al_2O_3, and metallic aluminum is obtained by the electrolytic reduction of Al_2O_3 using the *Hall–Heroult process* described inChapter 19 "Electrochemistry". Of the

group 13 elements, only aluminum is used on a large scale: for example, each Boeing 777 airplane is about 50% aluminum by mass.



Source: Thomas D. Kelly and Grecia R. Matos, "Historical Statistics for Mineral and Material Commodities in the United States," US Geological Survey Data Series 140, 2010, accessed July 20, 2011,http://pubs.usgs.gov/ds/2005/140/.

The other members of group 13 are rather rare: gallium is approximately 5000 times less abundant than aluminum, and indium and thallium are even scarcer. Consequently, these metals are usually obtained as by-products in the processing of other metals. The extremely low melting point of gallium (29.6°C), however, makes it easy to separate from aluminum. Due to its low melting point and high boiling point, gallium is used as a liquid in thermometers that have a temperature range of almost 2200°C. Indium and thallium, the heavier group 13 elements, are found as trace impurities in sulfide ores of zinc and lead. Indium is used as a crushable seal for high-vacuum cryogenic devices, and its alloys are used as low-melting solders in electronic circuit boards. Thallium, on the other hand, is so toxic that the metal and its compounds have few uses. Both indium and thallium oxides are released in flue dust when sulfide ores are converted to metal oxides and SO_2. Until relatively recently, these and other toxic elements were allowed to disperse in the air, creating large "dead zones" downwind of a smelter. The flue dusts are now trapped and serve as a relatively rich source of elements such as In and Tl (as well as Ge, Cd, Te, and As).

Table 22.1 "Selected Properties of the Group 13 Elements" summarizes some important properties of the group 13 elements. Notice the large differences between boron and aluminum in size, ionization energy, electronegativity, and standard reduction potential, which is consistent with the observation that boron behaves chemically like a nonmetal and aluminum like a metal. All group 13 elements have ns^2np^1 valence electron configurations, and all tend to lose their three valence electrons to form compounds in the +3 oxidation state. The heavier elements in the group can also form compounds in the +1 oxidation state formed by the formal loss of the single *np* valence electron. Because the group 13 elements generally contain only six valence electrons in their neutral compounds, these compounds are all moderately strong Lewis acids.

Table 22.1 Selected Properties of the Group 13 Elements

Property	Boron	Aluminum*	Gallium	Indium	Thallium
atomic symbol	B	Al	Ga	In	Tl
atomic number	5	13	31	49	81
atomic mass (amu)	10.81	26.98	69.72	114.82	204.38
valence electron configuration†	$2s^22p^1$	$3s^23p^1$	$4s^24p^1$	$5s^25p^1$	$6s^26p^1$
melting point/boiling point (°C)	2075/4000	660/2519	29.7/2204	156.6/2072	304/1473
density (g/cm^3) at 25°C	2.34	2.70	5.91	7.31	11.8
atomic radius (pm)	87	118	136	156	156
first ionization energy (kJ/mol)	801	578	579	558	589
most common oxidation state	+3	+3	+3	+3	+1
ionic radius (pm)‡	−25	54	62	80	162
electron affinity (kJ/mol)	−27	−42	−40	−39	−37
electronegativity	2.0	1.6	1.8	1.8	1.8
standard reduction potential ($E°$, V)	−0.87	−1.66	−0.55	−0.34	+0.741 of M^{3+}(aq)
product of reaction with O_2	B_2O_3	Al_2O_3	Ga_2O_3	In_2O_3	Tl_2O
type of oxide	acidic	amphoteric	amphoteric	amphoteric	basic
product of reaction with	BN	AlN	GaN	InN	none

Property	Boron	Aluminum*	Gallium	Indium	Thallium
N_2					
product of reaction with X_2[§]	BX_3	Al_2X_6	Ga_2X_6	In_2X_6	TlX
***This is the name used in the United States; the rest of the world inserts an extra *i* and calls it *aluminium*.**					
[†]The configuration shown does not include filled *d* and *f* subshells.					
[‡]The values cited are for six-coordinate ions in the most common oxidation state, except for Al^{3+}, for which the value for the four-coordinate ion is given. The B^{3+} ion is not a known species; the radius cited is an estimated four-coordinate value.					
[§]X is Cl, Br, or I. Reaction with F_2 gives the trifluorides (MF_3) for all group 13 elements.					

Note the Pattern

Neutral compounds of the group 13 elements are electron deficient, so they are generally moderately strong Lewis acids.

In contrast to groups 1 and 2, the group 13 elements show no consistent trends in ionization energies, electron affinities, and reduction potentials, whereas electronegativities actually *increase* from aluminum to thallium. Some of these anomalies, especially for the series Ga, In, Tl, can be explained by the increase in the effective nuclear charge (Z_{eff}) that results from poor shielding of the nuclear charge by the filled $(n - 1)d^{10}$ and $(n - 2)f^{14}$ subshells. Consequently, although the actual nuclear charge increases by 32 as we go from indium to thallium, screening by the filled $5d$ and $4f$ subshells is so poor that Z_{eff} increases significantly from indium to thallium. Thus the first ionization energy of thallium is actually greater than that of indium.

Note the Pattern

Anomalies in periodic trends among Ga, In, and Tl can be explained by the increase in the effective nuclear charge due to poor shielding.

Reactions and Compounds of Boron

Elemental boron is a semimetal that is remarkably unreactive; in contrast, the other group 13 elements all exhibit metallic properties and reactivity. We therefore consider the reactions and compounds of boron separately from those of other elements in the group.

All group 13 elements have fewer valence electrons than valence orbitals, which generally results in delocalized, metallic bonding. With its high ionization energy, low electron affinity, low electronegativity, and small size, however, boron does not form a metallic lattice with delocalized valence electrons. Instead,

boron forms unique and intricate structures that contain *multicenter bonds*, in which a pair of electrons holds together three or more atoms.

Note the Pattern

Elemental boron forms multicenter bonds, whereas the other group 13 elements exhibit metallic bonding.

The basic building block of elemental boron is not the individual boron atom, as would be the case in a metal, but rather the B_{12} *icosahedron*. (For more information on B_{12}, see Chapter 7 "The Periodic Table and Periodic Trends", Section 7.4 "The Chemical Families".) Because these icosahedra do not pack together very well, the structure of solid boron contains voids, resulting in its low density (Figure 22.2 "Solid Boron Contains B"). Elemental boron can be induced to react with many nonmetallic elements to give binary compounds that have a variety of applications. For example, plates of boron carbide (B_4C) can stop a 30-caliber, armor-piercing bullet, yet they weigh 10%–30% less than conventional armor. Other important compounds of boron with nonmetals include boron nitride (BN), which is produced by heating boron with excess nitrogen (Equation 22.6); boron oxide (B_2O_3), which is formed when boron is heated with excess oxygen (Equation 22.7); and the boron trihalides (BX_3), which are formed by heating boron with excess halogen (Equation 22.8).

Equation 22.6

$$2B(s) + N2(g) \rightarrow D2BN(s)$$

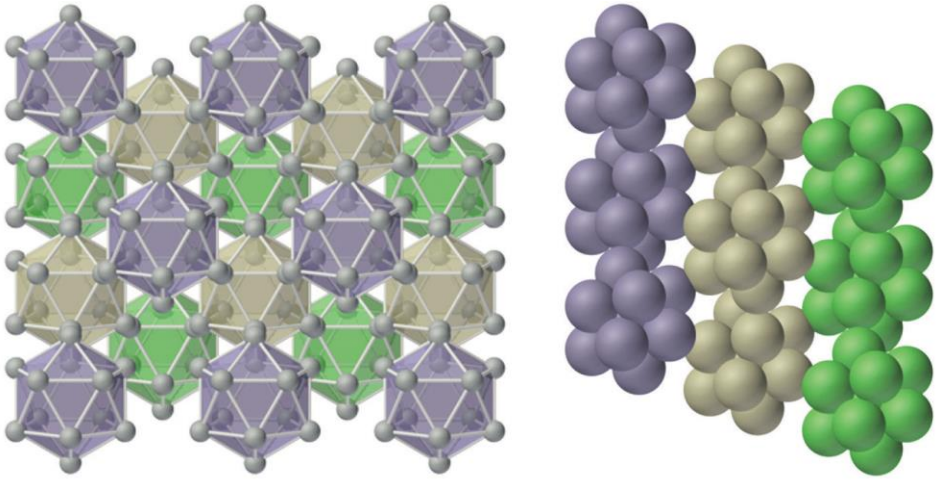
Equation 22.7

$$4B(s) + 3O2(g) \rightarrow D2B2O3(s)$$

Equation 22.8

$$2B(s) + 3X2(g) \rightarrow D2BX3(g)$$

Figure 22.2 *Solid Boron Contains B_{12} Icosahedra*



(a) Cubic close-packed (ccp) B_{12} (b) Side view (90° rotation)

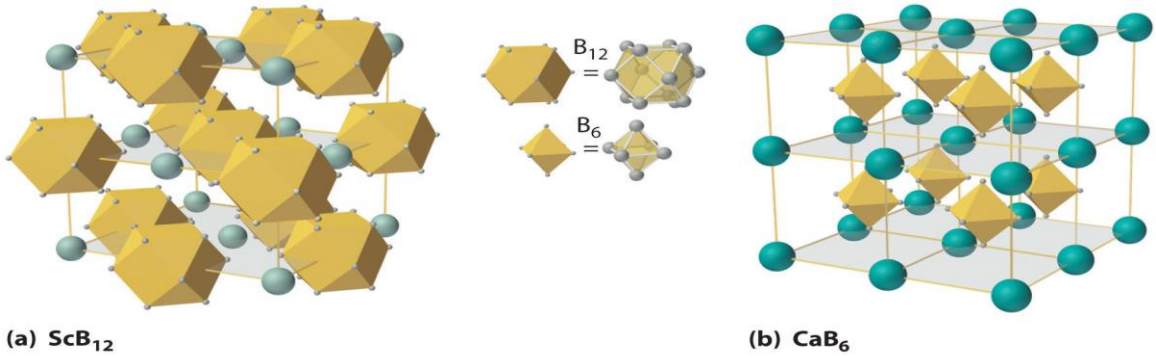
Unlike metallic solids, elemental boron consists of a regular array of B_{12} icosahedra rather than individual boron atoms. Note that each boron atom in the B_{12}icosahedron is connected to five other boron atoms within the B_{12} unit. (a) The allotrope of boron with the simplest structure is α-rhombohedral boron, which consists of B_{12} octahedra in an almost cubic close-packed lattice. (b) A side view of the structure shows that icosahedra do not pack as efficiently as spheres, making the density of solid boron less than expected.

As is typical of elements lying near the dividing line between metals and nonmetals, many compounds of boron are amphoteric, dissolving in either acid or base.

Boron nitride is similar in many ways to elemental carbon. With eight electrons, the B–N unit is *isoelectronic* with the C–C unit, and B and N have the same average size and electronegativity as C. The most stable form of BN is similar to graphite, containing six-membered B_3N_3 rings arranged in layers. At high temperature and pressure, hexagonal BN converts to a cubic structure similar to diamond, which is one of the hardest substances known. Boron oxide (B_2O_3) contains layers of trigonal planar BO_3groups (analogous to BX_3) in which the oxygen atoms bridge two boron atoms. It dissolves many metal and nonmetal oxides, including SiO_2, to give a wide range of commercially important borosilicate glasses. A small amount of CoO gives the deep blue color characteristic of “cobalt blue” glass.

At high temperatures, boron also reacts with virtually all metals to give *metal borides* that contain regular three-dimensional networks, or *clusters*, of boron atoms. The structures of two metal borides—ScB_{12} and CaB_6—are shown in Figure 22.3 "The Structures of ScB". Because metal-rich borides such as ZrB_2 and

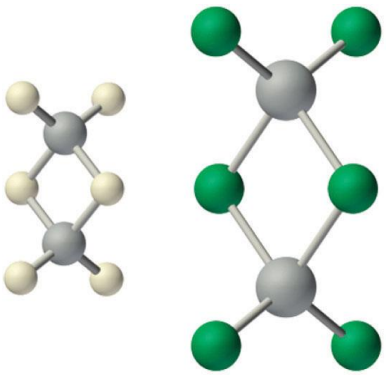
TiB_2 are hard and corrosion resistant even at high temperatures, they are used in applications such as turbine blades and rocket nozzles.



(a) The structure of ScB_{12} consists of B_{12} clusters and Sc atoms arranged in a faced-centered cubic lattice similar to that of NaCl, with B_{12} units occupying the anion positions and scandium atoms the cation positions. The B_{12} units here are not icosahedra but cubooctahedra, with alternating square and triangular faces. (b) The structure of CaB_6 consists of octahedral B_6 clusters and calcium atoms arranged in a body-centered cubic lattice similar to that of CsCl, with B_6 units occupying the anion positions and calcium atoms the cation positions.

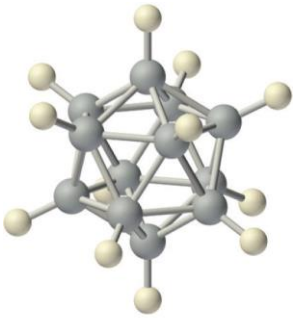
Boron hydrides were not discovered until the early 20th century, when the German chemist Alfred Stock undertook a systematic investigation of the binary compounds of boron and hydrogen, although binary hydrides of carbon, nitrogen, oxygen, and fluorine have been known since the 18th century. Between 1912 and 1936, Stock oversaw the preparation of a series of boron–hydrogen compounds with unprecedented structures that could not be explained with simple bonding theories. All these compounds contain multicenter bonds, as discussed in Chapter 21 "Periodic Trends and the " (Figure 21.5 "A Three-Center Bond Uses Two Electrons to Link Three Atoms"). The simplest example is diborane (B_2H_6), which contains two bridging hydrogen atoms (part (a) in Figure 22.4 "The Structures of Diborane (B"). An extraordinary variety of polyhedral boron–hydrogen clusters is now known; one example is the $B_{12}H_{12}^{2-}$ ion, which has a polyhedral structure similar to the icosahedral B_{12} unit of elemental boron, with a single hydrogen atom bonded to each boron atom.

Figure 22.4 The Structures of Diborane (B_2H_6) and Aluminum Chloride (Al_2Cl_6)

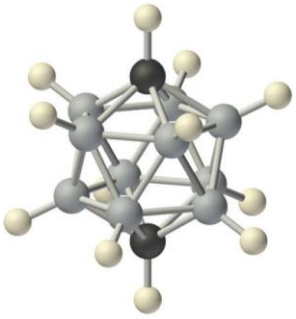


(a) B_2H_6 (b) Al_2Cl_6

(a) The hydrogen-bridged dimer B_2H_6 contains two three-center, two-electron bonds as described for the $B_2H_7^-$ ion in ***Figure 21.5 "A Three-Center Bond Uses Two Electrons to Link Three Atoms"****. (b) In contrast, the bonding in the halogen-bridged dimer Al_2Cl_6 can be described in terms of electron-pair bonds, in which a chlorine atom bonded to one aluminum atom acts as a Lewis base by donating a lone pair of electrons to another aluminum atom, which acts as a Lewis acid.*



$B_{12}H_{12}^{2-}$



$B_{10}C_2H_{12}$

A related class of polyhedral clusters, the carboranes, contain both CH and BH units; an example is shown here. Replacing the hydrogen atoms bonded to carbon with organic groups produces substances with

novel properties, some of which are currently being investigated for their use as liquid crystals and in cancer chemotherapy.

The enthalpy of combustion of diborane (B_2H_6) is −2165 kJ/mol, one of the highest values known:

Equation 22.9

$$B2H6(g) + 3O2(g) \rightarrow B2O3(s) + 3H2O(l) \qquad DHcomb = -2165\ kJ/mol$$

Consequently, the US military explored using boron hydrides as rocket fuels in the 1950s and 1960s. This effort was eventually abandoned because boron hydrides are unstable, costly, and toxic, and, most important, B_2O_3 proved to be highly abrasive to rocket nozzles. Reactions carried out during this investigation, however, showed that boron hydrides exhibit unusual reactivity.

Because boron and hydrogen have almost identical electronegativities, the reactions of boron hydrides are dictated by minor differences in the distribution of electron density in a given compound. In general, two distinct types of reaction are observed: electron-rich species such as the BH_4^- ion are reductants, whereas electron-deficient species such as B_2H_6 act as oxidants.

EXAMPLE 1

For each reaction, explain why the given products form.

a. $B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(l)$

b. $BCl_3(l) + 3H_2O(l) \rightarrow B(OH)_3(aq) + 3HCl(aq)$

a. $2BI3(s) + 3H2(g) - \rightarrow D16B12(s) + 6HI(g)$

Given: balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the reaction products form.

Solution:

a. Molecular oxygen is an oxidant. If the other reactant is a potential reductant, we expect that a redox reaction will occur. Although B_2H_6 contains boron in its highest oxidation state (+3), it also contains hydrogen in the −1 oxidation state (the hydride ion). Because hydride is a strong reductant, a redox reaction will probably occur. We expect that H^- will be

oxidized to H^+ and O_2 will be reduced to O^{2-}, but what are the actual products? A reasonable guess is B_2O_3 and H_2O, both stable compounds.

b. Neither BCl_3 nor water is a powerful oxidant or reductant, so a redox reaction is unlikely; a hydrolysis reaction is more probable. Nonmetal halides are acidic and react with water to form a solution of the hydrohalic acid and a nonmetal oxide or hydroxide. In this case, the most probable boron-containing product is boric acid [$B(OH)_3$].

c. We normally expect a boron trihalide to behave like a Lewis acid. In this case, however, the other reactant is elemental hydrogen, which usually acts as a reductant. The iodine atoms in BI_3 are in the lowest accessible oxidation state (−1), and boron is in the +3 oxidation state. Consequently, we can write a redox reaction in which hydrogen is oxidized and boron is reduced. Because compounds of boron in lower oxidation states are rare, we expect that boron will be reduced to elemental boron. The other product of the reaction must therefore be HI.

Exercise

Predict the products of the reactions and write a balanced chemical equation for each reaction.

a. $B_2H_6(g) + H_2O(l) \text{ - } \rightarrow \text{D}$

a. $BBr_3(l) + O_2(g) \rightarrow$

a. $B_2O_3(s) + Ca(s) \text{ - } \rightarrow \text{D}$

Answer: *a.* $B_2H_6(g) + H_2O(l) \text{ - } \rightarrow \text{D } 2B(OH)_3(s) + 6H_2(g)$

$BBr_3(l) + O_2(g) \rightarrow$ no reaction *a. b.* $6B_2O_3(s) + 18Ca(s) \text{ - } \rightarrow \text{D } B_{12}(s) + 18CaO(s)$

a. Reactions and Compounds of the Heavier Group 13 Elements

All four of the heavier group 13 elements (Al, Ga, In, and Tl) react readily with the halogens to form compounds with a 1:3 stoichiometry:

Equation 22.10

$2M(s) + 3X_2(s,l,g) \rightarrow 2MX_3(s) \text{ or } M_2X_6$

The reaction of Tl with iodine is an exception: although the product has the stoichiometry TlI_3, it is *not* thallium(III) iodide, but rather a thallium(I) compound, the Tl^+ salt of the triiodide ion (I_3^-). This compound forms because iodine is not a powerful enough oxidant to oxidize thallium to the +3 oxidation state.

Of the halides, only the fluorides exhibit behavior typical of an ionic compound: they have high melting points (>950°C) and low solubility in nonpolar solvents. In contrast, the trichorides, tribromides, and triiodides of aluminum, gallium, and indium, as well as $TlCl_3$ and $TlBr_3$, are more covalent in character and form halogen-bridged dimers (part (b) in Figure 22.4 "The Structures of Diborane (B"). Although the structure of these dimers is similar to that of diborane (B_2H_6), the bonding can be described in terms of electron-pair bonds rather than the delocalized electron-deficient bonding found in diborane. Bridging halides are poor electron-pair donors, so the group 13 trihalides are potent Lewis acids that react readily with Lewis bases, such as amines, to form a Lewis acid–base adduct:

Equation 22.11

$$Al_2Cl_6(soln) + 2(CH_3)_3N(soln) \rightarrow 2(CH_3)_3N{:}AlCl_3(soln)$$

In water, the halides of the group 13 metals hydrolyze to produce the metal hydroxide [$M(OH)_3$]:

Equation 22.12

$$MX_3(s) + 3H_2O(l) \rightarrow M(OH)_3(s) + 3HX(aq)$$

In a related reaction, $Al_2(SO_4)_3$ is used to clarify drinking water by the precipitation of hydrated $Al(OH)_3$, which traps particulates. The halides of the heavier metals (In and Tl) are less reactive with water because of their lower charge-to-radius ratio. Instead of forming hydroxides, they dissolve to form the hydrated metal complex ions: $[M(H_2O)_6]^{3+}$.

Note the Pattern

Of the group 13 halides, only the fluorides behave as typical ionic compounds.

Note the Pattern

Group 13 trihalides are potent Lewis acids that react with Lewis bases to form a Lewis acid–base adduct.

Like boron (Equation 22.7), all the heavier group 13 elements react with excess oxygen at elevated temperatures to give the trivalent oxide (M_2O_3), although Tl_2O_3 is unstable:

Equation 22.13

$$4M(s) + 3O2(g) \rightarrow D2M2O3(s)$$

Aluminum oxide (Al_2O_3), also known as alumina, is a hard, high-melting-point, chemically inert insulator used as a ceramic and as an abrasive in sandpaper and toothpaste. Replacing a small number of Al^{3+} ions in crystalline alumina with Cr^{3+}ions forms the gemstone ruby, whereas replacing Al^{3+} with a mixture of Fe^{2+}, Fe^{3+}, and Ti^{4+} produces blue sapphires. The gallium oxide compound $MgGa_2O_4$ gives the brilliant green light familiar to anyone who has ever operated a xerographic copy machine. All the oxides dissolve

in dilute acid, but Al_2O_3 and Ga_2O_3 are amphoteric, which is consistent with their location along the diagonal line of the periodic table, also dissolving in concentrated aqueous base to form solutions that contain $M(OH)_4^-$ ions.

Aluminum, gallium, and indium also react with the other group 16 elements (chalcogens) to form chalcogenides with the stoichiometry M_2Y_3. However, because Tl(III) is too strong an oxidant to form a stable compound with electron-rich anions such as S^{2-}, Se^{2-}, and Te^{2-}, thallium forms only the thallium(I) chalcogenides with the stoichiometry Tl_2Y. Only aluminum, like boron, reacts directly with N_2 (at very high temperatures) to give AlN, which is used in transistors and microwave devices as a nontoxic heat sink because of its thermal stability; GaN and InN can be prepared using other methods. All the metals, again except Tl, also react with the heavier group 15 elements (pnicogens) to form the so-called III–V compounds, such as GaAs. These are semiconductors, whose electronic properties, such as their band gaps, differ from those that can be achieved using either pure or doped group 14 elements. (For more information on band gaps, see Chapter 12 "Solids", Section 12.6 "Bonding in Metals and Semiconductors".) For example, nitrogen- and phosphorus-doped gallium arsenide ($GaAs_{1-x-y}P_xN_y$) is used in the displays of calculators and digital watches.

Note the Pattern

All group 13 oxides dissolve in dilute acid, but Al_2O_3 and Ga_2O_3 are amphoteric.

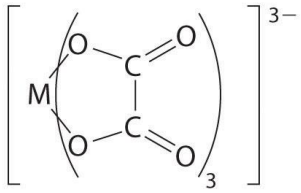
Unlike boron, the heavier group 13 elements do not react directly with hydrogen. Only the aluminum and gallium hydrides are known, but they must be prepared indirectly; AlH_3 is an insoluble, polymeric solid that is rapidly decomposed by water, whereas GaH_3 is unstable at room temperature.

Complexes of Group 13 Elements

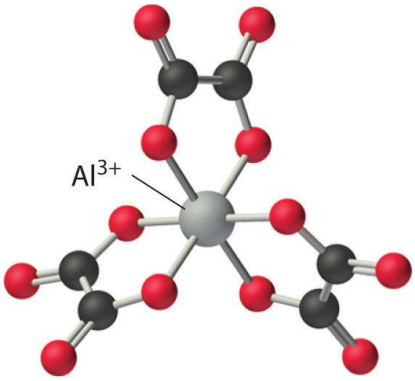
Boron has a relatively limited tendency to form complexes, but aluminum, gallium, indium, and, to some extent, thallium form many complexes. Some of the simplest are the hydrated metal ions $[M(H_2O)_6^{3+}]$, which are relatively strong Brønsted–Lowry acids that can lose a proton to form the $M(H_2O)_5(OH)^{2+}$ ion:

Equation 22.14

$$[M(H_2O)_6]^{3+}(aq) \rightarrow M(H_2O)_5(OH)^{2+}(aq) + H^+(aq)$$



Oxalate ion



Al^{3+}–oxalate complex

Group 13 metal ions also form stable complexes with species that contain two or more negatively charged groups, such as the oxalate ion. The stability of such complexes increases as the number of coordinating groups provided by the ligand increases.

EXAMPLE 2

For each reaction, explain why the given products form.

a. *a.* $2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(l) + Al_2O_3(s)$

$2Ga(s) + 6H_2O(l) + 2OH^-(aq) \rightarrow 3H_2(g) + 2Ga(OH)_4^-(aq)$

a. b. $In_2Cl_6(s) \rightarrow H2O(l)\ 2In^{3+}(aq) + 6Cl^-(aq)$

b. **Given:** balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the reaction products form.

Solution:

a. Aluminum is an active metal and a powerful reductant, and Fe_2O_3 contains Fe(III), a potential oxidant. Hence a redox reaction is probable, producing metallic Fe and Al_2O_3.

Because Al is a main group element that lies above Fe, which is a transition element, it should be a more active metal than Fe. Thus the reaction should proceed to the right. In fact, this is the thermite reaction, which is so vigorous that it produces molten Fe and can be used for welding. (For more information on the thermite reaction, see Chapter 5 "Energy Changes in Chemical Reactions", Section 5.2 "Enthalpy".)

b. Gallium lies immediately below aluminum in the periodic table and is amphoteric, so it will dissolve in either acid or base to produce hydrogen gas. Because gallium is similar to aluminum in many of its properties, we predict that gallium will dissolve in the strong base.

c. The metallic character of the group 13 elements increases with increasing atomic number. Indium trichloride should therefore behave like a typical metal halide, dissolving in water to form the hydrated cation.

Exercise

Predict the products of the reactions and write a balanced chemical equation for each reaction.

a. $LiH(s) + Al_2Cl_6(soln) \rightarrow$

b. $Al_2O_3(s) + OH^-(aq) \rightarrow$

c. $a.\ \ Al(s) + N_2(g)\ \text{-} \rightarrow \text{D}$

d. $Ga_2Cl_6(soln) + Cl^-(soln) \rightarrow$

Answer:

a. $8LiH(s) + Al_2Cl_6(soln) \rightarrow 2LiAlH_4(soln) + 6LiCl(s)$

b. $Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2Al(OH)_4^-(aq)$

c. $a.\ \ 2Al(s) + N_2(g)\ \text{-} \rightarrow \text{D}\ 2AlN(s)$

d. $Ga_2Cl_6(soln) + 2Cl^-(soln) \rightarrow 2GaCl_4^-(soln)$

Summary

Isolation of the group 13 elements requires a large amount of energy because compounds of the group 13 elements with oxygen are thermodynamically stable. Boron behaves chemically like a nonmetal, whereas its heavier congeners exhibit metallic behavior. Many of the inconsistencies observed in the properties of the group 13 elements can be explained by the increase in Z_{eff} that arises from poor shielding of the nuclear charge by the filled $(n - 1)d^{10}$ and $(n - 2)f^{14}$ subshells. Instead of forming a metallic lattice with delocalized

valence electrons, boron forms unique aggregates that contain multicenter bonds, including *metal borides*, in which boron is bonded to other boron atoms to form three-dimensional networks or *clusters* with regular geometric structures. All neutral compounds of the group 13 elements are electron deficient and behave like Lewis acids. The trivalent halides of the heavier elements form halogen-bridged dimers that contain electron-pair bonds, rather than the delocalized electron-deficient bonds characteristic of diborane. Their oxides dissolve in dilute acid, although the oxides of aluminum and gallium are amphoteric. None of the group 13 elements reacts directly with hydrogen, and the stability of the hydrides prepared by other routes decreases as we go down the group. In contrast to boron, the heavier group 13 elements form a large number of complexes in the +3 oxidation state.

KEY TAKEAWAYS

- Compounds of the group 13 elements with oxygen are thermodynamically stable.
- Many of the anomalous properties of the group 13 elements can be explained by the increase in Z_{eff} moving down the group.

CONCEPTUAL PROBLEMS

1. None of the group 13 elements was isolated until the early 19th century, even though one of these elements is the most abundant metal on Earth. Explain why the discovery of these elements came so late and describe how they were finally isolated.
2. Boron and aluminum exhibit very different chemistry. Which element forms complexes with the most ionic character? Which element is a metal? a semimetal? What single property best explains the difference in their reactivity?
3. The usual oxidation state of boron and aluminum is +3, whereas the heavier elements in group 13 have an increasing tendency to form compounds in the +1 oxidation state. Given that all group 13 elements have an ns^2np^1 electron configuration, how do you explain this difference between the lighter and heavier group 13 elements?
4. Do you expect the group 13 elements to be highly reactive in air? Why or why not?
5. Which of the group 13 elements has the least metallic character? Explain why.
6. Boron forms multicenter bonds rather than metallic lattices with delocalized valence electrons. Why does it prefer this type of bonding? Does this explain why boron behaves like a semiconductor rather than a metal? Explain your answer.

7. Because the B–N unit is isoelectronic with the C–C unit, compounds that contain these units tend to have similar chemistry, although they exhibit some important differences. Describe the differences in physical properties, conductivity, and reactivity of these two types of compounds.
8. Boron has a strong tendency to form clusters. Does aluminum have this same tendency? Why or why not?
9. Explain why a B–O bond is much stronger than a B–C bond.
10. The electron affinities of boron and aluminum are −27 and −42 kJ/mol, respectively. Contrary to the usual periodic trends, the electron affinities of the remaining elements in group 13 are between those of B and Al. How do you explain this apparent anomaly?
11. The reduction potentials of B and Al in the +3 oxidation state are −0.87 V and −1.66 V, respectively. Do you expect the reduction potentials of the remaining elements of group 13 to be greater than or less than these values? How do you explain the differences between the expected values and those given in Table 22.1 "Selected Properties of the Group 13 Elements"?
12. The compound Al_2Br_6 is a halide-bridged dimer in the vapor phase, similar to diborane (B_2H_6). Draw the structure of Al_2Br_6 and then compare the bonding in this compound with that found in diborane. Explain the differences.
13. The compound AlH_3 is an insoluble, polymeric solid that reacts with strong Lewis bases, such as Me_3N, to form adducts with 10 valence electrons around aluminum. What hybrid orbital set is formed to allow this to occur?

ANSWERS

1. The high stability of compounds of the group 13 elements with oxygen required powerful reductants such as metallic potassium to be isolated. Al and B were initially prepared by reducing molten $AlCl_3$ and B_2O_3, respectively, with potassium.
2.
3.
4.
5. Due to its low electronegativity and small size, boron is an unreactive semimetal rather than a metal.
6.

7. The B–N bond is significantly more polar than the C–C bond, which makes B–N compounds more reactive and generally less stable than the corresponding carbon compounds. Increased polarity results in less delocalization and makes the planar form of BN less conductive than graphite.
8.
9. Partial pi bonding between O and B increases the B–O bond strength.
10.
11. Periodic trends predict that the cations of the heavier elements should be easier to reduce, so the elements should have less negative reduction potentials. In fact, the reverse is observed because the heavier elements have anomalously high Z_{eff} values due to poor shielding by filled $(n - 1)d$ and $(n - 2)f$ subshells.
12.
13. dsp^3

STRUCTURE AND REACTIVITY

1. Is $B(OH)_3$ a strong or a weak acid? Using bonding arguments, explain why.
2. Using bonding arguments, explain why organoaluminum compounds are expected to be potent Lewis acids that react rapidly with weak Lewis bases.
3. Imagine that you are studying chemistry prior to the discovery of gallium, element 31. Considering its position in the periodic table, predict the following properties of gallium:

a. chemical formulas of its most common oxide, most common chloride, and most common hydride

b. solubility of its oxide in water and the acidity or basicity of the resulting solution

c. the principal ion formed in aqueous solution

4. The halides of Al, Ga, In, and Tl dissolve in water to form acidic solutions containing the hydrated metal ions, but only the halides of aluminum and gallium dissolve in aqueous base to form soluble metal-hydroxide complexes. Show the formulas of the soluble metal–hydroxide complexes and of the hydrated metal ions. Explain the difference in their reactivities.
5. Complete and balance each chemical equation.

a. $a.\quad BCl_3(g) + H_2(g) \text{ - } \rightarrow \text{D}$

b. $6C_2H_4(g) + B_2H_6(g) \rightarrow$

c. $B_2H_6(g) + 3Cl_2(g) \rightarrow$

d. $B_2H_6(g) + 2(C_2H_5)_2S(g) \rightarrow$

6. Complete and balance each chemical equation.

a. $a.\quad BBr_3(g) + H_2(g) - \rightarrow D$

b. $BF_3(g) + F^-(g) \rightarrow$

c. $LiH(s) + B_2H_6(g) \rightarrow$

d. $B(OH)_3(s) + NaOH(aq) \rightarrow$

7. Write a balanced chemical equation for each reaction.

a. the dissolution of Al_2O_3 in dilute acid

b. the dissolution of Ga_2O_3 in concentrated aqueous base

c. the dissolution of Tl_2O in concentrated aqueous acid

d. $Ga(l) + S_8(s)$

e. $Tl(s) + H_2S(g)$

8. Write a balanced chemical equation for the reaction that occurs between Al and each species.

a. Cl_2

b. O_2

c. S

d. N_2

e. H_2O

f. $H^+(aq)$

9. Write a balanced chemical equation that shows how you would prepare each compound from its respective elements or other common compounds.

a. In_2I_6

b. $B(OH)_3$

c. Ga_2O_3

d. $[Tl(H_2O)_6]^{3+}$

e. $Al(OH)_4^-$

f. In_4C_3

10. Write a balanced chemical equation that shows how you would prepare each compound from its respective elements or other common compounds.

a. BCl_3

b. $InCl_3$

c. Tl_2S

d. $Al(OH)_3$

e. In_2O_3

f. AlN

11. Diborane is a spontaneously flammable, toxic gas that is prepared by reacting $NaBH_4$with BF_3. Write a balanced chemical equation for this reaction.

12. Draw the Lewis electron structure of each reactant and product in each chemical equation. Then describe the type of bonding found in each reactant and product.

13. *a.* $4B(s) + 3O_2(g) \rightarrow 2B_2O_3(s)$

14. Draw the Lewis electron structure of each reactant and product in each chemical equation. Then describe the type of bonding found in each reactant and product.

a. $B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(l)$

b. $B_2H_6(g) + 6CH_3CH{=}CH_2(g) \rightarrow 2[B(CH_2CH_2CH_3)_3](l)$

ANSWERS

1.

2.

3.

4.

5.

a. *a.* $12BCl_3(g) + 18H_2(g) \rightarrow B_{12}(s) + 36HCl(g)$ $6C_2H_4(g) + B_2H_6(g) \rightarrow 2B(C_2H_5)_3(l)$

b. $6B_2H_6(g) + 18Cl_2(g) \rightarrow B_{12}(s) + 36HCl(g)$

c. $B_2H_6(g) + 2(C_2H_5)_2S(g) \rightarrow 2H_3B{\cdot}S(C_2H_5)_2(l)$

6.

7.

a. $Al_2O_3(s) + 6H_3O^+(aq) + 3H_2O(l) \rightarrow 2Al(H_2O)_6^{3+}(aq)$

b. $Ga_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2Ga(OH)_4^-(aq)$

c. $Tl_2O(s) + 2H^+(aq) + 9H_2O(l) \rightarrow 2Tl(H_2O)_6^+(aq)$

d. $16Ga(l) + 3S_8(s) \rightarrow 8Ga_2S_3(s)$

e. $2Tl(s) + H_2S(g) \rightarrow Tl_2S(s) + H_2(g)$

8.

9.

a. $a.\quad 2In(s) + 3I_2(s) - \rightarrow D\ In_2I_6(s) B_{12}(s) + 18Cl_2(g) \rightarrow 12BCl_3(l)$

$BCl_3(l) + 3H_2O(l) \rightarrow B(OH)_3(aq) + 3HCl(aq)$

b. $4Ga(l) + 3O_2(g) - \rightarrow D\ 2Ga_2O_3(s)$

c. $2Tl(s) + 3Cl_2(g) \rightarrow 2TlCl_3(s)$; $TlCl_3(s) + 6H_2O(l) \rightarrow Tl(H_2O_6)^{3+}(aq) + 3Cl^-(aq)$

d. $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$; $2Al(s) + 2NaOH(aq) + 6H_2O(l) \rightarrow 2Al(OH)_4^- + 3H_2(g) + 2Na^+(aq)$

22.2 The Elements of Group 14

LEARNING OBJECTIVE

1. To understand the trends in properties and reactivity of the group 14 elements.

The elements of group 14 show a greater range of chemical behavior than any other family in the periodic table. Three of the five elements—carbon, tin, and lead—have been known since ancient times. For example, some of the oldest known writings are Egyptian hieroglyphics written on papyrus with ink made from *lampblack*, a finely divided carbon soot produced by the incomplete combustion of hydrocarbons (Figure 22.5 "Very Small Particles of Noncrystalline Carbon Are Used to Make Black Ink").*Activated carbon* is an even more finely divided form of carbon that is produced from the thermal decomposition of organic materials, such as sawdust. Because it adsorbs many organic and sulfur-containing compounds, activated carbon is used to decolorize foods, such as sugar, and to purify gases and wastewater.

(a) Since ancient times, ink sticks have been the major source of black ink in Asia. Plant oils or resinous woods such as pine are burned, and the resulting soot (lampblack) is collected, mixed with binders such as animal glues and minerals, compressed into a solid stick, and allowed to dry. Liquid ink is made by rubbing the ink stick against the surface of a special stone ink dish with small

amounts of water. (b) A 19th-century Japanese painting illustrates how ink is made from an ink stick.

Tin and lead oxides and sulfides are easily reduced to the metal by heating with charcoal, a discovery that must have occurred by accident when prehistoric humans used rocks containing their ores for a cooking fire. However, because tin and copper ores are often found together in nature, their alloy—*bronze*—was probably discovered before either element, a discovery that led to the Bronze Age. The heaviest element in group 14, lead, is such a soft and malleable metal that the ancient Romans used thin lead foils as writing tablets, as well as lead cookware and lead pipes for plumbing. (Recall that the atomic symbols for tin and lead come from their Latin names: Sn for*stannum* and Pb for *plumbum*.)

Although the first glasses were prepared from silica (silicon oxide, SiO_2) around 1500 BC, elemental silicon was not prepared until 1824 because of its high affinity for oxygen. Jöns Jakob Berzelius was finally able to obtain amorphous silicon by reducing Na_2SiF_6 with molten potassium. The crystalline element, which has a shiny blue-gray luster, was not isolated until 30 yr later. The last member of the group 14 elements to be discovered was germanium, which was found in 1886 in a newly discovered silver-colored ore by the German chemist Clemens Winkler, who named the element in honor of his native country.

Preparation and General Properties of the Group 14 Elements

The natural abundance of the group 14 elements varies tremendously. Elemental carbon, for example, ranks only 17th on the list of constituents of Earth's crust. Pure graphite is obtained by reacting coke, an amorphous form of carbon used as a reductant in the production of steel, with silica to give silicon carbide (SiC). This is then thermally decomposed at very high temperatures (2700°C) to give graphite:

Equation 22.15

$$SiO2(s) + 3C(s) \rightarrow DSiC(s) + 2CO(g)$$ *Equation 22.16*

$$SiC(s) \rightarrow DSi(s) + C(graphite)$$

One allotrope of carbon, diamond, is metastable under normal conditions, *with a* $DG \square fof$ 2.9 kJ/mol versus graphite. At pressures greater than 50,000 atm, however, the diamond structure is favored and is the most stable form of carbon. Because the structure of diamond is more compact than that of graphite, its density is significantly higher (3.51 g/cm^3 versus 2.2 g/cm^3). Because of its high thermal conductivity, diamond powder is used to transfer heat in electronic devices.

The most common sources of diamonds on Earth are ancient volcanic pipes that contain a rock called *kimberlite*, a lava that solidified rapidly from deep inside the Earth. Most kimberlite formations, however, are much newer than the diamonds they contain. In fact, the relative amounts of different carbon isotopes in diamond show that diamond is a chemical and geological "fossil" older than our solar system, which means that diamonds on Earth predate the existence of our sun. Thus diamonds were most likely created deep inside Earth from primordial grains of graphite present when Earth was formed (part (a) in Figure 22.6 "Crystalline Samples of Carbon and Silicon, the Lightest Group 14 Elements"). Gem-quality diamonds can now be produced synthetically and have chemical, optical, and physical characteristics identical to those of the highest-grade natural diamonds.

(a) The 78.86-carat Ahmadabad diamond, a historic Indian gem purchased in Gujarat in the 17th century by the French explorer Jean-Baptiste Tavernier and sold in 1995 for $4.3 million, is a rare example of a large single crystal of diamond, the less-stable allotrope of carbon. (b) Large single crystals of highly purified silicon are the basis of the modern electronics industry. They are sliced into very thin wafers that are highly polished and then cut into smaller pieces for use as chips.

Although oxygen is the most abundant element on Earth, the next most abundant is silicon, the next member of group 14. Pure silicon is obtained by reacting impure silicon with Cl_2 to give $SiCl_4$, followed by the fractional distillation of the impure $SiCl_4$ and reduction with H_2:

Equation 22.17

$$SiCl4(l) + 2H2(g) \rightarrow \text{D}Si(s) + 4HCl(g)$$

Several million tons of silicon are annually produced with this method. Amorphous silicon containing residual amounts of hydrogen is used in photovoltaic devices that convert light to electricity, and silicon-based solar cells are used to power pocket calculators, boats, and highway signs, where access to electricity by conventional methods is difficult or expensive. Ultrapure silicon and germanium form the basis of the modern electronics industry (part (b) in Figure 22.6 "Crystalline Samples of Carbon and Silicon, the Lightest Group 14 Elements").

In contrast to silicon, the concentrations of germanium and tin in Earth's crust are only 1–2 ppm. The concentration of lead, which is the end product of the nuclear decay of many radionuclides, is 13 ppm, making lead by far the most abundant of the heavy group 14 elements. (For more information on

radionuclides, see Chapter 20 "Nuclear Chemistry".) No concentrated ores of germanium are known; like indium, germanium is generally recovered from flue dusts obtained by processing the ores of metals such as zinc. Because germanium is essentially transparent to infrared radiation, it is used in optical devices. Tin and lead are soft metals that are too weak for structural applications, but because tin is flexible, corrosion resistant, and nontoxic, it is used as a coating in food packaging. A “tin can,” for example, is actually a steel can whose interior is coated with a thin layer (1–2 μm) of metallic tin. Tin is also used in superconducting magnets and low-melting-point alloys such as solder and pewter. Pure lead is obtained by heating galena (PbS) in air and reducing the oxide (PbO) to the metal with carbon, followed by electrolytic deposition to increase the purity:

Equation 22.18

$$PbS(s) + 3 2 O2(g) \rightarrow \mathrm{D} PbO(s) + SO2(g)$$

Equation 22.19

$$PbO(s) + C(s) \rightarrow \mathrm{D} Pb(l) + CO(g) \text{ or}$$

Equation 22.20

$$PbO(s) + CO(g) \rightarrow \mathrm{D} Pb(l) + CO2(g)$$

By far the single largest use of lead is in lead storage batteries. (For more information on batteries, see Chapter 19 "Electrochemistry".)

As you learned in Chapter 7 "The Periodic Table and Periodic Trends", the group 14 elements all have ns^2np^2 valence electron configurations. All form compounds in which they formally lose either the two *np* and the two *ns* valence electrons or just the two *np* valence electrons, giving a +4 or +2 oxidation state, respectively. Because covalent bonds decrease in strength with increasing atomic size and the ionization energies for the heavier elements of the group are higher than expected due to a higher Z_{eff}, the relative stability of the +2 oxidation state increases smoothly from carbon to lead.

Note the Pattern

The relative stability of the +2 oxidation state increases, and the tendency to form catenated compounds decreases, from carbon to lead in group 14.

Recall that many carbon compounds contain multiple bonds formed by π overlap of singly occupied 2*p* orbitals on adjacent atoms. (For more information on atomic orbitals, see Chapter 9 "Molecular Geometry and Covalent Bonding Models".) Compounds of silicon, germanium, tin, and lead with the same

stoichiometry as those of carbon, however, tend to have different structures and properties. For example, $CO_2$is a gas that contains discrete O=C=O molecules, whereas the most common form of SiO_2 is the high-melting solid known as quartz, the major component of sand. Instead of discrete SiO_2 molecules, quartz contains a three-dimensional network of silicon atoms that is similar to the structure of diamond but with an oxygen atom inserted between each pair of silicon atoms. Thus each silicon atom is linked to four other silicon atoms by bridging oxygen atoms. (For more information on the properties of solids, see Chapter 12 "Solids", Section 12.1 "Crystalline and Amorphous Solids".) The tendency to catenate—to form chains of like atoms—decreases rapidly as we go down group 14 because bond energies for both the E–E and E–H bonds decrease with increasing atomic number (where E is any group 14 element). Consequently, inserting a CH_2 group into a linear hydrocarbon such as *n*-hexane is exergonic ($\Delta G^\circ = -45$ kJ/mol), whereas inserting an SiH_2 group into the silicon analogue of *n*-hexane (Si_6H_{14}) actually costs energy ($\Delta G^\circ \approx +25$ kJ/mol). As a result of this trend, the thermal stability of catenated compounds decreases rapidly from carbon to lead.

In Table 22.2 "Selected Properties of the Group 14 Elements" we see, once again, that there is a large difference between the lightest element (C) and the others in size, ionization energy, and electronegativity. As in group 13, the second and third elements (Si and Ge) are similar, and there is a reversal in the trends for some properties, such as ionization energy, between the fourth and fifth elements (Sn and Pb). As for group 13, these effects can be explained by the presence of filled $(n - 1)d$ and $(n - 2)f$ subshells, whose electrons are relatively poor at screening the outermost electrons from the higher nuclear charge.

Table 22.2 Selected Properties of the Group 14 Elements

Property	Carbon	Silicon	Germanium	Tin	Lead
atomic symbol	C	Si	Ge	Sn	Pb
atomic number	6	14	32	50	82
atomic mass (amu)	12.01	28.09	72.64	118.71	207.2
valence electron configuration*	$2s^2 2p^2$	$3s^2 3p^2$	$4s^2 4p^2$	$5s^2 5p^2$	$6s^2 6p^2$
melting point/boiling point (°C)	4489 (at 10.3 MPa)/3825	1414/3265	939/2833	232/2602	327/1749
density (g/cm^3) at 25°C	2.2 (graphite), 3.51 (diamond)	2.33	5.32	7.27(white)	11.30
atomic radius (pm)	77 (diamond)	111	125	145	154

Property	Carbon	Silicon	Germanium	Tin	Lead
first ionization energy (kJ/mol)	1087	787	762	709	716
most common oxidation state	+4	+4	+4	+4	+4
ionic radius (pm)†	≈29	≈40	53	69	77.5
electron affinity (kJ/mol)	−122	−134	−119	−107	−35
electronegativity	2.6	1.9	2.0	2.0	1.8
standard reduction potential ($E°$, V) (for $EO_2 \rightarrow E$ in acidic solution)	0.21	−0.86	−0.18	−0.12	0.79
product of reaction with O_2	CO_2, CO	SiO_2	GeO_2	SnO_2	PbO
type of oxide	acidic (CO_2)	acidic neutral (CO)	amphoteric	amphoteric	amphoteric
product of reaction with N_2	none	Si_3N_4	none	Sn_3N_4	none
product of reaction with X_2‡	CX_4	SiX_4	GeX_4	SnX_4	PbX_2
product of reaction with H_2	CH_4	none	none	none	none
***The configuration shown does not include filled *d* and *f* subshells.**					
†The values cited are for six-coordinate +4 ions in the most common oxidation state, except for C^{4+} and Si^{4+}, for which values for the four-coordinate ion are estimated.					
‡X is Cl, Br, or I. Reaction with F_2 gives the tetrafluorides (EF_4) for all group 14 elements, where E represents any group 14 element.					

Note the Pattern

The group 14 elements follow the same pattern as the group 13 elements in their periodic properties.

Reactions and Compounds of Carbon

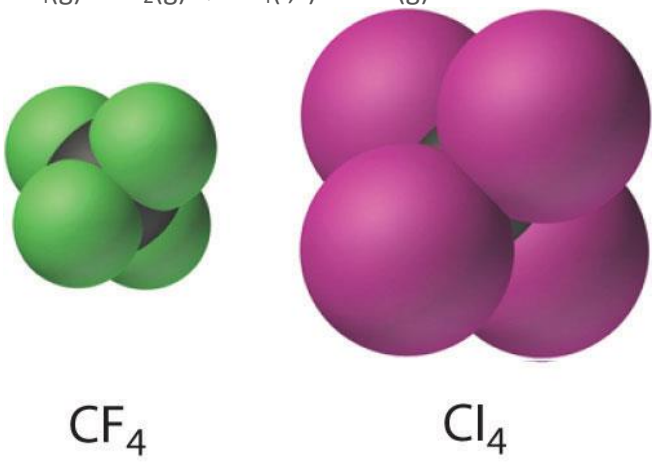
Carbon is the building block of all organic compounds, including biomolecules, fuels, pharmaceuticals, and plastics, whereas inorganic compounds of carbon include metal carbonates, which are found in substances as diverse as fertilizers and antacid tablets, halides, oxides, carbides, and carboranes. Like boron in group 13, the chemistry of carbon differs sufficiently from that of its heavier congeners to merit a separate discussion.

The structures of the allotropes of carbon—diamond, graphite, fullerenes, and nanotubes—are distinct, but they all contain simple electron-pair bonds (Figure 7.18 "Four Allotropes of Carbon"). Although it was originally believed that fullerenes were a new form of carbon that could be prepared only in the

laboratory, fullerenes have been found in certain types of meteorites. Another possible allotrope of carbon has also been detected in impact fragments of a carbon-rich meteorite; it appears to consist of long chains of carbon atoms linked by alternating single and triple bonds, $(-C{\equiv}C-C{\equiv}C-)_n$. Carbon nanotubes ("buckytubes") are being studied as potential building blocks for ultramicroscale detectors and molecular computers and as tethers for space stations. They are currently used in electronic devices, such as the electrically conducting tips of miniature electron guns for flat-panel displays in portable computers. Although all the carbon tetrahalides (CX_4) are known, they are generally not obtained by the direct reaction of carbon with the elemental halogens (X_2) but by indirect methods such as the following reaction, where X is Cl or Br:

Equation 22.21

$$CH_4(g) + 4X_2(g) \rightarrow CX_4(l,s) + 4HX(g)$$



The carbon tetrahalides all have the tetrahedral geometry predicted by the valence-shell electron-pair repulsion (VSEPR) model, as shown for CCl_4 and CI_4. Their stability decreases rapidly as the halogen increases in size because of poor orbital overlap and increased crowding. Because the C–F bond is about 25% stronger than a C–H bond, fluorocarbons are thermally and chemically more stable than the corresponding hydrocarbons, while having a similar hydrophobic character. A polymer of tetrafluoroethylene ($F_2C{=}CF_2$), analogous to polyethylene, is the nonstick Teflon lining found on many cooking pans, and similar compounds are used to make fabrics stain resistant (such as Scotch-Gard) or waterproof but breathable (such as Gore-Tex).

Note the Pattern

The stability of the carbon tetrahalides decreases with increasing size of the halogen due to increasingly poor orbital overlap and crowding.

Carbon reacts with oxygen to form either CO or CO_2, depending on the stoichiometry. Carbon monoxide is a colorless, odorless, and poisonous gas that reacts with the iron in hemoglobin to form an Fe–CO unit, which prevents hemoglobin from binding, transporting, and releasing oxygen in the blood (see Figure 23.26 "Binding of O" for myoglobin). In the laboratory, carbon monoxide can be prepared on a small scale by dehydrating formic acid with concentrated sulfuric acid:

Equation 22.22

$$HCO2H(l) - \rightarrow - - - - H2SO4(l)CO(g) + H3O + (aq) + HSO - 4$$

Carbon monoxide also reacts with the halogens to form the oxohalides (COX_2). Probably the best known of these is phosgene ($Cl_2C{=}O$), which is highly poisonous and was used as a chemical weapon during World War I:

Equation 22.23

$$CO(g) + Cl2(g) \rightarrow DCl2C = O(g)$$

Despite its toxicity, phosgene is an important industrial chemical that is prepared on a large scale, primarily in the manufacture of polyurethanes.

Carbon dioxide can be prepared on a small scale by reacting almost any metal carbonate or bicarbonate salt with a strong acid. As is typical of a nonmetal oxide, CO_2reacts with water to form acidic solutions containing carbonic acid (H_2CO_3). In contrast to its reactions with oxygen, reacting carbon with sulfur at high temperatures produces only carbon disulfide (CS_2):

Equation 22.24

$$C(s) + 2S(g) \rightarrow DCS2(g)$$

The selenium analogue CSe_2 is also known. Both have the linear structure predicted by the VSEPR model, and both are vile smelling (and in the case of CSe_2, highly toxic), volatile liquids. The sulfur and selenium analogues of carbon monoxide, CS and CSe, are unstable because the C≡Y bonds (Y is S or Se) are much weaker than the C≡O bond due to poorer π orbital overlap.

Note the Pattern

Pi bonds between carbon and the heavier chalcogenides are weak due to poor orbital overlap.

Binary compounds of carbon with less electronegative elements are called *carbides*. The chemical and physical properties of carbides depend strongly on the identity of the second element, resulting in three general classes: ionic carbides, interstitial carbides, and covalent carbides. The reaction of carbon at high

temperatures with electropositive metals such as those of groups 1 and 2 and aluminum produces *ionic carbides*, which contain discrete metal cations and carbon anions. The identity of the anions depends on the size of the second element. For example, smaller elements such as beryllium and aluminum give *methides* such as Be_2C and Al_4C_3, which formally contain the C^{4-} ion derived from methane (CH_4) by losing all four H atoms as protons. In contrast, larger metals such as sodium and calcium give carbides with stoichiometries of Na_2C_2 and CaC_2. Because these carbides contain the C_4^{-} ion, which is derived from acetylene (HC≡CH) by losing both H atoms as protons, they are more properly called *acetylides*. As discussed in Chapter 21 "Periodic Trends and the ", Section 21.4 "The Alkaline Earth Metals (Group 2)", reacting ionic carbides with dilute aqueous acid results in protonation of the anions to give the parent hydrocarbons: CH_4 or C_2H_2. For many years, miners' lamps used the reaction of calcium carbide with water to produce a steady supply of acetylene, which was ignited to provide a portable lantern.

The reaction of carbon with most transition metals at high temperatures produces *interstitial carbides*. Due to the less electropositive nature of the transition metals, these carbides contain covalent metal–carbon interactions, which result in different properties: most interstitial carbides are good conductors of electricity, have high melting points, and are among the hardest substances known. Interstitial carbides exhibit a variety of nominal compositions, and they are often nonstoichiometric compounds whose carbon content can vary over a wide range. Among the most important are tungsten carbide (WC), which is used industrially in high-speed cutting tools, and cementite (Fe_3C), which is a major component of steel.

Elements with an electronegativity similar to that of carbon form *covalent carbides*, such as silicon carbide (SiC; Equation 22.15) and boron carbide (B_4C). These substances are extremely hard, have high melting points, and are chemically inert. For example, silicon carbide is highly resistant to chemical attack at temperatures as high as 1600°C. Because it also maintains its strength at high temperatures, silicon carbide is used in heating elements for electric furnaces and in variable-temperature resistors.

Note the Pattern

Carbides formed from group 1 and 2 elements are ionic. Transition metals form interstitial carbides with covalent metal–carbon interactions, and covalent carbides are chemically inert.

EXAMPLE 3

For each reaction, explain why the given product forms.

a. $CO(g) + Cl_2(g) \rightarrow Cl_2C{=}O(g)$

b. $CO(g) + BF_3(g) \rightarrow F_3B{:}C{\equiv}O(g)$

a. $Sr(s) + 2C(s) \text{ - } \rightarrow \text{D } SrC_2(s)$

Given: balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

Solution:

a. Because the carbon in CO is in an intermediate oxidation state (+2), CO can be either a reductant or an oxidant; it is also a Lewis base. The other reactant (Cl_2) is an oxidant, so we expect a redox reaction to occur in which the carbon of CO is further oxidized. Because Cl_2 is a two-electron oxidant and the carbon atom of CO can be oxidized by two electrons to the +4 oxidation state, the product is phosgene ($Cl_2C{=}O$).

b. Unlike Cl_2, BF_3 is not a good oxidant, even though it contains boron in its highest oxidation state (+3). Nor can BF_3 behave like a reductant. Like any other species with only six valence electrons, however, it is certainly a Lewis acid. Hence an acid–base reaction is the most likely alternative, especially because we know that CO can use the lone pair of electrons on carbon to act as a Lewis base. The most probable reaction is therefore the formation of a Lewis acid–base adduct.

c. Typically, both reactants behave like reductants. Unless one of them can also behave like an oxidant, no reaction will occur. We know that Sr is an active metal because it lies far to the left in the periodic table and that it is more electropositive than carbon. Carbon is a nonmetal with a significantly higher electronegativity; it is therefore more likely to accept electrons in a redox reaction. We conclude, therefore, that Sr will be oxidized, and C will be reduced. Carbon forms ionic carbides with active metals, so the reaction will produce a species formally containing either C^{4-} or C_2^{2-}. Those that contain C^{4-} usually involve small, highly charged metal ions, so Sr^{2+} will produce the acetylide (SrC_2) instead.

Exercise

Predict the products of the reactions and write a balanced chemical equation for each reaction.

a. $a.$ $C(s) + excess\ O_2(g) \text{ - } \rightarrow$ D

b. $C(s) + H_2O(l) \rightarrow$

c. $NaHCO_3(s) + H_2SO_4(aq) \rightarrow$

Answer:

a. $a.$ $C(s) + excess\ O_2(g) \text{ - } \rightarrow$ D $CO_2(g)$

b. $C(s) + H_2O(l) \rightarrow$ no reaction

c. $NaHCO_3(s) + H_2SO_4(aq) \rightarrow CO_2(g) + NaHSO_4(aq) + H_2O(l)$

Reactions and Compounds of the Heavier Group 14 Elements

Although silicon, germanium, tin, and lead in their +4 oxidation states often form binary compounds with the same stoichiometry as carbon, the structures and properties of these compounds are usually significantly different from those of the carbon analogues. Silicon and germanium are both semiconductors with structures analogous to diamond. Tin has two common allotropes: white (β) tin has a metallic lattice and metallic properties, whereas gray (α) tin has a diamond-like structure and is a semiconductor. The metallic β form is stable above 13.2°C, and the nonmetallic α form is stable below 13.2°C. Lead is the only group 14 element that is metallic in both structure and properties under all conditions.

Based on its position in the periodic table, we expect silicon to be amphoteric. In fact, it dissolves in strong aqueous base to produce hydrogen gas and solutions of silicates, but the only aqueous acid that it reacts with is hydrofluoric acid, presumably due to the formation of the stable SiF_6^{2-} ion. Germanium is more metallic in its behavior than silicon. For example, it dissolves in hot oxidizing acids, such as HNO_3 and H_2SO_4, but in the absence of an oxidant, it does not dissolve in aqueous base. Although tin has an even more metallic character than germanium, lead is the only element in the group that behaves purely as a metal. Acids do not readily attack it because the solid acquires a thin protective outer layer of a Pb^{2+} salt, such as $PbSO_4$.

All group 14 dichlorides are known, and their stability increases dramatically as the atomic number of the central atom increases. Thus CCl_2 is dichlorocarbene, a highly reactive, short-lived intermediate that can be made in solution but cannot be isolated in pure form using standard techniques; $SiCl_2$ can be isolated at very low temperatures, but it decomposes rapidly above −150°C, and $GeCl_2$ is relatively stable at

temperatures below 20°C. In contrast, $SnCl_2$ is a polymeric solid that is indefinitely stable at room temperature, whereas $PbCl_2$ is an insoluble crystalline solid with a structure similar to that of $SnCl_2$.

Note the Pattern

The stability of the group 14 dichlorides increases dramatically from carbon to lead.

Although the first four elements of group 14 form tetrahalides (MX_4) with all the halogens, only fluorine is able to oxidize lead to the +4 oxidation state, giving PbF_4. The tetrahalides of silicon and germanium react rapidly with water to give amphoteric oxides (where M is Si or Ge):

Equation 22.25

$$MX_4(s,l) + 2H_2O(l) \rightarrow MO_2(s) + 4HX(aq)$$

In contrast, the tetrahalides of tin and lead react with water to give hydrated metal ions.

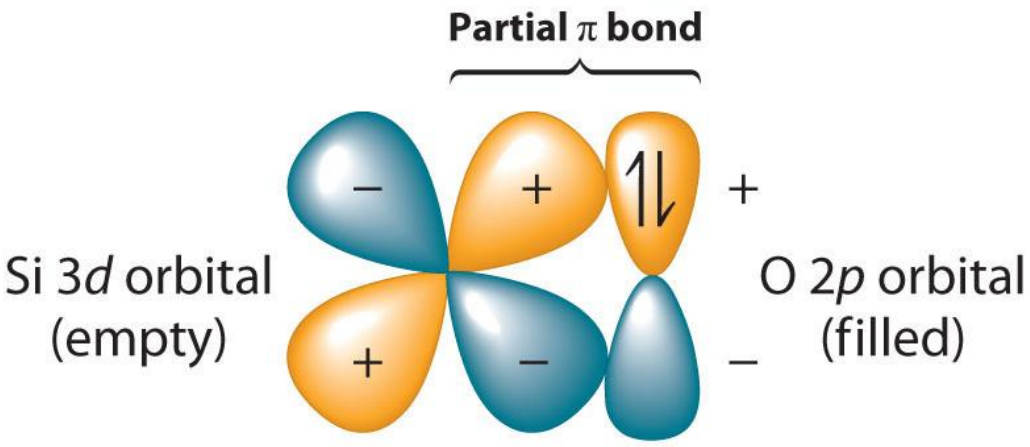
Because of the stability of its +2 oxidation state, lead reacts with oxygen or sulfur to form PbO or PbS, respectively, whereas heating the other group 14 elements with excess O_2 or S_8 gives the corresponding dioxides or disulfides, respectively. The dioxides of the group 14 elements become increasingly basic as we go down the group.

Note the Pattern

The dioxides of the group 14 elements become increasingly basic down the group.

Because the Si–O bond is even stronger than the C–O bond (~452 kJ/mol versus ~358 kJ/mol), silicon has a strong affinity for oxygen. The relative strengths of the C–O and Si–O bonds contradict the generalization that bond strengths decrease as the bonded atoms become larger. This is because we have thus far assumed that a formal single bond between two atoms can always be described in terms of a single pair of shared electrons. In the case of Si–O bonds, however, the presence of relatively low-energy, empty *d* orbitals on Si and nonbonding electron pairs in the *p* or *spn* hybrid orbitals of O results in a partial π bond (Figure 22.7 "Pi Bonding between Silicon and Oxygen"). Due to its partial π double bond character, the Si–O bond is significantly stronger and shorter than would otherwise be expected. A similar interaction with oxygen is also an important feature of the chemistry of the elements that follow silicon in the third period (P, S, and Cl). Because the Si–O bond is unusually strong, silicon–oxygen compounds dominate the chemistry of silicon.

Figure 22.7 Pi Bonding between Silicon and Oxygen

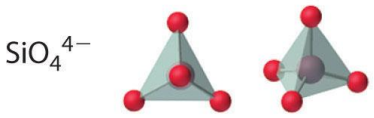


Silicon has relatively low-energy, empty 3d orbitals that can interact with filled 2phybrid orbitals on oxygen. This interaction results in a partial π bond in which both electrons are supplied by oxygen, giving the Si–O bond partial double bond character and making it significantly stronger (and shorter) than expected for a single bond.

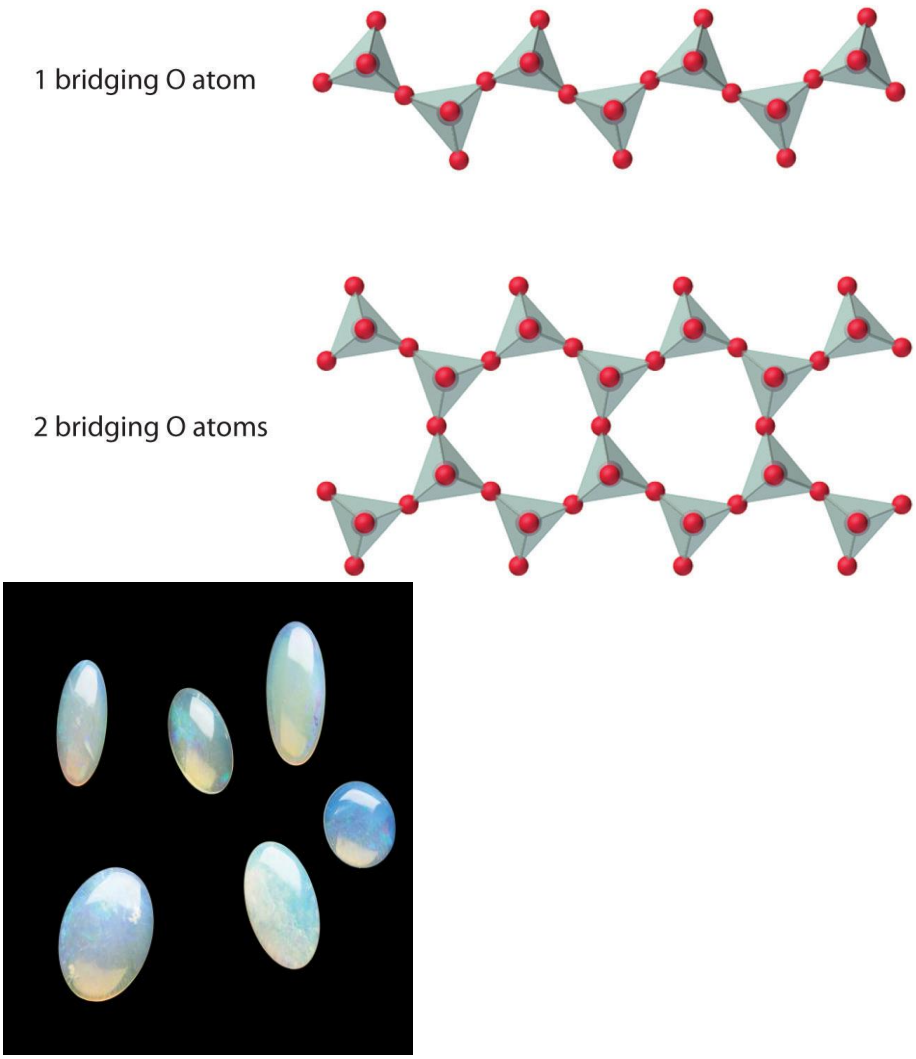
Note the Pattern

Because silicon–oxygen bonds are unusually strong, silicon–oxygen compounds dominate the chemistry of silicon.

Compounds with anions that contain only silicon and oxygen are called *silicates*, whose basic building block is the SiO_4^{4-} unit:



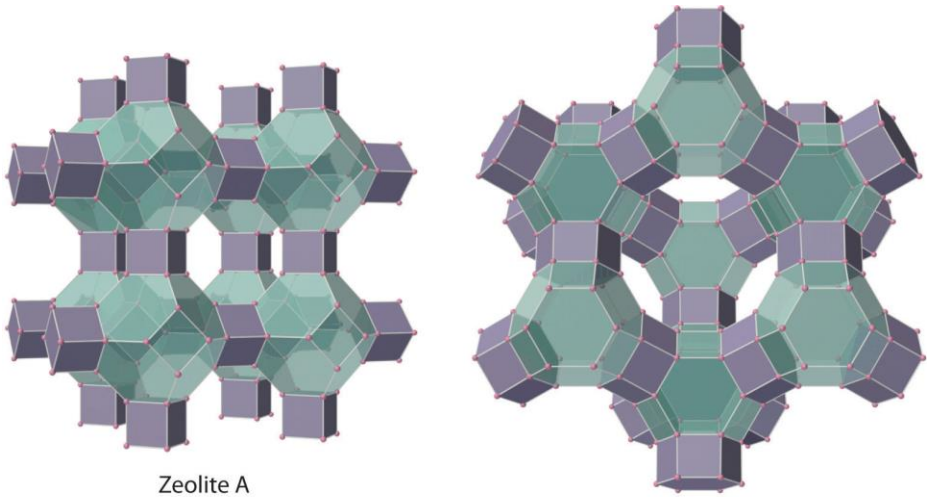
The number of oxygen atoms shared between silicon atoms and the way in which the units are linked vary considerably in different silicates. Converting one of the oxygen atoms from terminal to bridging generates chains of silicates, while converting two oxygen atoms from terminal to bridging generates double chains. In contrast, converting three or four oxygens to bridging generates a variety of complex layered and three-dimensional structures, respectively.



Opal gemstones.

The silicates include many glasses as well as the gemstone known as *opal*, which typically contains 10%–15% water. In a large and important class of materials called *aluminosilicates*, some of the Si atoms are replaced by Al atoms to give aluminosilicates such as *zeolites*, whose three-dimensional framework structures have large cavities connected by smaller tunnels (Figure 22.8 "Zeolites Are Aluminosilicates with Large Cavities Connected by Channels"). Because the cations in zeolites are readily exchanged, zeolites are used in laundry detergents as water-softening agents: the more loosely bound Na^+ ions inside the zeolite cavities are displaced by the more highly charged Mg^{2+} and Ca^{2+} ions present in hard water, which bind more tightly. Zeolites are also used as catalysts and for water purification.

Figure 22.8 *Zeolites Are Aluminosilicates with Large Cavities Connected by Channels*



Zeolite A

Faujasite

The cavities normally contain hydrated cations that are loosely bound to the oxygen atoms of the negatively charged framework by electrostatic interactions. The sizes and arrangements of the channels and cavities differ in different types of zeolites. For example, in zeolite A the aluminosilicate cages are arranged in a cubic fashion, and the channels connecting the cavities intersect at right angles. In contrast, the cavities in faujasite are much larger, and the channels intersect at 120° angles. In these idealized models, the oxygen atoms that connect each pair of silicon atoms have been omitted.

Silicon and germanium react with nitrogen at high temperature to form *nitrides*(M_3N_4):

Equation 22.26

$$3Si(l) + 2N_2(g) \rightarrow Si_3N_4(s)$$

Silicon nitride has properties that make it suitable for high-temperature engineering applications: it is strong, very hard, and chemically inert, and it retains these properties to temperatures of about 1000°C. Because of the diagonal relationship between boron and silicon, metal silicides and metal borides exhibit many similarities. Although metal silicides have structures that are as complex as those of the metal borides and carbides, few silicides are structurally similar to the corresponding borides due to the significantly larger size of Si (atomic radius 111 pm versus 87 pm for B). Silicides of active metals, such as Mg_2Si, are ionic compounds that contain the Si^{4-} ion. They react with aqueous acid to form silicon hydrides such as SiH_4:

Equation 22.27

$$Mg_2Si(s) + 4H^+(aq) \rightarrow 2Mg^{2+}(aq) + SiH_4(g)$$

Unlike carbon, catenated silicon hydrides become thermodynamically less stable as the chain lengthens. Thus straight-chain and branched *silanes* (analogous to alkanes) are known up to only $n = 10$; the germanium analogues (*germanes*) are known up to $n = 9$. In contrast, the only known hydride of tin is SnH_4, and it slowly decomposes to elemental Sn and H_2 at room temperature. The simplest lead hydride (PbH_4) is so unstable that chemists are not even certain it exists. Because E=E and E≡E bonds become weaker with increasing atomic number (where E is any group 14 element), simple silicon, germanium, and tin analogues of alkenes, alkynes, and aromatic hydrocarbons are either unstable (Si=Si and Ge=Ge) or unknown. Silicon-based life-forms are therefore likely to be found only in science fiction.

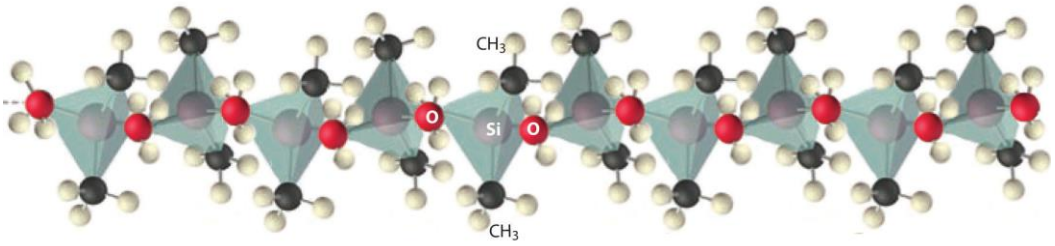
Note the Pattern

The stability of group 14 hydrides decreases down the group, and E=E and E≡E bonds become weaker.

The only important organic derivatives of lead are compounds such as tetraethyllead [$(CH_3CH_2)_4Pb$]. Because the Pb–C bond is weak, these compounds decompose at relatively low temperatures to produce alkyl radicals (R·), which can be used to control the rate of combustion reactions. For 60 yr, hundreds of thousands of tons of lead were burned annually in automobile engines, producing a mist of lead oxide particles along the highways that constituted a potentially serious public health problem. (Example 6 in Section 22.3 "The Elements of Group 15 (The Pnicogens)" examines this problem.) The use of catalytic converters reduced the amount of carbon monoxide, nitrogen oxides, and hydrocarbons released into the atmosphere through automobile exhausts, but it did nothing to decrease lead emissions. Because lead poisons catalytic converters, however, its use as a gasoline additive has been banned in most of the world.

Compounds that contain Si–C and Si–O bonds are stable and important. High-molecular-mass polymers called *silicones* contain an (Si–O–)n backbone with organic groups attached to Si (Figure 22.9 "Silicones Are Polymers with Long Chains of Alternating Silicon and Oxygen Atoms"). The properties of silicones are determined by the chain length, the type of organic group, and the extent of cross-linking between the chains. Without cross-linking, silicones are waxes or oils, but cross-linking can produce flexible materials used in sealants, gaskets, car polishes, lubricants, and even elastic materials, such as the plastic substance known as Silly Putty.

Figure 22.9 *Silicones Are Polymers with Long Chains of Alternating Silicon and Oxygen Atoms*



The structure of a linear silicone polymer is similar to that of quartz, but two of the oxygen atoms attached to each silicon atom are replaced by the carbon atoms of organic groups, such as the methyl groups (–CH_3) shown here. The terminal silicon atoms are bonded to three methyl groups. Silicones can be oily, waxy, flexible, or elastic, depending on the chain length, the extent of cross-linking between the chains, and the type of organic group.

EXAMPLE 4

For each reaction, explain why the given products form.

a. $Pb(s) + Cl_2(g) \rightarrow PbCl_2(s)$

a. $Mg_2Si(s) + 4H_2O(l) \rightarrow SiH_4(g) + 2Mg(OH)_2(s)$

b. $GeO_2(s) + 4OH^-(aq) \rightarrow GeO_4^{4-}(aq) + 2H_2O(l)$

Given: balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

Solution:

A. Lead is a metal, and chlorine is a nonmetal that is a strong oxidant. Thus we can expect a redox reaction to occur in which the metal acts as a reductant. Although lead can form compounds in the +2 and +4 oxidation states, Pb^{4+} is a potent oxidant (the inert-pair effect). Because lead prefers the +2 oxidation state and chlorine is a weaker oxidant than fluorine, we expect $PbCl_2$ to be the product.

a. This is the reaction of water with a metal silicide, which formally contains the Si^{4-} ion. Water can act as either an acid or a base. Because the other compound is a base, we expect an acid–base reaction to occur in which water acts as an acid. Because Mg_2Si

contains Si in its lowest possible oxidation state, however, an oxidation–reduction reaction is also a possibility. But water is a relatively weak oxidant, so an acid–base reaction is more likely. The acid (H_2O) transfers a proton to the base (Si^{4-}), which can accept four protons to form SiH_4. Proton transfer from water produces the OH^- ion, which will combine with Mg^{2+} to give magnesium hydroxide.

b. We expect germanium dioxide (GeO_2) to be amphoteric because of the position of germanium in the periodic table. It should dissolve in strong aqueous base to give an anionic species analogous to silicate.

Exercise

Predict the products of the reactions and write a balanced chemical equation for each reaction.

a. $a. \quad PbO2(s)- \rightarrow DPbO(s) +12O2(g)$

b. $GeCl_4(s) + H_2O(l) \rightarrow$

c. $Sn(s) + HCl(aq) \rightarrow$

Answer:

$a. \quad PbO2(s)- \rightarrow DPbO(s) +12O2(g)$ $GeCl_4(s) + 2H_2O(l) \rightarrow GeO_2(s) + 4HCl(aq)$

b. $Sn(s) + 2HCl(aq) \rightarrow Sn^{2+}(aq) + H_2(g) + 2Cl^-(aq)$

Summary

The group 14 elements show the greatest range of chemical behavior of any group in the periodic table. Because the covalent bond strength decreases with increasing atomic size and greater-than-expected ionization energies due to an increase in Z_{eff}, the stability of the +2 oxidation state increases from carbon to lead. The tendency to form multiple bonds and to catenate decreases as the atomic number increases. The stability of the carbon tetrahalides decreases as the halogen increases in size because of poor orbital overlap and steric crowding. Carbon forms three kinds of carbides with less electronegative elements: ionic carbides, which contain metal cations and C^{4-} (methide) or C_2^{2-} (acetylide) anions; interstitial carbides, which are characterized by covalent metal–carbon interactions and are among the hardest substances known; and covalent carbides, which have three-dimensional covalent network structures that make them extremely hard, high melting, and chemically inert. Consistent with periodic trends, metallic behavior increases down the group. Silicon has a tremendous affinity for oxygen because of partial Si–O π bonding. Dioxides of the group 14 elements become increasingly basic down the group and their metallic

character increases. Silicates contain anions that consist of only silicon and oxygen. Aluminosilicates are formed by replacing some of the Si atoms in silicates by Al atoms; aluminosilicates with three-dimensional framework structures are called zeolites. Nitrides formed by reacting silicon or germanium with nitrogen are strong, hard, and chemically inert. The hydrides become thermodynamically less stable down the group. Moreover, as atomic size increases, multiple bonds between or to the group 14 elements become weaker. Silicones, which contain an Si–O backbone and Si–C bonds, are high-molecular-mass polymers whose properties depend on their compositions.

KEY TAKEAWAY

- The group 14 elements show the greatest diversity in chemical behavior of any group; covalent bond strengths decease with increasing atomic size, and ionization energies are greater than expected, increasing from C to Pb.

CONCEPTUAL PROBLEMS

1. Why is the preferred oxidation state of lead +2 rather than +4? What do you expect the preferred oxidation state of silicon to be based on its position in the periodic table?
2. Carbon uses $p\pi$–$p\pi$ overlap to form compounds with multiple bonds, but silicon does not. Why? How does this same phenomenon explain why the heavier elements in group 14 do not form catenated compounds?
3. Diamond is both an electrical insulator and an excellent thermal conductor. Explain this property in terms of its bonding.
4. The lighter chalcogens (group 16) form π bonds with carbon. Does the strength of these π bonds increase or decrease with increasing atomic number of the chalcogen? Why?
5. The heavier group 14 elements can form complexes that contain expanded coordination spheres. How does this affect their reactivity compared with the reactivity of carbon? Is this a thermodynamic effect or a kinetic effect? Explain your answer.
6. Refer to Table 22.2 "Selected Properties of the Group 14 Elements" for the values of the electron affinities of the group 14 elements. Explain any discrepancies between these actual values and the expected values based on usual periodic trends.
7. Except for carbon, the elements of group 14 can form five or six electron-pair bonds. What hybrid orbitals are used to allow this expanded coordination? Why does carbon not form more than four electron-pair bonds?
8. Which of the group 14 elements is least stable in the +4 oxidation state? Why?

STRUCTURE AND REACTIVITY

1. Predict the products of each reaction and balance each chemical equation.

a. $CaC_2(s) + HCl(g) \rightarrow$

b. $a.\quad Pb(s) + Br_2(l) - \rightarrow D$

c. $(CH_3)_3N(l) + H_2O_2(aq) \rightarrow$

2. $d.\quad Pb(N_3)_2(s) - \rightarrow D$

3. Write a balanced chemical equation to indicate how you would prepare each compound.

a. SiF_6^{2-} from its elements and other common compounds

b. SiO_2 from $SiCl_4$

c. GeS_2 from its elements

d. $Si(CH_3)_4$ from Si

4. Write a balanced chemical equation to indicate how you would prepare each compound.

a. CO_2 from CuO

b. methane from Be_2C

c. $Si(OH)_4$ from Si

d. Si_3N_4 from Si

ANSWERS

1.

a. $CaC_2(s) + 2HCl(g) \rightarrow CaCl_2(s) + C_2H_2(g)\ a.\quad b.\quad Pb(s) + Br_2(l) - \rightarrow D\ PbBr_2(s)$

b.

c. $(CH_3)_3N(l) + H_2O_2(aq) \rightarrow (CH_3)_3N{-}O(l) + H_2O(l)$

2. $d.\quad Pb(N_3)_2(s) - \rightarrow D Pb(s) + 3N_2(g)$

3.

a. $e.\quad CuO(s) + CO(s) - \rightarrow D\ Cu(s) + CO_2(g)$

b. $Be_2C(s) + 4HCl(aq) \rightarrow 2BeCl_2(aq) + CH_4(g)$

c. $Si(s) + 2Cl_2(g) \rightarrow SiCl_4(l)$; $SiCl_4(l) + 4H_2O(l) \rightarrow Si(OH)_4(s) + 4HCl(aq)$

$a.\quad 3Si(s) + 2N_2(g) - \rightarrow D\ Si_3N_4(s)$

$a.\quad s) + 3C(s) - \rightarrow D\ In_4C_3(s)$

22.3 The Elements of Group 15 (The Pnicogens)

LEARNING OBJECTIVE

1. To understand the trends in properties and reactivity of the group 14 elements: the pnicogens.

Like the group 14 elements, the lightest member of group 15, nitrogen, is found in nature as the free element, and the heaviest elements have been known for centuries because they are easily isolated from their ores.

Antimony (Sb) was probably the first of the pnicogens to be obtained in elemental form and recognized as an element. Its atomic symbol comes from its Roman name: *stibium*. It is found in stibnite (Sb_2S_3), a black mineral that has been used as a cosmetic (an early form of mascara) since biblical times, and it is easily reduced to the metal in a charcoal fire (Figure 22.10 "The Ancient Egyptians Used Finely Ground Antimony Sulfide for Eye Makeup"). The Egyptians used antimony to coat copper objects as early as the third millennium BC, and antimony is still used in alloys to improve the tonal quality of bells.

(a) Crystals of the soft black mineral stibnite (Sb_2S_3) on a white mineral matrix. (b) A fragment of an Egyptian painting on limestone from the 16th–13th centuries BC shows the use of ground stibnite ("kohl") as black eye shadow. Small vases of ground stibnite have been found among the funeral goods buried with Egyptian pharaohs.

In the form of its yellow sulfide ore, *orpiment* (As_2S_3), arsenic (As) has been known to physicians and professional assassins since ancient Greece, although elemental arsenic was not isolated until centuries later. The history of bismuth (Bi), in contrast, is more difficult to follow because early alchemists often confused it with other metals, such as lead, tin, antimony, and even silver (due to its slightly pinkish-white luster). Its name comes from the old German *wismut*, meaning "white metal." Bismuth was finally isolated in the 15th century, and it was used to make movable type for printing shortly after the invention of the Gutenberg printing process in 1440. Bismuth is used in printing because it is one of the few substances known whose solid state is less dense than the liquid. Consequently, its alloys expand as they cool, filling a mold completely and producing crisp, clear letters for typesetting.

Phosphorus was discovered in 1669 by the German alchemist Hennig Brandt, who was looking for the "philosophers' stone," a mythical substance capable of converting base metals to silver or gold. Believing that human urine was the source of the key ingredient, Brandt obtained several dozen buckets of urine, which he allowed to putrefy. The urine was distilled to dryness at high temperature and then condensed; the last fumes were collected under water, giving a

waxy white solid that had unusual properties. For example, it glowed in the dark and burst into flames when removed from the water. (Unfortunately for Brandt, however, it did not turn lead into gold.) The element was given its current name (from the Greek *phos*, meaning "light," and *phoros*, meaning "bringing") in the 17th century. For more than a century, the only way to obtain phosphorus was the distillation of urine, but in 1769 it was discovered that phosphorus could be obtained more easily from bones. During the 19th century, the demand for phosphorus for matches was so great that battlefields and paupers' graveyards were systematically scavenged for bones. Early matches were pieces of wood coated with elemental phosphorus that were stored in an evacuated glass tube and ignited when the tube was broken (which could cause unfortunate accidents if the matches were kept in a pocket!). Unfortunately, elemental phosphorus is volatile and highly toxic. It is absorbed by the teeth and destroys bone in the jaw, leading to a painful and fatal condition called "phossy jaw," which for many years was accepted as an occupational hazard of working in the match industry.

Although nitrogen is the most abundant element in the atmosphere, it was the last of the pnicogens to be obtained in pure form. In 1772, Daniel Rutherford, working with Joseph Black (who discovered CO_2), noticed that a gas remained when CO_2 was removed from a combustion reaction. Antoine Lavoisier called the gas *azote*, meaning "no life," because it did not support life. When it was discovered that the same element was also present in nitric acid and nitrate salts such as KNO_3 (nitre), it was named nitrogen. About 90% of the nitrogen produced today is used to provide an inert atmosphere for processes or reactions that are oxygen sensitive, such as the production of steel, petroleum refining, and the packaging of foods and pharmaceuticals.

Preparation and General Properties of the Group 15 Elements

Because the atmosphere contains several trillion tons of elemental nitrogen with a purity of about 80%, it is a huge source of nitrogen gas. Distillation of liquefied air yields nitrogen gas that is more than 99.99% pure, but small amounts of very pure nitrogen gas can be obtained from the thermal decomposition of sodium azide:

Equation 22.28

$$2NaN3(s) \rightarrow D2Na(l) + 3N2(g)$$

In contrast, Earth's crust is relatively poor in nitrogen. The only important nitrogen ores are large deposits of KNO_3 and $NaNO_3$ in the deserts of Chile and Russia, which were apparently formed when ancient alkaline lakes evaporated. Consequently, virtually all nitrogen compounds produced on an industrial scale use atmospheric nitrogen as the starting material. Phosphorus, which constitutes only

about 0.1% of Earth's crust, is much more abundant in ores than nitrogen. Like aluminum and silicon, phosphorus is always found in combination with oxygen, and large inputs of energy are required to isolate it.

The other three pnicogens are much less abundant: arsenic is found in Earth's crust at a concentration of about 2 ppm, antimony is an order of magnitude less abundant, and bismuth is almost as rare as gold. All three elements have a high affinity for the chalcogens and are usually found as the sulfide ores (M_2S_3), often in combination with sulfides of other heavy elements, such as copper, silver, and lead. Hence a major source of antimony and bismuth is flue dust obtained by smelting the sulfide ores of the more abundant metals.

In group 15, as elsewhere in the *p* block, we see large differences between the lightest element (N) and its congeners in size, ionization energy, electron affinity, and electronegativity (Table 22.3 "Selected Properties of the Group 15 Elements"). The chemical behavior of the elements can be summarized rather simply: nitrogen and phosphorus behave chemically like nonmetals, arsenic and antimony behave like semimetals, and bismuth behaves like a metal. With their ns^2np^3 valence electron configurations, all form compounds by losing either the three *np* valence electrons to form the +3 oxidation state or the three *np* and the two *ns* valence electrons to give the +5 oxidation state, whose stability decreases smoothly from phosphorus to bismuth. In addition, the relatively large magnitude of the electron affinity of the lighter pnicogens enables them to form compounds in the −3 oxidation state (such as NH_3 and PH_3), in which three electrons are formally added to the neutral atom to give a filled *np* subshell. Nitrogen has the unusual ability to form compounds in nine different oxidation states, including −3, +3, and +5. Because neutral covalent compounds of the trivalent pnicogens contain a lone pair of electrons on the central atom, they tend to behave as Lewis bases.

Table 22.3 Selected Properties of the Group 15 Elements

Property	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
atomic symbol	N	P	As	Sb	Bi
atomic number	7	15	33	51	83
atomic mass (amu)	14.01	30.97	74.92	121.76	209.98
valence electron configuration*	$2s^22p^3$	$3s^23p^3$	$4s^24p^3$	$5s^25p^3$	$6s^26p^3$
melting point/boiling	−210/−196	44.15/281*c*	817 (at 3.70	631/1587	271/1564

Property	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
point (°C)			MPa)/603 (sublimes)†		
density (g/cm3) at 25°C	1.15 (g/L)	1.82†	5.75‡	6.68	9.79
atomic radius (pm)	56	98	114	133	143
first ionization energy (kJ/mol)	1402	1012	945	831	703
common oxidation state(s)	−3 to +5	+5, +3, −3	+5, +3	+5, +3	+3
ionic radius (pm)§	146 (−3), 16 (+3)	212 (−3), 44 (+3)	58 (+3)	76 (+3), 60 (+5)	103 (+3)
electron affinity (kJ/mol)	0	−72	−78	−101	−91
electronegativity	3.0	2.2	2.2	2.1	1.9
standard reduction potential ($E°$, V) ($E^{V} \rightarrow E^{III}$ in acidic solution)‖	+0.93	−0.28	+0.56	+0.65	—
product of reaction with O_2	NO_2, NO	P_4O_6, P_4O_{10}	As_4O_6	Sb_2O_5	Bi_2O_3
type of oxide	acidic (NO_2), neutral (NO, N_2O)	acidic	acidic	amphoteric	basic
product of reaction with N_2	—	none	none	none	none
product of reaction with X_2	none	PX_3, PX_5	AsF_5, AsX_3	SbF_5, $SbCl_5$, $SbBr_3$, SbI_3	BiF_5, BiX_3
product of reaction with H_2	none	none	none	none	none
***The configuration shown does not include filled *d* and *f* subshells.**					
†For white phosphorus.					
‡For gray arsenic.					
§The values cited are for six-coordinate ions in the indicated oxidation states. The N^{5+}, P^{5+}, and As^{5+} ions are not known species.					
‖The chemical form of the elements in these oxidation states varies considerably. For N, the reaction is $NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O$; for P and As, it is $H_3EO_4 + 2H^+ + 2e^- \rightarrow H_3EO_3 + H_2O$; and for Sb it is $Sb_2O_5 + 4e^- + 10H^+ \rightarrow 2Sb^{3+} + 5H_2O$.					

Note the Pattern

In group 15, the stability of the +5 oxidation state decreases from P to Bi.

Note the Pattern

Because neutral covalent compounds of the trivalent group 15 elements have a lone pair of electrons on the central atom, they tend to be Lewis bases.

Reactions and Compounds of Nitrogen

Like carbon, nitrogen has four valence orbitals (one 2*s* and three 2*p*), so it can participate in at most four electron-pair bonds by using sp^3 hybrid orbitals. Unlike carbon, however, nitrogen does not form long chains because of repulsive interactions between lone pairs of electrons on *adjacent* atoms. These interactions become important at the shorter internuclear distances encountered with the smaller, second-period elements of groups 15, 16, and 17. (For more information on internuclear distance, see Chapter 7 "The Periodic Table and Periodic Trends", Section 7.2 "Sizes of Atoms and Ions" and Chapter 8 "Ionic versus Covalent Bonding", Section 8.2 "Ionic Bonding".) Stable compounds with N–N bonds are limited to chains of no more than three N atoms, such as the azide ion (N_3^-). Nitrogen is the only pnicogen that normally forms multiple bonds with itself and other second-period elements, using π overlap of adjacent *np* orbitals. Thus the stable form of elemental nitrogen is N_2, whose N≡N bond is so strong ($D_{N\equiv N}$ = 942 kJ/mol) compared with the N–N and N=N bonds (D_{N-N} = 167 kJ/mol; $D_{N=N}$ = 418 kJ/mol) that all compounds containing N–N and N=N bonds are thermodynamically unstable with respect to the formation of N_2. In fact, the formation of the N≡N bond is so thermodynamically favored that virtually all compounds containing N–N bonds are potentially explosive. Again in contrast to carbon, nitrogen undergoes only two important chemical reactions at room temperature: it reacts with metallic lithium to form lithium nitride, and it is reduced to ammonia by certain microorganisms. (For more information lithium, seeChapter 21 "Periodic Trends and the ".) At higher temperatures, however, N_2 reacts with more electropositive elements, such as those in group 13, to give binary nitrides, which range from covalent to ionic in character. Like the corresponding compounds of carbon, binary compounds of nitrogen with oxygen, hydrogen, or other nonmetals are usually covalent molecular substances.

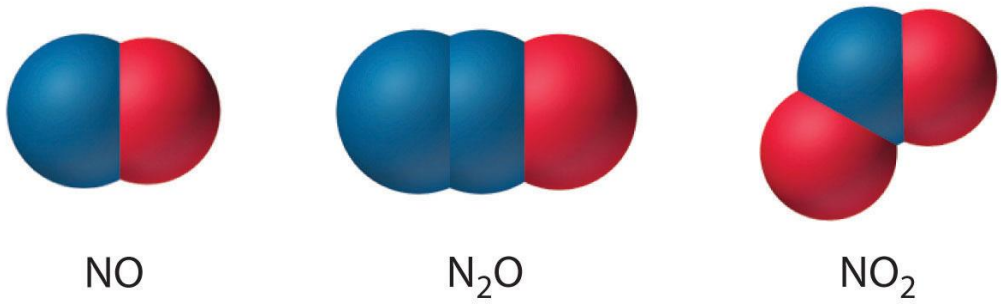
Few binary molecular compounds of nitrogen are formed by direct reaction of the elements. At elevated temperatures, N_2 reacts with H_2 to form ammonia, with O_2 to form a mixture of NO and NO_2, and with carbon to form *cyanogen* (N≡C–C≡N); elemental nitrogen does not react with the halogens or the other chalcogens. Nonetheless, all the binary nitrogen halides (NX_3) are known. Except for NF_3, all are toxic,

thermodynamically unstable, and potentially explosive, and all are prepared by reacting the halogen with NH_3 rather than N_2. Both nitrogen monoxide (NO) and nitrogen dioxide (NO_2) are thermodynamically unstable, with positive free energies of formation. Unlike NO, NO_2 reacts readily with excess water, forming a 1:1 mixture of nitrous acid (HNO_2) and nitric acid (HNO_3):

Equation 22.29

$$2NO_2(g) + H_2O(l) \rightarrow HNO_2(aq) + HNO_3(aq)$$

Nitrogen also forms N_2O (dinitrogen monoxide, or nitrous oxide), a linear molecule that is isoelectronic with CO_2 and can be represented as $^-N{=}N^+{=}O$. Like the other two oxides of nitrogen, nitrous oxide is thermodynamically unstable. The structures of the three common oxides of nitrogen are as follows:



Note the Pattern

Few binary molecular compounds of nitrogen are formed by the direct reaction of the elements.

At elevated temperatures, nitrogen reacts with highly electropositive metals to form*ionic nitrides*, such as Li_3N and Ca_3N_2. These compounds consist of ionic lattices formed by M^{n+} and N^{3-} ions. Just as boron forms interstitial borides and carbon forms interstitial carbides, with less electropositive metals nitrogen forms a range of*interstitial nitrides*, in which nitrogen occupies holes in a close-packed metallic structure. Like the interstitial carbides and borides, these substances are typically very hard, high-melting materials that have metallic luster and conductivity.

Nitrogen also reacts with semimetals at very high temperatures to produce *covalent nitrides*, such as Si_3N_4 and BN, which are solids with extended covalent network structures similar to those of graphite or diamond. Consequently, they are usually high melting and chemically inert materials.

Ammonia (NH_3) is one of the few thermodynamically stable binary compounds of nitrogen with a nonmetal. It is not flammable in air, but it burns in an O_2 atmosphere:

Equation 22.30

$$4NH_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(g)$$

About 10% of the ammonia produced annually is used to make fibers and plastics that contain amide bonds, such as nylons and polyurethanes, while 5% is used in explosives, such as ammonium nitrate, TNT (trinitrotoluene), and nitroglycerine. Large amounts of anhydrous liquid ammonia are used as fertilizer. Nitrogen forms two other important binary compounds with hydrogen. Hydrazoic acid (HN_3), also called hydrogen azide, is a colorless, highly toxic, and explosive substance. Hydrazine (N_2H_4) is also potentially explosive; it is used as a rocket propellant and to inhibit corrosion in boilers.

Note the Pattern

B, C, and N all react with transition metals to form interstitial compounds that are hard, high-melting materials.

EXAMPLE 5

For each reaction, explain why the given products form when the reactants are heated.

a. $Sr(s) + N_2O(g) \rightarrow SrO(s) + N_2(g)$

b. $NH_4NO_2(s) \rightarrow N_2(g) + 2H_2O(g)$

a. $Pb(NO_3)_2(s) \rightarrow PbO_2(s) + 2NO_2(g)$

Given: balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

Solution:

a. As an alkali metal, strontium is a strong reductant. If the other reactant can act as an oxidant, then a redox reaction will occur. Nitrous oxide contains nitrogen in a low oxidation state (+1), so we would not normally consider it an oxidant. Nitrous oxide is, however, thermodynamically unstable ($\Delta H_f > 0$ and $\Delta G_f > 0$), and it can be

b. reduced to N_2, which is a stable species. Consequently, we predict that a redox reaction will occur.

c. When a substance is heated, a decomposition reaction probably will occur, which often involves the release of stable gases. In this case, ammonium nitrite contains nitrogen in two different oxidation states (−3 and +3), so an internal redox reaction is a possibility.

Due to its thermodynamic stability, N_2 is the probable nitrogen-containing product, whereas we predict that H and O will combine to form H_2O.

d. Again, this is probably a thermal decomposition reaction. If one element is in an usually high oxidation state and another in a low oxidation state, a redox reaction will probably occur. Lead nitrate contains the Pb^{2+} cation and the nitrate anion, which contains nitrogen in its highest possible oxidation state (+5). Hence nitrogen can be reduced, and we know that lead can be oxidized to the +4 oxidation state. Consequently, it is likely that lead(II) nitrate will decompose to lead(IV) oxide and nitrogen dioxide when heated. Even though PbO_2 is a powerful oxidant, the release of a gas such as NO_2 can often drive an otherwise unfavorable reaction to completion (Le Châtelier's principle). Note, however, that PbO_2 will probably decompose to PbO at high temperatures.

Exercise

Predict the product(s) of each reaction and write a balanced chemical equation for each reaction.

a. $NO(g) + H_2O(l) \text{ - } \rightarrow \text{D}$

b. $NH_4NO_3(s) \text{ - } \rightarrow \text{D}$

c. $Sr(s) + N_2(g) \rightarrow$

Answer: *a.* $NO(g) + H_2O(l) \text{ - } \rightarrow \text{D}$ *no reaction*

$NH_4NO_3(s) \text{ - } \rightarrow \text{D}\ N_2O(g) + 2H_2O(g)$

$3Sr(s) + N_2(g) \rightarrow Sr_3N_2(s)$

Reactions and Compounds of the Heavier Pnicogens

Like the heavier elements of group 14, the heavier pnicogens form catenated compounds that contain only single bonds, whose stability decreases rapidly as we go down the group. For example, phosphorus exists as multiple allotropes, the most common of which is *white phosphorus*, which consists of P_4 tetrahedra and behaves like a typical nonmetal. As is typical of a molecular solid, white phosphorus is volatile, has a low melting point (44.1°C), and is soluble in nonpolar solvents. It is highly strained, with bond angles of only 60°, which partially explains why it is so reactive and so easily converted to more stable allotropes. Heating white phosphorus for several days converts it to *red phosphorus*, a polymer that is air stable, virtually insoluble, denser than white phosphorus, and higher melting, properties that make it much safer

to handle. A third allotrope of phosphorus, *black phosphorus*, is prepared by heating the other allotropes under high pressure; it is even less reactive, denser, and higher melting than red phosphorus. As expected from their structures, white phosphorus is an electrical insulator, and red and black phosphorus are semiconductors. The three heaviest pnicogens—arsenic, antimony, and bismuth—all have a metallic luster, but they are brittle (not ductile) and relatively poor electrical conductors.

Note the Pattern

As in group 14, the heavier group 15 elements form catenated compounds that contain only single bonds, whose stability decreases as we go down the group.

The reactivity of the heavier pnicogens decreases as we go down the column. Phosphorus is by far the most reactive of the pnicogens, forming binary compounds with every element in the periodic table except antimony, bismuth, and the noble gases. Phosphorus reacts rapidly with O_2, whereas arsenic burns in pure O_2 if ignited, and antimony and bismuth react with O_2 only when heated. None of the pnicogens reacts with nonoxidizing acids such as aqueous HCl, but all dissolve in oxidizing acids such as HNO_3. Only bismuth behaves like a metal, dissolving in HNO_3 to give the hydrated Bi^{3+} cation.

Note the Pattern

The reactivity of the heavier group 15 elements decreases as we go down the column.

The heavier pnicogens can use energetically accessible 3*d*, 4*d*, or 5*d* orbitals to formdsp^3 or d^2sp^3 hybrid orbitals for bonding. Consequently, these elements often have coordination numbers of 5 or higher. Phosphorus and arsenic form halides (e.g., $AsCl_5$) that are generally covalent molecular species and behave like typical nonmetal halides, reacting with water to form the corresponding oxoacids (in this case, H_3AsO_4). All the pentahalides are potent Lewis acids that can expand their coordination to accommodate the lone pair of a Lewis base:

Equation 22.31

$$AsF_5(soln) + F^-(soln) \rightarrow AsF_6^-(soln)$$

In contrast, bismuth halides have extended lattice structures and dissolve in water to produce hydrated ions, consistent with the stronger metallic character of bismuth.

Except for BiF_3, which is essentially an ionic compound, the trihalides are volatile covalent molecules with a lone pair of electrons on the central atom. Like the pentahalides, the trihalides react rapidly with water. In the cases of phosphorus and arsenic, the products are the corresponding acids, H_3PO_3 and H_3AsO_3, where E is P or As:

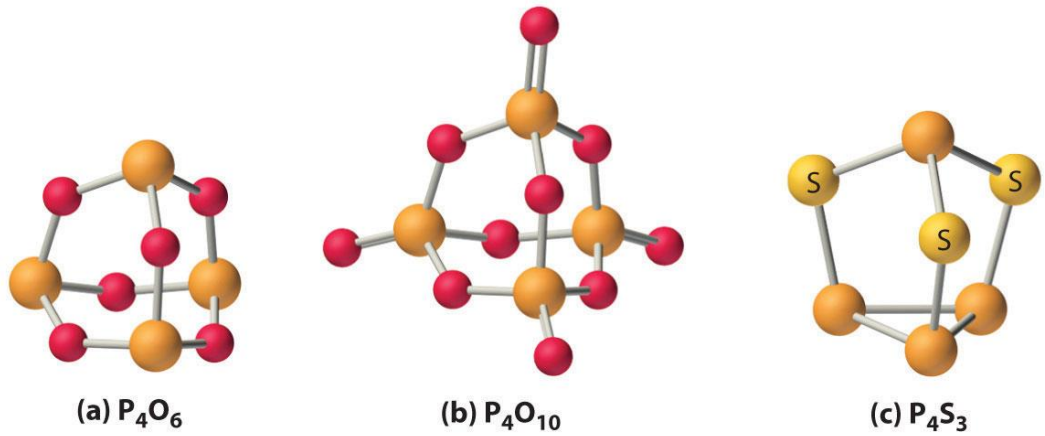
Equation 22.32

$EX_3(l) + 3H_2O(l) \rightarrow H_3EO_3(aq) + 3HX(aq)$

Phosphorus halides are also used to produce insecticides, flame retardants, and plasticizers.

With energetically accessible *d* orbitals, phosphorus and, to a lesser extent, arsenic are able to form π bonds with second-period atoms such as N and O. This effect is even more important for phosphorus than for silicon, resulting in very strong P–O bonds and even stronger P=O bonds. The first four elements in group 15 also react with oxygen to produce the corresponding oxide in the +3 oxidation state. Of these oxides, P_4O_6 and As_4O_6 have cage structures formed by inserting an oxygen atom into each edge of the P_4 or As_4 tetrahedron (part (a) in Figure 22.11 "The Structures of Some Cage Compounds of Phosphorus"), and they behave like typical nonmetal oxides. For example, P_4O_6 reacts with water to form phosphorous acid (H_3PO_3). Consistent with its position between the nonmetal and metallic oxides, Sb_4O_6 is amphoteric, dissolving in either acid or base. In contrast, Bi_2O_3 behaves like a basic metallic oxide, dissolving in acid to give solutions that contain the hydrated Bi^{3+} ion. The two least metallic elements of the heavier pnicogens, phosphorus and arsenic, form very stable oxides with the formula E_4O_{10} in the +5 oxidation state (part (b) in Figure 22.11 "The Structures of Some Cage Compounds of Phosphorus"). In contrast, Bi_2O_5 is so unstable that there is no absolute proof it exists.

Figure 22.11 *The Structures of Some Cage Compounds of Phosphorus*



(a, b) The structures of P_4O_6 and P_4O_{10} are both derived from the structure of white phosphorus (P_4) by inserting an oxygen atom into each of the six edges of the P_4tetrahedron; P_4O_{10} contains an additional terminal oxygen atom bonded to each phosphorus atom. (c) The structure of P_4S_3 is also derived from the structure of P_4 by inserting three sulfur atoms into three adjacent edges of the tetrahedron.

The heavier pnicogens form sulfides that range from molecular species with three-dimensional cage structures, such as P_4S_3 (part (c) in Figure 22.11 "The Structures of Some Cage Compounds of Phosphorus"), to layered or ribbon structures, such as $Sb_2S_3$and Bi_2S_3, which are semiconductors. Reacting the heavier pnicogens with metals produces substances whose properties vary with the metal content. Metal-rich*phosphides* (such as M_4P) are hard, high-melting, electrically conductive solids with a metallic luster, whereas phosphorus-rich phosphides (such as MP_{15}) are lower melting and less thermally stable because they contain catenated P*n* units. Many organic or organometallic compounds of the heavier pnicogens containing one to five alkyl or aryl groups are also known. Because of the decreasing strength of the pnicogen–carbon bond, their thermal stability decreases from phosphorus to bismuth.

Note the Pattern

Phosphorus has the greatest ability to form π bonds with elements such as O, N, and C.

Note the Pattern

The thermal stability of organic or organometallic compounds of group 15 decreases down the group due to the decreasing strength of the pnicogen–carbon bond.

EXAMPLE 6

For each reaction, explain why the given products form.

a. $Bi(s) + 32Br(l) \rightarrow BiBr3(s)$

b. $2(CH_3)_3As(l) + O_2(g) \rightarrow 2(CH_3)_3As{=}O(s)$

c. $PBr_3(l) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HBr(aq)$ $As(s) + Ga(s) - \rightarrow D\ GaAs(s)$

Given: balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the reaction products form.

Solution:

a. Bromine is an oxidant, and bismuth is a metal that can be oxidized. Hence a redox reaction is likely to occur. To identify the product, recall that bismuth can form compounds in either the +3 or +5 oxidation state. The heaviest pnicogen, bismuth is rather difficult to

oxidize to the +5 oxidation state because of the inert-pair effect. Hence the product will probably be bismuth(III) bromide.

b. Trimethylarsine, with a lone pair of electrons on the arsenic atom, can act as either a Lewis base or a reductant. If arsenic is oxidized by two electrons, then oxygen must be reduced, most probably by two electrons to the −2 oxidation state. Because As(V) forms strong bonds to oxygen due to π bonding, the expected product is $(CH_3)_3As{=}O$.

c. Phosphorus tribromide is a typical nonmetal halide. We expect it to react with water to produce an oxoacid of P(III) and the corresponding hydrohalic acid. [1]

d. Gallium is a metal with a strong tendency to act as a reductant and form compounds in the +3 oxidation state. In contrast, arsenic is a semimetal. It can act as a reductant to form compounds in the +3 or +5 oxidation state, or it can act as an oxidant, accepting electrons to form compounds in the −3 oxidation state. If a reaction occurs, then a binary compound will probably form with a 1:1 ratio of the elements. GaAs is an example of a III-V compound, many of which are used in the electronics industry. (For more information on electrical properties, seeChapter 12 "Solids".)

Exercise

Predict the products of each reaction and write a balanced chemical equation for each reaction.

a. $PCl_5(s) + H_2O(l) \rightarrow$

b. $Bi_2O_5(s) \text{ - } \rightarrow \text{D}$

c. $Ca_3P_2(s) + H^+(aq) \rightarrow$

d. $NaNH_2(s) + PH_3(soln) \rightarrow$

Answer:

a. $PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$

b. *a.* $Bi_2O_5(s) \text{ - } \rightarrow \text{D } Bi_2O_3(s) + O_2(g)$

c. $Ca_3P_2(s) + 6H^+(aq) \rightarrow 2PH_3(g) + 3Ca^{2+}(aq)$

d. $NaNH_2(s) + PH_3(soln) \rightarrow NaPH_2(s) + NH_3(soln)$

Summary

In group 15, nitrogen and phosphorus behave chemically like nonmetals, arsenic and antimony behave like semimetals, and bismuth behaves like a metal. Nitrogen forms compounds in nine different oxidation

states. The stability of the +5 oxidation state decreases from phosphorus to bismuth because of the inert-pair effect. Due to their higher electronegativity, the lighter pnicogens form compounds in the −3 oxidation state. Because of the presence of a lone pair of electrons on the pnicogen, neutral covalent compounds of the trivalent pnicogens are Lewis bases. Nitrogen does not form stable catenated compounds because of repulsions between lone pairs of electrons on adjacent atoms, but it does form multiple bonds with other second-period atoms. Nitrogen reacts with electropositive elements to produce solids that range from covalent to ionic in character. Reaction with electropositive metals produces ionic nitrides, reaction with less electropositive metals produces interstitial nitrides, and reaction with semimetals produces covalent nitrides. The reactivity of the pnicogens decreases with increasing atomic number. Compounds of the heavier pnicogens often have coordination numbers of 5 or higher and use dsp^3 or d^2sp^3 hybrid orbitals for bonding. Because phosphorus and arsenic have energetically accessible *d* orbitals, these elements form π bonds with second-period atoms such as O and N. Phosphorus reacts with metals to produce phosphides. Metal-rich phosphides are hard, high-melting, electrically conductive solids with metallic luster, whereas phosphorus-rich phosphides, which contain catenated phosphorus units, are lower melting and less thermally stable.

KEY TAKEAWAY

- The reactivity of the heavier group 15 elements decreases down the group, as does the stability of their catenated compounds.

CONCEPTUAL PROBLEMS

1. Nitrogen is the first diatomic molecule in the second period of elements. Why is N_2 the most stable form of nitrogen? Draw its Lewis electron structure. What hybrid orbitals are used to describe the bonding in this molecule? Is the molecule polar?
2. The polymer (SN)*n* has metallic luster and conductivity. Are the constituent elements in this polymer metals or nonmetals? Why does the polymer have metallic properties?
3. Except for NF_3, all the halides of nitrogen are unstable. Explain why NF_3 is stable.
4. Which of the group 15 elements forms the most stable compounds in the +3 oxidation state? Explain why.
5. Phosphorus and arsenic react with the alkali metals to produce salts with the composition M_3Z_{11}. Compare these products with those produced by reaction of P and As with the alkaline earth metals. What conclusions can you draw about the types of structures favored by the heavier elements in this part of the periodic table?

1. PF_3 reacts with F_2 to produce PF_5, which in turn reacts with F^- to give salts that contain the PF_6^- ion. In contrast, NF_3 does not react with F_2, even under extreme conditions; NF_5 and the NF_6^- ion do not exist. Why?
2. Red phosphorus is safer to handle than white phosphorus, reflecting their dissimilar properties. Given their structures, how do you expect them to compare with regard to reactivity, solubility, density, and melting point?
3. Bismuth oxalate [$Bi_2(C_2O_4)_3$] is a poison. Draw its structure and then predict its solubility in H_2O, dilute HCl, and dilute HNO_3. Predict its combustion products. Suggest a method to prepare bismuth oxalate from bismuth.
4. Small quantities of NO can be obtained in the laboratory by reaction of the iodide ion with acidic solutions of nitrite. Write a balanced chemical equation that represents this reaction.
5. Although pure nitrous acid is unstable, dilute solutions in water are prepared by adding nitrite salts to aqueous acid. Write a balanced chemical equation that represents this type of reaction.
6. Metallic versus nonmetallic behavior becomes apparent in reactions of the elements with an oxidizing acid, such as HNO_3. Write balanced chemical equations for the reaction of each element of group 15 with nitric acid. Based on the products, predict which of these elements, if any, are metals and which, if any, are nonmetals.
7. Predict the product(s) of each reaction and then balance each chemical equation.

a. $P_4O_{10}(s) + H_2O(l) \rightarrow$

b. $AsCl_3(l) + H_2O(l) \rightarrow$

c. $Bi_2O_3(s) + H_2O(l) \rightarrow$

d. $Sb_4O_6(s) + OH^-(aq) \rightarrow$

e. $a.\ \left(C_2H_5\right)_3Sb(l) + O_2(g)$ - → D

f. $SbCl_3(s) + LiAlH_4(soln) \rightarrow$

8. $a.\ Ca(s) + N_2O(g)$ - → D

9. Write a balanced chemical equation to show how you would prepare each compound.

a. H_3PO_4 from P

b. Sb_2O_5 from Sb

c. SbH_3 from Sb

ANSWERS

1.
2.
3.
4.
5. $NaNO_2(s) + HCl(aq) \rightarrow HNO_2(aq) + NaCl(aq)$
6.
7.

a. $P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$

b. $AsCl_3(l) + 3H_2O(l) \rightarrow H_3AsO_3(aq) + 3HCl(aq)$

c. $Bi_2O_3(s) + 3H_2O(l) \rightarrow 2Bi(OH)_3(s)$

d. $Sb_4O_6(s) + 4OH^-(aq) + 2H_2O(l) \rightarrow 4H_2SbO_3^-(aq)$

e. $2(C_2H_5)_3Sb(l) + 21O_2(g) \rightarrow 12CO_2(g) + 15H_2O(g) + Sb_2O_3(s)$

f. $4SbCl_3(s) + 3LiAlH_4(soln) \rightarrow 4SbH_3(g) + 3LiCl(soln) + 3AlCl_3(soln)$

a. $Ca(s) + N_2O(g) \rightarrow CaO(s) + N_2(g)$

22.4 The Elements of Group 16 (The Chalcogens)

LEARNING OBJECTIVE

1. To understand the trends in properties and reactivity of the group 16 elements: the chalcogens.

The chalcogens are the first group in the *p* block to have no stable metallic elements. All isotopes of polonium (Po), the only metal in group 16, are radioactive, and only one element in the group, tellurium (Te), can even be described as a semimetal. As in groups 14 and 15, the lightest element of group 16, oxygen, is found in nature as the free element.

Of the group 16 elements, only sulfur was known in ancient times; the others were not discovered until the late 18th and 19th centuries. Sulfur is frequently found as yellow crystalline deposits of essentially pure S_8 in areas of intense volcanic activity or around hot springs. As early as the 15th century BC, sulfur was used as a fumigant in Homeric

Greece because, when burned, it produces SO_2 fumes that are toxic to most organisms, including vermin hiding in the walls and under the floors of houses. Hence references to sulfur are common in ancient literature, frequently in the context of religious purification. In fact, the association of sulfur with the divine was so pervasive that the prefixes *thio-* (meaning "sulfur") and *theo-* (meaning "god") have the same root in ancient Greek. Though used primarily in the production of sulfuric acid, sulfur is also used to manufacture gunpowder and as a cross-linking agent for rubber, which enables rubber to hold its shape but retain its flexibility.

Note the Pattern

Group 16 is the first group in the *p* block with no stable metallic elements.

Oxygen was not discovered until 1771, when the Swedish pharmacist Carl Wilhelm Scheele found that heating compounds such as KNO_3, Ag_2CO_3, and HgO produced a colorless, odorless gas that supported combustion better than air. The results were not published immediately, however, so Scheele's work remained unknown until 1777. Unfortunately, this was nearly two years *after* a paper by the English chemist Joseph Priestley had been published, describing the isolation of the same gas by using a magnifying glass to focus the sun's rays on a sample of HgO. Oxygen is used primarily in the steel industry during the conversion of crude iron to steel using the Bessemer process. (For more information on the Bessemer process, see Chapter 23 "The ".) Another important industrial use of oxygen is in the production of TiO_2, which is commonly used as a white pigment in paints, paper, and plastics.

Tellurium was discovered accidentally in 1782 by the Austrian chemist Franz Joseph Müller von Reichenstein, the chief surveyor of mines in Transylvania who was also responsible for the analysis of ore samples. The silvery-white metal had the same density as antimony but very different properties. Because it was difficult to analyze, Müller called it *metallum problematicum* (meaning "difficult metal"). The name *tellurium* (from the Latin*tellus*, meaning "earth") was coined by another Austrian chemist, Martin Klaproth, who demonstrated in 1798 that Müller's "difficult metal" was actually a new element. Tellurium is used to color glass and ceramics, in the manufacture of blasting caps, and in thermoelectric devices.

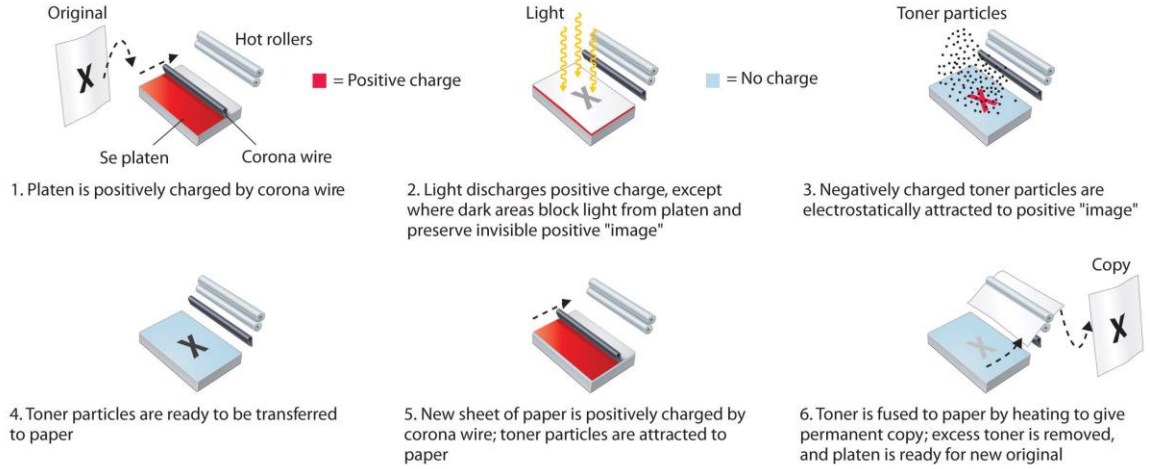
Selenium (Se) was first isolated in 1817 by the Swedish chemist Jöns Jakob Berzelius, who also discovered silicon. He had invested money in a sulfuric acid plant and decided to investigate a foul-smelling contaminant that formed a red precipitate. Although he initially thought the contaminant was tellurium, further study showed that it was actually a new element similar to tellurium. To emphasize the similarities, Berzelius named the new element selenium (after the Greek *selene*, meaning "moon"). Selenium is used primarily as a minor ingredient to decolorize glass. Because it is

photosensitive, selenium is also used to capture images in the photocopying process (Figure 22.12 "The Chemistry of Photocopying").

Jöns Jakob Berzelius (1779–1848)

Berzelius was born into a well-educated Swedish family, but both parents died when he was young. He studied medicine at the University of Uppsala, where his experiments with electroshock therapy caused his interests to turn to electrochemistry. Berzelius devised the system of chemical notation that we use today. In addition, he discovered six elements (cerium, thorium, selenium, silicon, titanium, and zirconium).

Figure 22.12 *The Chemistry of Photocopying*



Because amorphous selenium is a photosensitive semiconductor, exposing an electrostatically charged Se film to light causes the positive charge on the film to be discharged in all areas that are white in the original. Dark areas in the original block the light and generate an invisible, positively charged image. To produce an image on paper, negatively charged toner particles are attracted to the positive image, transferred to a negatively charged sheet of blank paper, and fused with the paper at high temperature to give a permanent image.

The heaviest chalcogen, polonium, was isolated after an extraordinary effort by Marie Curie. (For more information on radioactivity and polonium, see Chapter 1 "Introduction to Chemistry", Section 1.5 "The Atom".) Although she was never able to obtain macroscopic quantities of the element, which she named for her native country of Poland, she demonstrated that its chemistry required it to be assigned to group 16. Marie Curie was awarded a second Nobel Prize in Chemistry in 1911 for the discovery of radium and polonium.

Preparation and General Properties of the Group 16 Elements

Oxygen is by far the most abundant element in Earth's crust and in the hydrosphere (about 44% and 86% by mass, respectively). The same process that is used to obtain nitrogen from the atmosphere produces pure oxygen. Oxygen can also be obtained by the electrolysis of water, the decomposition of alkali metal or alkaline earth peroxides or superoxides, or the thermal decomposition of simple inorganic salts, such as potassium chlorate in the presence of a catalytic amount of MnO_2:

Equation 22.33

$$2KClO3(s) \square \ DMnO2(s)2KCl(s) + 3O2(g)$$

(For more information on electrolysis, see Chapter 19 "Electrochemistry". For more information on the alkali metals and the alkaline earth metals, see Chapter 21 "Periodic Trends and the ".)

Unlike oxygen, sulfur is not very abundant, but it is found as elemental sulfur in rock formations overlying salt domes, which often accompany petroleum deposits (Figure 2.22 "Top 25 Chemicals Produced in the United States in 2002*"). Sulfur is also recovered from H_2S and organosulfur compounds in crude oil and coal and from metal sulfide ores such as *pyrite* (FeS_2).

Because selenium and tellurium are chemically similar to sulfur, they are usually found as minor contaminants in metal sulfide ores and are typically recovered as by-products. Even so, they are as abundant in Earth's crust as silver, palladium, and gold. One of the best sources of selenium and tellurium is the "slime" deposited during the electrolytic purification of copper. Both of these elements are notorious for the vile odors of many of their compounds. For example, when the body absorbs even trace amounts of tellurium, dimethyltellurium [$(CH_3)_2Te$] is produced and slowly released in the breath and perspiration, resulting in an intense garlic-like smell that is commonly called "tellurium breath."

With their ns^2np^4 electron configurations, the chalcogens are two electrons short of a filled valence shell. Thus in reactions with metals, they tend to acquire two additional electrons to form compounds in the −2 oxidation state. This tendency is greatest for oxygen, the chalcogen with the highest electronegativity. The heavier, less electronegative chalcogens can lose either four *np*electrons or four *np* and two *ns* electrons to form compounds in the +4 and +6 oxidation state, respectively, as shown in Table 22.4 "Selected Properties of the Group 16 Elements". As with the other groups, the lightest member in the group, in this case oxygen, differs greatly from the others in size, ionization energy, electronegativity, and electron affinity, so its chemistry is unique. Also as in the other groups, the second and third members (sulfur and

selenium) have similar properties because of shielding effects. Only polonium is metallic, forming either the hydrated Po^{2+} or Po^{4+} ion in aqueous solution, depending on conditions.

Table 22.4 Selected Properties of the Group 16 Elements

Property	Oxygen	Sulfur	Selenium	Tellurium	Polonium
atomic symbol	O	S	Se	Te	Po
atomic number	8	16	34	52	84
atomic mass (amu)	16.00	32.07	78.96	127.60	209
valence electron configuration*	$2s^2 2p^4$	$3s^2 3p^4$	$4s^2 4p^4$	$5s^2 5p^4$	$6s^2 6p^4$
melting point/boiling point (°C)	−219/−183	115/445	221/685	450/988	254/962
density (g/cm³) at 25°C	1.31 (g/L)	2.07	4.81	6.24	9.20
atomic radius (pm)	48	88	103	123	135
first ionization energy (kJ/mol)	1314	1000	941	869	812
normal oxidation state(s)	−2	+6, +4, −2	+6, +4, −2	+6, +4, −2	+2 (+4)
ionic radius (pm)†	140 (−2)	184 (−2), 29 (+6)	198 (−2), 42 (+6)	221 (−2), 56 (+6)	230 (−2), 97 (+4)
electron affinity (kJ/mol)	−141	−200	−195	−190	−180
electronegativity	3.4	2.6	2.6	2.1	2.0
standard reduction potential ($E°$, V) ($E^0 \rightarrow H_2E$ in acidic solution)	+1.23	+0.14	−0.40	−0.79	−1.00
product of reaction with O_2	—	SO_2	SeO_2	TeO_2	PoO_2
type of oxide	—	acidic	acidic	amphoteric	basic
product of reaction with N_2	NO, NO_2	none	none	none	none
product of reaction with X_2	O_2F_2	SF_6, S_2Cl_2, S_2Br_2	SeF_6, SeX_4	TeF_6, TeX_4	PoF_4, $PoCl_2$, $PoBr_2$
product of reaction with H_2	H_2O	H_2S	H_2Se	none	none
***The configuration shown does not include filled *d* and *f* subshells.**					
†The values cited for the hexacations are for six-coordinate ions and are only estimated values.					

Reactions and Compounds of Oxygen

As in groups 14 and 15, the lightest group 16 member has the greatest tendency to form multiple bonds. Thus elemental oxygen is found in nature as a diatomic gas that contains a net double bond: O=O. As with nitrogen, electrostatic repulsion between lone pairs of electrons on adjacent atoms prevents oxygen from

forming stable catenated compounds. In fact, except for O_2, all compounds that contain O–O bonds are potentially explosive. Ozone, peroxides, and superoxides are all potentially dangerous in pure form. Ozone (O_3), one of the most powerful oxidants known, is used to purify drinking water because it does not produce the characteristic taste associated with chlorinated water. Hydrogen peroxide (H_2O_2) is so thermodynamically unstable that it has a tendency to undergo explosive decomposition when impure:

Equation 22.34

$$2H2O2(l) \rightarrow 2H2O(l) + O2(g) \qquad DG° = -119\ kJ/mol$$

Note the Pattern

As in groups 14 and 15, the lightest element in group 16 has the greatest tendency to form multiple bonds. *Despite the strength of the O = O bond* ($DO2 = 494\ kJ/mol$), O_2 *is extremely reactive, reacting* directly with nearly all other elements except the noble gases. Some properties of O_2 and related species, such as the peroxide and superoxide ions, are in Table 22.5 "Some Properties of O". With few exceptions, the chemistry of oxygen is restricted to negative oxidation states because of its high electronegativity (χ = 3.4). Unlike the other chalcogens, oxygen does not form compounds in the +4 or +6 oxidation state. Oxygen is second only to fluorine in its ability to stabilize high oxidation states of metals in both ionic and covalent compounds. For example, AgO is a stable solid that contains silver in the unusual Ag(II) state, whereas OsO_4 is a volatile solid that contains Os(VIII). Because oxygen is so electronegative, the O–H bond is highly polar, creating a large bond dipole moment that makes hydrogen bonding much more important for compounds of oxygen than for similar compounds of the other chalcogens.

Table 22.5 Some Properties of O_2 and Related Diatomic Species

Species	Bond Order	Number of Unpaired e-	O–O Distance (pm)*
O_2^+	2.5	1	112
O_2	2	2	121
O_2^-	1.5	1	133
O_2^{2-}	1	0	149
***Source of data: Lauri Vaska, "Dioxygen-Metal Complexes: Toward a Unified View,"*Accounts of Chemical Research* 9 (1976): 175.**			

Metal oxides are usually basic, and nonmetal oxides are acidic, whereas oxides of elements that lie on or near the diagonal band of semimetals are generally amphoteric. A few oxides, such as CO and PbO_2, are neutral and do not react with water, aqueous acid, or aqueous base. Nonmetal oxides are typically

covalent compounds in which the bonds between oxygen and the nonmetal are polarized ($E^{\delta+}$–$O^{\delta-}$). Consequently, a lone pair of electrons on a water molecule can attack the partially positively charged E atom to eventually form an oxoacid. An example is reacting sulfur trioxide with water to form sulfuric acid:

Equation 22.35

$H_2O(l) + SO_3(g) \rightarrow H_2SO_4(aq)$

The oxides of the semimetals and of elements such as Al that lie near the metal/nonmetal dividing line are amphoteric, as we expect:

Equation 22.36

$Al_2O_3(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2O(l)$

Equation 22.37

$Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2Al(OH)_4^-(aq)$

Note the Pattern

Oxides of metals tend to be basic, oxides of nonmetals tend to be acidic, and oxides of elements in or near the diagonal band of semimetals are generally amphoteric.

EXAMPLE 7

For each reaction, explain why the given products form.

a. $Ga_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2Ga(OH)_4^-(aq)$

b. $3H_2O_2(aq) + 2MnO_4^-(aq) + 2H^+(aq) \rightarrow 3O_2(g) + 2MnO_2(s) + 4H_2O(l)$

a. $KNO_3(s)$ - $\rightarrow$ D $KNO(s) + O_2(g)$

Given: balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

Solution:

a. Gallium is a metal. We expect the oxides of metallic elements to be basic and therefore not to react with aqueous base. A close look at the periodic table, however, shows that gallium is close to the diagonal line of semimetals. Moreover, aluminum, the

element immediately above gallium in group 13, is amphoteric. Consequently, we predict that gallium will behave like aluminum (Equation 22.37).

b. Hydrogen peroxide is an oxidant that can accept two electrons per molecule to give two molecules of water. With a strong oxidant, however, H_2O_2 can also act as a reductant, losing two electrons (and two protons) to produce O_2. Because the other reactant is permanganate, which is a potent oxidant, the only possible reaction is a redox reaction in which permanganate is the oxidant and hydrogen peroxide is the reductant. Recall that reducing permanganate often gives MnO_2, an insoluble brown solid. Reducing MnO_4^- to MnO_2 is a three-electron reduction, whereas the oxidation of H_2O_2 to O_2 is a two-electron oxidation.

c. This is a thermal decomposition reaction. Because KNO_3 contains nitrogen in its highest oxidation state (+5) and oxygen in its lowest oxidation state (−2), a redox reaction is likely. Oxidation of the oxygen in nitrate to atomic oxygen is a two-electron process per oxygen atom. Nitrogen is likely to accept two electrons because oxoanions of nitrogen are known only in the +5 (NO_3^-) and +3 (NO_2^-) oxidation states.

Exercise

Predict the product(s) of each reaction and write a balanced chemical equation for each reaction.

a. $SiO_2(s) + H^+(aq) \rightarrow$

b. $NO(g) + O_2(g) \rightarrow$

c. $SO_3(g) + H_2O(l) \rightarrow$

d. $H_2O_2(aq) + I^-(aq) \rightarrow$

Answer:

a. $SiO_2(s) + H^+(aq) \rightarrow$ no reaction

b. $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

c. $O_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$

d. $H_2O_2(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2OH^-(aq)$

Reactions and Compounds of the Heavier Chalcogens

Because most of the heavier chalcogens (group 16) and pnicogens (group 15) are nonmetals, they often form similar compounds. For example, both third-period elements of these groups (phosphorus and sulfur) form catenated compounds and form multiple allotropes. Consistent with periodic trends, the tendency to catenate decreases as we go down the column.

Sulfur and selenium both form a fairly extensive series of catenated species. For example, elemental sulfur forms S_8 rings packed together in a complex "crankshaft" arrangement (Figure 18.15 "Two Forms of Elemental Sulfur and a Thermodynamic Cycle Showing the Transition from One to the Other"), and molten sulfur contains long chains of sulfur atoms connected by S–S bonds. Moreover, both sulfur and selenium form polysulfides (S_n^{2-}) and polyselenides (Se_n^{2-}), with $n \leq 6$. The only stable allotrope of tellurium is a silvery white substance whose properties and structure are similar to those of one of the selenium allotropes. Polonium, in contrast, shows no tendency to form catenated compounds. The striking decrease in structural complexity from sulfur to polonium is consistent with the decrease in the strength of single bonds and the increase in metallic character as we go down the group.

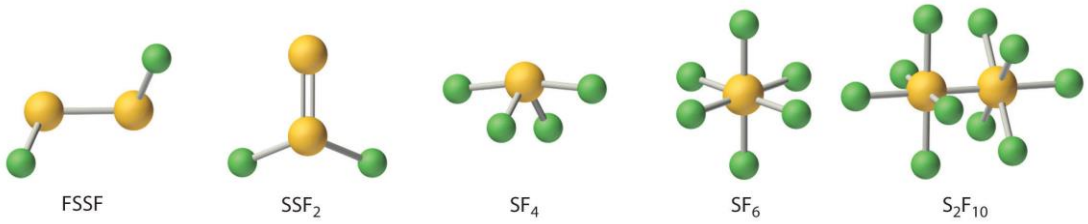
As in group 15, the reactivity of elements in group 16 decreases from lightest to heaviest. For example, selenium and tellurium react with most elements but not as readily as sulfur does. As expected for nonmetals, sulfur, selenium, and tellurium do not react with water, aqueous acid, or aqueous base, but all dissolve in strongly oxidizing acids such as HNO_3 to form oxoacids such as H_2SO_4. In contrast to the other chalcogens, polonium behaves like a metal, dissolving in dilute HCl to form solutions that contain the Po^{2+} ion.

Note the Pattern

Just as with the other groups, the tendency to catenate, the strength of single bonds, and reactivity decrease down the group.

Fluorine reacts directly with all chalcogens except oxygen to produce the hexafluorides (YF_6), which are extraordinarily stable and unreactive compounds. Four additional stable fluorides of sulfur are known; thus sulfur oxidation states range from +1 to +6 (Figure 22.13 "The Structures of the Known Fluorides of Sulfur"). In contrast, only four fluorides of selenium (SeF_6, SeF_4, FSeSeF, and $SeSeF_2$) and only three of tellurium (TeF_4, TeF_6, and Te_2F_{10}) are known.

Figure 22.13 *The Structures of the Known Fluorides of Sulfur*



Five stable sulfur fluorides are known, containing sulfur in oxidation states ranging from +1 to +6. All are volatile molecular compounds that vary tremendously in stability and toxicity. Although both SF_6 and S_2F_{10} are very stable, S_2F_{10} is toxic and SF_6 is not. The other three are highly reactive substances.

Direct reaction of the heavier chalcogens with oxygen at elevated temperatures gives the dioxides (YO_2), which exhibit a dramatic range of structures and properties. The dioxides become increasingly metallic in character down the group, as expected, and the coordination number of the chalcogen steadily increases. Thus SO_2 is a gas that contains V-shaped molecules (as predicted by the valence-shell electron-pair repulsion model), SeO_2 is a white solid with an infinite chain structure (each Se is three coordinate), TeO_2 is a light yellow solid with a network structure in which each Te atom is four coordinate, and PoO_2 is a yellow ionic solid in which each Po^{4+} ion is eight coordinate.

The dioxides of sulfur, selenium, and tellurium react with water to produce the weak, diprotic oxoacids (H_2YO_3—sulfurous, selenous, and tellurous acid, respectively). Both sulfuric acid and selenic acid (H_2SeO_4) are strong acids, but telluric acid [$Te(OH)_6$] is quite different. Because tellurium is larger than either sulfur or selenium, it forms weaker π bonds to oxygen. As a result, the most stable structure for telluric acid is $Te(OH)_6$, with six Te–OH bonds rather than Te=O bonds. Telluric acid therefore behaves like a weak *triprotic* acid in aqueous solution, successively losing the hydrogen atoms bound to three of the oxygen atoms. As expected for compounds that contain elements in their highest accessible oxidation state (+6 in this case), sulfuric, selenic, and telluric acids are oxidants. Because the stability of the highest oxidation state decreases with increasing atomic number, telluric acid is a stronger oxidant than sulfuric acid.

Note the Pattern

The stability of the highest oxidation state of the chalcogens decreases down the column.

Sulfur and, to a lesser extent, selenium react with carbon to form an extensive series of compounds that are structurally similar to their oxygen analogues. For example, $CS_2$and CSe_2 are both volatile liquids that

contain C=S or C=Se bonds and have the same linear structure as CO_2. Because these double bonds are significantly weaker than the C=O bond, however, CS_2, CSe_2, and related compounds are less stable and more reactive than their oxygen analogues. The chalcogens also react directly with nearly all metals to form compounds with a wide range of stoichiometries and a variety of structures. Metal chalcogenides can contain either the simple chalcogenide ion (Y^{2-}), as in Na_2S and FeS, or polychalcogenide ions (Y_n^{2-}), as in FeS_2 and Na_2S_5.

Note the Pattern

The dioxides of the group 16 elements become increasingly basic, and the coordination number of the chalcogen steadily increases down the group.

Ionic chalcogenides like Na_2S react with aqueous acid to produce *binary hydrides* such as hydrogen sulfide (H_2S). Because the strength of the Y–H bond decreases with increasing atomic radius, the stability of the binary hydrides decreases rapidly down the group. It is perhaps surprising that hydrogen sulfide, with its familiar rotten-egg smell, is much more toxic than hydrogen cyanide (HCN), the gas used to execute prisoners in the "gas chamber." Hydrogen sulfide at relatively low concentrations deadens the olfactory receptors in the nose, which allows it to reach toxic levels without detection and makes it especially dangerous.

EXAMPLE 8

For each reaction, explain why the given product forms or no reaction occurs.

a. $SO_2(g) + Cl_2(g) \rightarrow SO_2Cl_2(l)$

b. $SF_6(g) + H_2O(l) \rightarrow$ no reaction

c. $2Se(s) + Cl_2(g) \rightarrow Se_2Cl_2(l)$

Given: balanced chemical equations

Asked for: why the given products (or no products) form

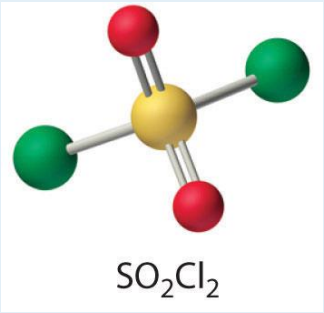
Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the reaction products form or why no reaction occurs.

Solution:

a. One of the reactants (Cl_2) is an oxidant. If the other reactant can be oxidized, then a redox reaction is likely. Sulfur dioxide contains sulfur in the +4 oxidation state, which is 2 less than its maximum

oxidation state. Sulfur dioxide is also known to be a mild reducing agent in aqueous solution, producing sulfuric acid as the oxidation product. Hence a redox reaction is probable. The simplest reaction is the formation of SO_2Cl_2(sulfuryl chloride), which is a tetrahedral species with two S–Cl and two S=O bonds.



b. Sulfur hexafluoride is a nonmetallic halide. Such compounds normally react vigorously with water to produce an oxoacid of the nonmetal and the corresponding hydrohalic acid. In this case, however, we have a highly stable species, presumably because all of sulfur's available orbitals are bonding orbitals. Thus SF_6 is not likely to react with water.

c. Here we have the reaction of a chalcogen with a halogen. The halogen is a good oxidant, so we can anticipate that a redox reaction will occur. Only fluorine is capable of oxidizing the chalcogens to a +6 oxidation state, so we must decide between $SeCl_4$ and Se_2Cl_2 as the product. The stoichiometry of the reaction determines which of the two is obtained: $SeCl_4$ or Se_2Cl_2.

Exercise

Predict the products of each reaction and write a balanced chemical equation for each reaction.

a. $Te(s) + Na(s) \text{ - } \rightarrow$ DSF_4(g) + H_2O(l) →

b. $CH_3SeSeCH_3$(soln) + K(s) →

c. Li_2Se(s) + H^+(aq) →

Answer:

a. Te(s) + 2Na(s) → Na_2Te(s)

b. SF_4(g) + $3H_2O$(l) → H_2SO_3(aq) + 4HF(aq)

c. $CH_3SeSeCH_3$(soln) + 2K(s) → $2KCH_3Se$(soln)

d. Li_2Se(s) + $2H^+$(aq) → H_2Se(g) + $2Li^+$(aq)

Summary

Because the electronegativity of the chalcogens decreases down the group, so does their tendency to acquire two electrons to form compounds in the −2 oxidation state. The lightest member, oxygen, has the greatest tendency to form multiple bonds with other elements. It does not form stable catenated compounds, however, due to repulsions between lone pairs of electrons on adjacent atoms. Because of its high electronegativity, the chemistry of oxygen is generally restricted to compounds in which it has a negative oxidation state, and its bonds to other elements tend to be highly polar. Metal oxides are usually basic, and nonmetal oxides are acidic, whereas oxides of elements along the dividing line between metals and nonmetals are amphoteric. The reactivity, the strength of multiple bonds to oxygen, and the tendency to form catenated compounds all decrease down the group, whereas the maximum coordination numbers increase. Because Te=O bonds are comparatively weak, the most stable oxoacid of tellurium contains six Te–OH bonds. The stability of the highest oxidation state (+6) decreases down the group. Double bonds between S or Se and second-row atoms are weaker than the analogous C=O bonds because of reduced orbital overlap. The stability of the binary hydrides decreases down the group.

KEY TAKEAWAYS

- The chalcogens have no stable metallic elements.
- The tendency to catenate, the strength of single bonds, and the reactivity all decrease moving down the group.

CONCEPTUAL PROBLEMS

1. Unlike the other chalcogens, oxygen does not form compounds in the +4 or +6 oxidation state. Why?
2. Classify each oxide as basic, acidic, amphoteric, or neutral.

a. CaO

b. SO_2

c. NO

d. Rb_2O

e. PbO_2

3. Classify each oxide as basic, acidic, amphoteric, or neutral.

a. BaO

b. Br_2O

c. SnO

d. B_2O_3

e. Sb_2O_3

4. Polarization of an oxide affects its solubility in acids or bases. Based on this, do you expect RuO_2 to be an acidic, a basic, or a neutral oxide? Is the compound covalent? Justify your answers.

5. Arrange CrO_3, Al_2O_3, Sc_2O_3, and BaO in order of increasing basicity.

6. As the atomic number of the group 16 elements increases, the complexity of their allotropes decreases. What factors account for this trend? Which chalcogen do you expect to polymerize the most readily? Why?

7. Arrange H_3BO_3, HIO_4, and HNO_2 in order of increasing acid strength.

8. Of OF_2, SO_2, P_4O_6, SiO_2, and Al_2O_3, which is most ionic?

9. Of CO_2, NO_2, O_2, SO_2, Cl_2O, H_2O, NH_3, and CH_4, which do you expect to have the

a. most polar covalent bond(s)?

b. least polar covalent bond(s)?

10. Of Na_2O_2, MgO, Al_2O_3, and SiO_2, which is most acidic?

11. Give an example of

a. a covalent hydride that engages in strong hydrogen bonding.

b. an amphoteric oxide.

12. The Si–O bond is shorter and stronger than expected. What orbitals are used in this bond? Do you expect Si to interact with Br in the same way? Why or why not?

ANSWERS

1. Oxygen has the second highest electronegativity of any element; consequently, it prefers to share or accept electrons from other elements. Only with fluorine does oxygen form compounds in positive oxidation states.

2.

3.

a. basic

b. acidic

c. amphoteric

d. acidic

e. amphoteric

4.

5. $CrO_3 < Al_2O_3 < Sc_2O_3 < BaO$

6.

7. $H_3BO_3 < HNO_2 < HIO_4$

8.

9. Most polar: H_2O; least polar: O_2

10.

11.

a. H_2O, HF, or NH_3

b. SnO or Al_2O_3

12.

STRUCTURE AND REACTIVITY

1. Considering its position in the periodic table, predict the following properties of selenium:

a. chemical formulas of its most common oxide, most common chloride, and most common hydride

b. solubility of its hydride in water, and the acidity or basicity of the resulting solution

c. the principal ion formed in aqueous solution

2. Using arguments based on electronegativity, explain why ZnO is amphoteric. What product would you expect when ZnO reacts with an aqueous

a. acid?

b. base?

3. Write a balanced chemical equation for the reaction of sulfur with

a. $O_2(g)$.

b. $S^{2-}(aq)$.

c. $F_2(g)$.

d. $HNO_3(aq)$.

ANSWER

1.

2.

3.

a. $a.\ \ S_8 + 8O_2 \text{ - } \rightarrow \text{D } 8SO_2(g)$ $S_8(s) + 8S^{2-}(aq) \rightarrow 8S_2^{2-}(aq)$

b. $S_8(s) + 24F_2(g) \rightarrow 8SF_6(g)$

c. $S_8(s) + 48HNO_3(aq) \rightarrow 8H_2SO_4(aq) + 48NO_2(g) + 16H_2O(l)$

22.5 The Elements of Group 17 (The Halogens)

LEARNING OBJECTIVE

1. To understand the periodic trends and reactivity of the group 17 elements: the halogens.

Because the halogens are highly reactive, none is found in nature as the free element. Hydrochloric acid, which is a component of *aqua regia* (a mixture of HCl and HNO_3that dissolves gold), and the mineral fluorspar (CaF_2) were well known to alchemists, who used them in their quest for gold. Despite their presence in familiar substances, none of the halogens was even recognized as an element until the 19th century.

Note the Pattern

Because the halogens are highly reactive, none is found in nature as the free element.

Chlorine was the first halogen to be obtained in pure form. In 1774, Carl Wilhelm Scheele (the codiscoverer of oxygen) produced chlorine by reacting hydrochloric acid with manganese dioxide. Scheele was convinced, however, that the pale green gas he collected over water was a compound of oxygen and hydrochloric acid. In 1811, Scheele's "compound" was identified as a new element, named from the Greek *chloros*, meaning "yellowish green" (the same stem as in *chlorophyll*, the green pigment in plants). That same year, a French industrial chemist, Bernard Courtois, accidentally added too much sulfuric acid to the residue obtained from burned seaweed. A deep purple vapor was released, which had a biting aroma similar to that of Scheele's "compound." The purple substance was identified as a new element, named iodine from the Greek *iodes*, meaning "violet." Bromine was discovered soon after by a young French chemist, Antoine Jérôme Balard, who isolated a deep red liquid with a strong chlorine-like odor from brine from the salt marshes near Montpellier in southern France. Because many of its properties were intermediate between those of chlorine and iodine, Balard initially thought he had isolated a compound of the two (perhaps ICl). He soon realized, however, that he had discovered a new element, which he named bromine from the Greek *bromos*, meaning "stench." Currently, organic chlorine compounds, such as PVC (polyvinylchloride), consume about 70% of

the Cl_2 produced annually; organobromine compounds are used in much smaller quantities, primarily as fire retardants.

Because of the unique properties of its compounds, fluorine was believed to exist long before it was actually isolated. The mineral fluorspar (now called *fluorite* [CaF_2]) had been used since the 16th century as a "flux," a low-melting-point substance that could dissolve other minerals and ores. In 1670, a German glass cutter discovered that heating fluorspar with strong acid produced a solution that could etch glass. The solution was later recognized to contain the acid of a new element, which was named fluorine in 1812. Elemental fluorine proved to be very difficult to isolate, however, because both HF and F_2 are extraordinarily reactive and toxic. After being poisoned three times while trying to isolate the element, the French chemist Henri Moissan succeeded in 1886 in electrolyzing a sample of KF in anhydrous HF to produce a pale green gas (Figure 22.14 "Isolation of Elemental Fluorine"). For this achievement, among others, Moissan narrowly defeated Mendeleev for the Nobel Prize in Chemistry in 1906. Large amounts of fluorine are now consumed in the production of *cryolite*(Na_3AlF_6), a key intermediate in the production of aluminum metal. Fluorine is also found in teeth as *fluoroapatite* [$Ca_5(PO_4)_3F$], which is formed by reacting hydroxyapatite [$Ca_5(PO_4)_3OH$] in tooth enamel with fluoride ions in toothpastes, rinses, and drinking water.

oxidizing impurities, which generate detectable amounts of ozone when the crystals are crushed.

Preparation and General Properties of the Group 17 Elements

All the halogens except iodine are found in nature as salts of the halide ions (X^-), so the methods used for preparing F_2, Cl_2, and Br_2 all involve oxidizing the halide. Reacting CaF_2 with concentrated sulfuric acid produces gaseous hydrogen fluoride:

Equation 22.38

$$CaF_2(s) + H_2SO_4(l) \rightarrow CaSO_4(s) + 2HF(g)$$

Fluorine is produced by the electrolysis of a 1:1 mixture of HF and $K^+HF_2^-$ at 60–300°C in an apparatus made of Monel, a highly corrosion-resistant nickel–copper alloy:

Equation 22.39

$$KHF2 \cdot HF(l) - \rightarrow - - - - - electrolysis F2(g) + H2(g)$$

Fluorine is one of the most powerful oxidants known, and both F_2 and HF are highly corrosive. Consequently, the production, storage, shipping, and handling of these gases pose major technical challenges.

Although chlorine is significantly less abundant than fluorine, elemental chlorine is produced on an enormous scale. Fortunately, large subterranean deposits of rock salt (NaCl) are found around the world (Figure 22.15 "A Subterranean Salt Mine"), and seawater consists of about 2% NaCl by mass, providing an almost inexhaustible reserve. Inland salt lakes such as the Dead Sea and the Great Salt Lake are even richer sources, containing about 23% and 8% NaCl by mass, respectively. Chlorine is prepared industrially by the chloralkali process, which uses the following reaction:

Equation 22.40

$$2NaCl(aq) + 2H2O(l) \xrightarrow{\text{electrolysis}} 2NaOH(aq) + Cl2(g) + H2(g)$$

Bromine is much less abundant than fluorine or chlorine, but it is easily recovered from seawater, which contains about 65 mg of Br^- per liter. Salt lakes and underground brines are even richer sources; for example, the Dead Sea contains 4 g of Br^- per liter. Iodine is the least abundant of the nonradioactive halogens, and it is a relatively rare element. Because of its low electronegativity, iodine tends to occur in nature in an oxidized form. Hence most commercially important deposits of iodine, such as those in the Chilean desert, are iodate salts such as $Ca(IO_3)_2$. The production of iodine from such deposits therefore requires *reduction* rather than oxidation. The process is typically carried out in two steps: reduction of iodate to iodide with sodium hydrogen sulfite, followed by reaction of iodide with additional iodate:

Equation 22.41

$$2IO_3^-(aq) + 6HSO_3^-(aq) \rightarrow 2I^-(aq) + 6SO_4^{2-}(aq) + 6H^+(aq)$$

Equation 22.42

$$5I^-(aq) + IO_3^-(aq) + 6H^+(aq) \rightarrow 3I_2(s) + 3H_2O(l)$$

Because the halogens all have ns^2np^5 electron configurations, their chemistry is dominated by a tendency to accept an additional electron to form the closed-shell ion (X^-). Only the electron affinity and the bond dissociation energy of fluorine differ significantly from the expected periodic trends shown in Table 22.6 "Selected Properties of the Group 17 Elements". Electron–electron repulsion is important in fluorine because of its small atomic volume, making the electron affinity of fluorine less than that of chlorine. Similarly, repulsions between electron pairs on adjacent atoms are responsible for the unexpectedly low F–F bond dissociation energy. (As discussed earlier, this effect is also responsible for the weakness of O–O, N–N, and N–O bonds.)

Note the Pattern

Oxidative strength decreases down group 17.

Note the Pattern

Electrostatic repulsions between lone pairs of electrons on *adjacent* atoms cause single bonds between N, O, and F to be weaker than expected.

Table 22.6 Selected Properties of the Group 17 Elements

Property	Fluorine	Chlorine	Bromine	Iodine	Astatine
atomic symbol	F	Cl	Br	I	At
atomic number	9	17	35	53	85
atomic mass (amu)	19.00	35.45	79.90	126.90	210
valence electron configuration*	$2s^2 2p^5$	$3s^2 3p^5$	$4s^2 4p^5$	$5s^2 5p^5$	$6s^2 6p^5$
melting point/boiling point (°C)	−220/−188	−102/−34.0	−7.2/58.8	114/184	302/—
density (g/cm³) at 25°C	1.55 $(g/L$	2.90 (g/L)	3.10	4.93	—
atomic radius (pm)	42	79	94	115	127
first ionization energy (kJ/mol)	1681	1251	1140	1008	926
normal oxidation state(s)	−1	−1 (+1, +3, +5, +7)	−1 (+1, +3, +5, +7)	−1 (+1, +3, +5, +7)	−1, +1
ionic radius (pm)†	133	181	196	220	—
electron affinity (kJ/mol)	−328	−349	−325	−295	−270
electronegativity	4.0	3.2	3.0	2.7	2.2
standard reduction potential ($E°$, V) ($X_2 \rightarrow X^-$ in basic solution)	+2.87	+1.36	+1.07	+0.54	+0.30
dissociation energy of X_2(g) (kJ/mol)	158.8	243.6	192.8	151.1	~80
product of reaction with O_2	O_2F_2	none	none	none	none
type of oxide	acidic	acidic	acidic	acidic	acidic
product of reaction with N_2	none	none	none	none	none
product of reaction with H_2	HF	HCl	HBr	HI	HAt
***The configuration shown does not include filled *d* and *f* subshells.**					
†The values cited are for the six-coordinate anion (X^-).					

Because it is the most electronegative element in the periodic table, fluorine forms compounds in only the −1 oxidation state. Notice, however, that all the halogens except astatine have electronegativities greater than 2.5, making their chemistry exclusively that of nonmetals. The halogens all have relatively high

ionization energies, but the energy required to remove electrons decreases substantially as we go down the column. Hence the heavier halogens also form compounds in positive oxidation states (+1, +3, +5, and +7), derived by the formal loss of *ns* and *np* electrons.

Note the Pattern

Because ionization energies decrease down the group, the heavier halogens form compounds in positive oxidation states (+1, +3, +5, and +7).

Reactions and Compounds of the Halogens

Fluorine is the most reactive element in the periodic table, forming compounds with every other element except helium, neon, and argon. The reactions of fluorine with most other elements range from vigorous to explosive; only O_2, N_2, and Kr react slowly. There are three reasons for the high reactivity of fluorine:

1. Because fluorine is so electronegative, it is able to remove or at least share the valence electrons of virtually any other element.
2. Because of its small size, fluorine tends to form very strong bonds with other elements, making its compounds thermodynamically stable.
3. The F–F bond is weak due to repulsion between lone pairs of electrons on adjacent atoms, reducing both the thermodynamic and kinetic barriers to reaction.

With highly electropositive elements, fluorine forms ionic compounds that contain the closed-shell F^- ion. In contrast, with less electropositive elements (or with metals in very high oxidation states), fluorine forms covalent compounds that contain terminal F atoms, such as SF_6. Because of its high electronegativity and $2s^22p^5$ valence electron configuration, fluorine normally participates in only one electron-pair bond. Only a very strong Lewis acid, such as AlF_3, can share a lone pair of electrons with a fluoride ion, forming AlF_6^{3-}.

The halogens (X_2) react with metals (M) according to the general equation

Equation 22.43

$$M(s,l) + nX_2(s,l,g) \rightarrow MX_n(s,l)$$

For elements that exhibit multiple oxidation states fluorine tends to produce the highest possible oxidation state and iodine the lowest. For example, vanadium reacts with the halogens to give VF_5, VCl_4, VBr_4, and VI_3.

Metal halides in the +1 or +2 oxidation state, such as CaF_2, are typically ionic halides, which have high melting points and are often soluble in water. As the oxidation state of the metal increases, so does the

covalent character of the halide due to polarization of the M–X bond. With its high electronegativity, fluoride is the least polarizable, and iodide, with the lowest electronegativity, is the most polarizable of the halogens. Halides of small trivalent metal ions such as Al^{3+} tend to be relatively covalent. For example, $AlBr_3$ is a volatile solid that contains bromide-bridged Al_2Br_6 molecules. In contrast, the halides of larger trivalent metals, such as the lanthanides, are essentially ionic. For example, indium tribromide ($InBr_3$) and lanthanide tribromide ($LnBr_3$) are all high-melting-point solids that are quite soluble in water.

Note the Pattern

As the oxidation state of the metal increases, the covalent character of the corresponding metal halides also increases due to polarization of the M–X bond.

All halogens react vigorously with hydrogen to give the hydrogen halides (HX). Because the H–F bond in HF is highly polarized ($H^{\delta+}$–$F^{\delta-}$), liquid HF has extensive hydrogen bonds, giving it an unusually high boiling point and a high dielectric constant. As a result, liquid HF is a polar solvent that is similar in some ways to water and liquid ammonia; after a reaction, the products can be recovered simply by evaporating the HF solvent. (Hydrogen fluoride must be handled with extreme caution, however, because contact of HF with skin causes extraordinarily painful burns that are slow to heal.) Because fluoride has a high affinity for silicon, aqueous hydrofluoric acid is used to etch glass, dissolving SiO_2 to give solutions of the stable SiF_6^{2-} ion.

Except for fluorine, all the halogens react with water in a disproportionation reaction, where X is Cl, Br, or I:

Equation 22.44

$$X_2(g,l,s) + H_2O(l) \rightarrow H^+(aq) + X^-(aq) + HOX(aq)$$

The most stable oxoacids are the *perhalic acids*, which contain the halogens in their highest oxidation state (+7). The acid strengths of the oxoacids of the halogens increase with increasing oxidation state, whereas their stability and acid strength decrease down the group. Thus perchloric acid ($HOClO_3$, usually written as $HClO_4$) is a more potent acid and stronger oxidant than perbromic acid. Although all the oxoacids are strong oxidants, some, such as $HClO_4$, react rather slowly at low temperatures. Consequently, mixtures of the halogen oxoacids or oxoanions with organic compounds are potentially explosive if they are heated or even agitated mechanically to initiate the reaction. Because of the danger of explosions, *oxoacids and oxoanions of the halogens should never be allowed to come into contact with organic compounds*.

Note the Pattern

Both the acid strength and the oxidizing power of the halogen oxoacids decrease down the group.

The halogens react with one another to produce *interhalogen compounds*, such as ICl_3, BrF_5, and IF_7. In all cases, the heavier halogen, which has the lower electronegativity, is the central atom. The maximum oxidation state and the number of terminal halogens increase smoothly as the ionization energy of the central halogen decreases and the electronegativity of the terminal halogen increases. Thus depending on conditions, iodine reacts with the other halogens to form IF_n (n = 1–7), ICl or ICl_3, or IBr, whereas bromine reacts with fluorine to form only BrF, BrF_3, and BrF_5 but not BrF_7. The interhalogen compounds are among the most powerful Lewis acids known, with a strong tendency to react with halide ions to give complexes with higher coordination numbers, such as the IF_8^- ion:

Equation 22.45

$$IF_7(l) + KF(s) \rightarrow KIF_8(s)$$

All group 17 elements form compounds in odd oxidation states (−1, +1, +3, +5, +7). The interhalogen compounds are also potent oxidants and strong fluorinating agents; contact with organic materials or water can result in an explosion.

Note the Pattern

All group 17 elements form compounds in odd oxidation states (−1, +1, +3, +5, +7), but the importance of the higher oxidation states generally decreases down the group.

EXAMPLE 9

For each reaction, explain why the given products form.

a. $ClF_3(g) + Cl_2(g) \rightarrow 3ClF(g)$

b. $2KI(s) + 3H_2SO_4(aq) \rightarrow I_2(aq) + SO_2(g) + 2KHSO_4(aq) + 2H_2O(l)$

c. $Pb(s) + 2BrF_3(l) \rightarrow PbF_4(s) + 2BrF(g)$

Given: balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

Solution:

a. When the reactants have the same element in two different oxidation states, we expect the product to have that element in an intermediate oxidation state. We have Cl^{3+} and Cl^{0} as reactants, so a possible product would have Cl in either the +1 or +2 oxidation state. From our discussion, we know that +1 is much more likely. In this case, Cl_2 is behaving like a reductant rather than an oxidant.

b. At first glance, this appears to be a simple acid–base reaction, in which sulfuric acid transfers a proton to I^- to form HI. Recall, however, that I^- can be oxidized to I_2. Sulfuric acid contains sulfur in its highest oxidation state (+6), so it is a good oxidant. In this case, the redox reaction predominates.

c. This is the reaction of a metallic element with a very strong oxidant. Consequently, a redox reaction will occur. The only question is whether lead will be oxidized to Pb(II) or Pb(IV). Because BrF_3 is a powerful oxidant and fluorine is able to stabilize high oxidation states of other elements, it is likely that PbF_4 will be the product. The two possible reduction products for BrF_3 are BrF and Br_2. The actual product will likely depend on the ratio of the reactants used. With excess BrF_3, we expect the more oxidized product (BrF). With lower ratios of oxidant to lead, we would probably obtain Br_2 as the product.

Exercise

Predict the products of each reaction and write a balanced chemical equation for each reaction.

a. $CaCl_2(s) + H_3PO_4(l) \rightarrow$

b. $GeO_2(s) + HF(aq) \rightarrow$

c. $Fe_2O_3(s) + HCl(g) - \rightarrow$ D

d. $NaClO_2(aq) + Cl_2(g) \rightarrow$

Answer:

a. $CaCl_2(s) + H_3PO_4(l) \rightarrow 2HCl(g) + Ca(HPO_4)(soln)$

b. $GeO_2(s) + 6HF(aq) \rightarrow GeF_6^{2-}(aq) + 2H_2O(l) + 2H^+(aq)$

c. $Fe_2O_3(s) + 6HCl(g) - \rightarrow$ D $2FeCl_3(s$

d. $) + 3H_2O(g)$

e. $2NaClO_2(aq) + Cl_2(g) \rightarrow 2ClO_2(g) + 2NaCl(aq)$

Summary

The halogens are so reactive that none is found in nature as the free element; instead, all but iodine are found as halide salts with the X^- ion. Their chemistry is exclusively that of nonmetals. Consistent with periodic trends, ionization energies decrease down the group. Fluorine, the most reactive element in the periodic table, has a low F–F bond dissociation energy due to repulsions between lone pairs of electrons on adjacent atoms. Fluorine forms ionic compounds with electropositive elements and covalent compounds with less electropositive elements and metals in high oxidation states. All the halogens react with hydrogen to produce hydrogen halides. Except for F_2, all react with water to form oxoacids, including the *perhalic acids*, which contain the halogens in their highest oxidation state. Halogens also form *interhalogen compounds*; the heavier halogen, with the lower electronegativity, is the central atom.

KEY TAKEAWAY

- The halogens are highly reactive.
- All halogens have relatively high ionization energies, and the acid strength and oxidizing power of their oxoacids decreases down the group.

CONCEPTUAL PROBLEMS

1. The lightest elements of groups 15, 16, and 17 form unusually weak single bonds. Why are their bonds so weak?
2. Fluorine has an anomalously low F–F bond energy. Why? Why does fluorine form compounds only in the −1 oxidation state, whereas the other halogens exist in multiple oxidation states?
3. Compare AlI_3, $InCl_3$, GaF_3, and $LaBr_3$ with respect to the type of M–X bond formed, melting point, and solubility in nonpolar solvents.
4. What are the formulas of the interhalogen compounds that will most likely contain the following species in the indicated oxidation states: I (+3), Cl (+3), I (−1), Br (+5)?
5. Consider this series of bromides: $AlBr_3$, $SiBr_4$, and PBr_5. Does the ionic character of the bond between the Br atoms and the central atom decrease or increase in this series?
6. Chromium forms compounds in the +6, +3, and +2 oxidation states. Which halogen would you use to produce each oxidation state? Justify your selections.
7. Of ClF_7, BrF_5, IF_7, BrF_3, ICl_3, IF_3, and IF_5, which one is least likely to exist? Justify your selection.

ANSWERS

1. Electrostatic repulsions between lone pairs on adjacent atoms decrease bond strength.

2.

3.

4.

5. Ionic character decreases as Δχ decreases from Al to P.

6.

7. ClF_7

STRUCTURE AND REACTIVITY

1. SiF_4 reacts easily with NaF to form SiF_6^{2-}. In contrast, CF_4 is totally inert and shows no tendency to form CF_6^{2-} under even extreme conditions. Explain this difference.
2. Predict the products of each reaction and then balance each chemical equation.

a. $Xe(g) + \text{excess } F_2(g) \rightarrow$

b. $Se(s) + Cl_2(g) \rightarrow$

c. $SO_2(g) + Br_2(g) \rightarrow$

d. $NaBH_4(s) + BF_3(soln) \rightarrow$

3. Write a balanced chemical equation for the reaction of aqueous HF with

a. SiO_2.

b. Na_2CO_3.

c. CaO.

4. Oxyhalides of sulfur, such as the *thionyl halides* (SOX_2, where X is F, Cl, or Br), are well known. Because the thionyl halides react vigorously with trace amounts of water, they are used for dehydrating hydrated metal salts. Write a balanced chemical equation to show the products of reaction of $SOCl_2$ with water.
5. Write a balanced chemical equation describing each reaction.

a. the burning of sulfur in a chlorine atmosphere

b. the dissolution of iodine in a potassium iodide solution

c. the hydrolysis of PCl_3

d. the preparation of HF from calcium fluoride and sulfuric acid

e. the thermal decomposition of $KClO_3$

f. the oxidation of sulfide ion by elemental iodine

6. Write the complete Lewis electron structure, the type of hybrid used by the central atom, and the number of lone pair electrons present on the central atom for each compound.

a. CF_4

b. PCl_3

c. XeF_4

ANSWERS

1. Carbon has no low energy *d* orbitals that can be used to form a set of d^2sp^3 hybrid orbitals. It is also so small that it is impossible for six fluorine atoms to fit around it at a distance that would allow for formation of strong C–F bonds.

2.

3.

a. $SiO_2(s) + 6HF(aq) \rightarrow SiF_6^{2-}(aq) + 2H^+(aq) + 2H_2O(l)$

b. $Na_2CO_3(s) + 2HF(aq) \rightarrow CO_2(g) + 2NaF(aq) + H_2O(l)$

c. $CaO(s) + 2HF(aq) \rightarrow CaF_2(s) + H_2O(l)$

4.

5.

a. $S_8(s) + 4Cl_2(g) \rightarrow 4S_2Cl_2(l)$

b. $I_2(s) + KI(aq) \rightarrow I_3^-(aq) + K^+(aq)$

c. $PCl_3(l) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HCl(aq)$

d. $CaF_2(s) + H_2SO_4(aq) \rightarrow 2HF(aq) + CaSO_4(s)$

e. $a.\quad 2KClO_3(s) \text{ - } \rightarrow \text{D } 2KCl(s) + 3O_2(g)$

f. $8S^{2-}(aq) + 8I_2(aq) \rightarrow S_8(s) + 16I^-(aq)$

22.6 The Elements of Group 18 (The Noble Gases)

LEARNING OBJECTIVE

1. To understand the trends in properties and reactivity of the group 18 elements: the noble gases.

The noble gases were all isolated for the first time within a period of only five years at the end of the 19th century. Their very existence was not suspected until the 18th century, when early work on the composition of air suggested that it contained small amounts of gases in addition to oxygen, nitrogen, carbon dioxide, and water vapor. Helium

was the first of the noble gases to be identified, when the existence of this previously unknown element on the sun was demonstrated by new spectral lines seen during a solar eclipse in 1868. (For more information on spectroscopy, see Chapter 6 "The Structure of Atoms".) Actual samples of helium were not obtained until almost 30 years later, however. In the 1890s, the English physicist J. W. Strutt (Lord Rayleigh) carefully measured the density of the gas that remained after he had removed all O_2, CO_2, and water vapor from air and showed that this residual gas was slightly denser than pure N_2 obtained by the thermal decomposition of ammonium nitrite. In 1894, he and the Scottish chemist William Ramsay announced the isolation of a new "substance" (not necessarily a new element) from the residual nitrogen gas. Because they could not force this substance to decompose or react with anything, they named it *argon* (Ar), from the Greek *argos*, meaning "lazy." Because the measured molar mass of argon was 39.9 g/mol, Ramsay speculated that it was a member of a new group of elements located on the right side of the periodic table between the halogens and the alkali metals. He also suggested that these elements should have a preferred valence of 0, intermediate between the +1 of the alkali metals and the −1 of the halogens.

J. W. Strutt (Lord Rayleigh) (1842–1919)

Lord Rayleigh was one of the few members of British higher nobility to be recognized as an outstanding scientist. Throughout his youth, his education was repeatedly interrupted by his frail health, and he was not expected to reach maturity. In 1861 he entered Trinity College, Cambridge, where he excelled at mathematics. A severe attack of rheumatic fever took him abroad, but in 1873 he succeeded to the barony and was compelled to devote his time to the management of his estates. After leaving the entire management to his younger brother, Lord Rayleigh was able to devote his time to science. He was a recipient of honorary science and law degrees from Cambridge University.

Sir William Ramsay (1852–1916)

Born and educated in Glasgow, Scotland, Ramsay was expected to study for the Calvanist ministry. Instead, he became interested in chemistry while reading about the manufacture of gunpowder. Ramsay earned his PhD in organic chemistry at the University of Tübingen in Germany in 1872. When he returned to England, his interests turned first to physical chemistry and then to inorganic chemistry. He is best known for his work on the oxides of nitrogen and for the discovery of the noble gases with Lord Rayleigh.

In 1895, Ramsey was able to obtain a terrestrial sample of helium for the first time. Then, in a single year (1898), he discovered the next three noble gases: krypton (Kr), from the Greek *kryptos*, meaning "hidden," was identified by its orange and green emission lines; neon (Ne), from the Greek *neos*, meaning "new," had bright red emission lines; and

xenon (Xe), from the Greek *xenos*, meaning "strange," had deep blue emission lines. The last noble gas was discovered in 1900 by the German chemist Friedrich Dorn, who was investigating radioactivity in the air around the newly discovered radioactive elements radium and polonium. The element was named radon (Rn), and Ramsay succeeded in obtaining enough radon in 1908 to measure its density (and thus its atomic mass). For their discovery of the noble gases, Rayleigh was awarded the Nobel Prize in Physics and Ramsay the Nobel Prize in Chemistry in 1904. Because helium has the lowest boiling point of any substance known (4.2 K), it is used primarily as a cryogenic liquid. Helium and argon are both much less soluble in water (and therefore in blood) than N_2, so scuba divers often use gas mixtures that contain these gases, rather than N_2, to minimize the likelihood of the "bends," the painful and potentially fatal formation of bubbles of $N_2(g)$ that can occur when a diver returns to the surface too rapidly.

Preparation and General Properties of the Group 18 Elements

Fractional distillation of liquid air is the only source of all the noble gases except helium. Although helium is the second most abundant element in the universe (after hydrogen), the helium originally present in Earth's atmosphere was lost into space long ago because of its low molecular mass and resulting high mean velocity. Natural gas often contains relatively high concentrations of helium (up to 7%), however, and it is the only practical terrestrial source.

The elements of group 18 all have closed-shell valence electron configurations, either ns^2np^6 or $1s^2$ for He. Consistent with periodic trends in atomic properties, these elements have high ionization energies that decrease smoothly down the group. From their electron affinities, the data in Table 22.7 "Selected Properties of the Group 18 Elements" indicate that the noble gases are unlikely to form compounds in negative oxidation states. A potent oxidant is needed to oxidize noble gases and form compounds in positive oxidation states. Like the heavier halogens, xenon and perhaps krypton should form covalent compounds with F, O, and possibly Cl, in which they have *even* formal oxidation states (+2, +4, +6, and possibly +8). These predictions actually summarize the chemistry observed for these elements.

Table 22.7 Selected Properties of the Group 18 Elements

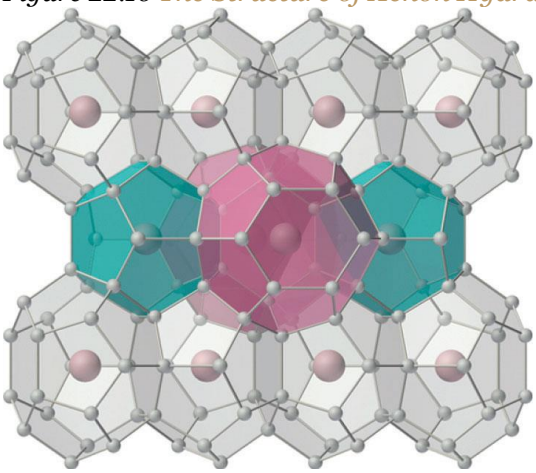
Property	Helium	Neon	Argon	Krypton	Xenon	Radon
atomic symbol	He	Ne	Ar	Kr	Xe	Rn
atomic number	2	10	18	36	54	86
atomic mass (amu)	4.00	20.18	39.95	83.80	131.29	222
valence electron configuration*	$1s^2$	$2s^22p^6$	$3s^23p^6$	$4s^24p^6$	$5s^25p^6$	$6s^26p^6$

Property	Helium	Neon	Argon	Krypton	Xenon	Radon
triple point/boiling point (°C)	—/−269†	−249 (at 43 kPa)/−246	−189 (at 69 kPa)/−189	−157/−153	−112 (at 81.6 kPa)/−108	−71/−62
density (g/L) at 25°C	0.16	0.83	1.63	3.43	5.37	9.07
atomic radius (pm)	31	38	71	88	108	120
first ionization energy (kJ/mol)	2372	2081	1521	1351	1170	1037
normal oxidation state(s)	0	0	0	0 (+2)	0 (+2, +4, +6, +8)	0 (+2)
electron affinity (kJ/mol)	> 0	> 0	> 0	> 0	> 0	> 0
electronegativity	—	—	—	—	2.6	—
product of reaction with O_2	none	none	none	none	none	none
type of oxide	—	—	—	—	acidic	—
product of reaction with N_2	none	none	none	none	none	none
product of reaction with X_2	none	none	none	KrF_2	XeF_2, XeF_4, XeF_6	RnF_2
product of reaction with H_2	none	none	none	none	none	none
***The configuration shown does not include filled *d* and *f* subshells.**						
†This is the normal boiling point of He. Solid He does not exist at 1 atm pressure, so no melting point can be given.						

Reactions and Compounds of the Noble Gases

For many years, it was thought that the only compounds the noble gases could form were *clathrates*. Clathrates are solid compounds in which a gas, the guest, occupies holes in a lattice formed by a less volatile, chemically dissimilar substance, the host (Figure 22.16 "The Structure of Xenon Hydrate, a Clathrate"). Because clathrate formation does not involve the formation of chemical bonds between the guest (Xe) and the host molecules (H_2O, in the case of xenon hydrate), the guest molecules are immediately released when the clathrate is melted or dissolved. In addition to the noble gases, many other species form stable clathrates. One of the most interesting is methane hydrate, large deposits of which occur naturally at the bottom of the oceans. It is estimated that the amount of methane in such deposits could have a major impact on the world's energy needs later in this century.

Figure 22.16 *The Structure of Xenon Hydrate, a Clathrate*



Small gaseous atoms or molecules such as Xe or CH_4 can occupy cavities in a lattice of hydrogen-bonded water molecules to produce a stable structure with a fixed stoichiometry (in this case, $Xe·5.75H_2O$). (The hydrogen atoms of the water molecules have been omitted for clarity.) Warming the solid hydrate or decreasing the pressure of the gas causes it to collapse, with the evolution of gas and the formation of liquid water.

"Burning snowballs."*Like xenon, methane (CH_4) forms a crystalline clathrate with water: methane hydrate. When the solid is warmed, methane is released and can be ignited to give what appears to be burning snow.*

The widely held belief in the intrinsic lack of reactivity of the noble gases was challenged when Neil Bartlett, a British professor of chemistry at the University of British Columbia, showed that PtF_6, a compound used in the Manhattan Project, could oxidize O_2. Because the ionization energy of xenon (1170 kJ/mol) is actually lower than that of O_2, Bartlett recognized that PtF_6should also be able to oxidize xenon. When he mixed colorless xenon gas with deep red PtF_6 vapor, yellow-orange crystals immediately formed (Figure 22.17 "The Synthesis of the First Chemical Compound of Xenon"). Although Bartlett initially postulated that they were $Xe^+PtF_6^-$, it is now generally agreed that the reaction also involves the transfer of a fluorine atom to xenon to give the XeF^+ ion:

Equation 22.46

$$Xe(g) + PtF_6(g) \rightarrow [XeF^+][PtF_5^-](s)$$

Subsequent work showed that xenon reacts directly with fluorine under relatively mild conditions to give XeF_2, XeF_4, or XeF_6, depending on conditions; one such reaction is as follows:

Equation 22.47

$Xe(g) + 2F_2(g) \rightarrow XeF_4(s)$

The ionization energies of helium, neon, and argon are so high (Table 22.7 "Selected Properties of the Group 18 Elements") that no stable compounds of these elements are known. The ionization energies of krypton and xenon are lower but still very high; consequently only highly electronegative elements (F, O, and Cl) can form stable compounds with xenon and krypton without being oxidized themselves. Xenon reacts directly with only two elements: F_2 and Cl_2. Although $XeCl_2$ and KrF_2 can be prepared directly from the elements, they are substantially less stable than the xenon fluorides.

Note the Pattern

The ionization energies of helium, neon, and argon are so high that no stable compounds of these elements are known.

Because halides of the noble gases are powerful oxidants and fluorinating agents, they decompose rapidly after contact with trace amounts of water, and they react violently with organic compounds or other reductants. The xenon fluorides are also Lewis acids; they react with the fluoride ion, the only Lewis base that is not oxidized immediately on contact, to form anionic complexes. For example, reacting cesium fluoride with XeF_6produces $CsXeF_7$, which gives Cs_2XeF_8 when heated:

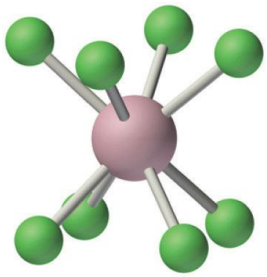
Equation 22.48

$XeF_6(s) + CsF(s) \rightarrow CsXeF_7(s)$

Equation 22.49

$$2CsXeF7(s) \rightarrow DCs2XeF8(s) + XeF6(g)$$

The XeF_8^{2-} ion contains eight-coordinate xenon and has the square antiprismatic structure shown here, which is essentially identical to that of the IF_8^- ion. Cs_2XeF_8 is surprisingly stable for a polyatomic ion that contains xenon in the +6 oxidation state, decomposing only at temperatures greater than 300°C. Major factors in the stability of Cs_2XeF_8 are almost certainly the formation of a stable ionic lattice and the high coordination number of xenon, which protects the central atom from attack by other species. (Recall from Section 22.4 "The Elements of Group 16 (The Chalcogens)" that this latter effect is responsible for the extreme stability of SF_6.)



XeF_8^{2-}

For a previously "inert" gas, xenon has a surprisingly high affinity for oxygen, presumably because of π bonding between O and Xe. Consequently, xenon forms an extensive series of oxides and oxoanion salts. For example, hydrolysis of either XeF_4 or XeF_6 produces XeO_3, an explosive white solid:

Equation 22.50

$$XeF_6(aq) + 3H_2O(l) \rightarrow XeO_3(aq) + 6HF(aq)$$

Treating a solution of XeO_3 with ozone, a strong oxidant, results in further oxidation of xenon to give either XeO_4, a colorless, explosive gas, or the surprisingly stable perxenate ion (XeO_6^{4-}), both of which contain xenon in its highest possible oxidation state (+8). The chemistry of the xenon halides and oxides is best understood by analogy to the corresponding compounds of iodine. For example, XeO_3 is isoelectronic with the iodate ion (IO_3^-), and XeF_8^{2-} is isoelectronic with the IF_8^- ion.

Note the Pattern

Xenon has a high affinity for both fluorine and oxygen.

Because the ionization energy of radon is less than that of xenon, in principle radon should be able to form an even greater variety of chemical compounds than xenon. Unfortunately, however, radon is so radioactive that its chemistry has not been extensively explored.

EXAMPLE 10

On a virtual planet similar to Earth, at least one isotope of radon is not radioactive. A scientist explored its chemistry and presented her major conclusions in a trailblazing paper on radon compounds, focusing on the kinds of compounds formed and their stoichiometries. Based on periodic trends, how did she summarize the chemistry of radon?

Given: nonradioactive isotope of radon

Asked for: summary of its chemistry

Strategy:

Based on the position of radon in the periodic table and periodic trends in atomic properties, thermodynamics, and kinetics, predict the most likely reactions and compounds of radon.

Solution:

We expect radon to be significantly easier to oxidize than xenon. Based on its position in the periodic table, however, we also expect its bonds to other atoms to be weaker than those formed by xenon. Radon should be more difficult to oxidize to its highest possible oxidation state (+8) than xenon because of the inert-pair effect. Consequently, radon should form an extensive series of fluorides, including RnF_2, RnF_4, RnF_6, and possibly RnF_8 (due to its large radius). The ion RnF_8^{2-} should also exist. We expect radon to form a series of oxides similar to those of xenon, including RnO_3 and possibly RnO_4. The biggest surprise in radon chemistry is likely to be the existence of stable chlorides, such as $RnCl_2$ and possibly even $RnCl_4$.

Exercise

Predict the stoichiometry of the product formed by reacting XeF_6 with a 1:1 stoichiometric amount of KF and propose a reasonable structure for the anion.

Answer: $KXeF_7$; the xenon atom in XeF_7^- has 16 valence electrons, which according to the valence-shell electron-pair repulsion model could give either a square antiprismatic structure with one fluorine atom missing or a pentagonal bipyramid if the $5s^2$ electrons behave like an inert pair that does not participate in bonding.

Summary

The noble gases have a closed-shell valence electron configuration. The ionization energies of the noble gases decrease with increasing atomic number. Only highly electronegative elements can form stable compounds with the noble gases in positive oxidation states without being oxidized themselves. Xenon has a high affinity for both fluorine and oxygen, which form stable compounds that contain xenon in even oxidation states up to +8.

KEY TAKEAWAYS

- The noble gases are characterized by their high ionization energies and low electron affinities.
- Potent oxidants are needed to oxidize the noble gases to form compounds in positive oxidation states.

CONCEPTUAL PROBLEMS

1. The chemistry of the noble gases is largely dictated by a balance between two competing properties. What are these properties? How do they affect the reactivity of these elements?
2. Of the group 18 elements, only krypton, xenon, and radon form stable compounds with other atoms and then only with very electronegative elements. Why?
3. Give the type of hybrid orbitals used by xenon in each species.

a. XeF_2

b. XeF_4

c. XeO_3

d. $XeOF_4$

e. XeO_4

f. XeO_6^{4-}

4. Which element is the least metallic—B, Ga, Tl, Pb, Ne, or Ge?
5. Of Br, N, Ar, Bi, Se, He, and S, which would you expect to form positive ions most easily? negative ions most easily?
6. Of BCl_3, BCl_4^-, CH_4, $H_3N{\cdot}BF_3$, PCl_3, PCl_5, XeO_3, H_2O, and F^-, which species do you expect to be

a. electron donors?

b. electron acceptors?

c. neither electron donors nor acceptors?

d. both electron donors and acceptors?

7. Of HCl, $HClO_4$, HBr, H_2S, HF, KrF_2, and PH_3, which is the strongest acid?
8. Of CF_4, NH_3, NF_3, H_2O, OF_2, SiF_4, H_2S, XeF_4, and SiH_4, which is the strongest base?

STRUCTURE AND REACTIVITY

1. Write a balanced chemical equation showing how you would prepare each compound from its elements and other common compounds.

a. XeF_2

b. XeF_4

c. XeF_6

d. $XeOF_4$

e. XeO_3

2. Write a balanced chemical equation showing how you would make each compound.

a. XeF_2 from Xe gas

b. $NaXeF_7$ from its elements

c. RnO_3 from Rn

3. In an effort to synthesize XeF_6, a chemist passed fluorine gas through a glass tube containing xenon gas. However, the product was not the one expected. What was the actual product?

4. Write a balanced chemical equation to describe the reaction of each species with water.

a. B_2H_6

b. F_2

c. C^{4+}

5. Using heavy water (D_2O) as the source of deuterium, how could you prepare each compound?

a. $LiAlD_4$

b. D_2SO_4

c. SiD_4

d. DF

6. Predict the product(s) of each reaction and write a balanced chemical equation for each reaction.

a. $Al_2O_3(s)$ in $OH^-(aq)$

b. $Ar(g) + F_2(g)$

c. $PI_3(s) + H_2O(l)$

d. $H_3PO_3(l) + OH^-(aq)$

e. $Bi(s)$ + excess $Br_2(l)$

ANSWERS

1.

a. $Xe(g) + F_2(g) \rightarrow XeF_2(s)$

b. $Xe(g) + 2F_2(g) \rightarrow XeF_4(s)$

c. $Xe(g) + 3F_2(g) \rightarrow XeF_6(s)$

d. $2XeF_6(s) + SiO_2(s) \rightarrow 2XeOF_4(l) + SiF_4(l)$

e. $XeF_6(s) + 3H_2O(l) \rightarrow XeO_3(s) + 6HF(aq)$

2.

3. SiF_4; $SiO_2(s) + 2F_2(g) \rightarrow SiF_4(l) + 2O_2(g)$
4.
5.

a. $2Na(s) + 2D_2O(l) \rightarrow D_2(g) + 2NaOD(aq)$

   $2Li(s) + D_2(g) \rightarrow 2LiD(s)$

   $4LiD(s) + AlCl_3(soln) \rightarrow LiAlD_4(s) + 3LiCl(soln)$

b. $D_2O(l) + SO_3(g) \rightarrow D_2SO_4(l)$

c. $SiCl_4(l) + LiAlD_4(s)$ [from part (a)] $\rightarrow SiD_4(g) + LiCl(s) + AlCl_3(s)$

d. $CaF_2(s) + D_2SO_4(l)$ [from part (b)] $\rightarrow 2DF(g) + CaSO_4(s)$

22.7 End-of-Chapter Material

APPLICATION PROBLEMS

1. Borax ($Na_2B_4O_5(OH)_4 \cdot 8H_2O$) is used as a flux during welding operations. As brass is heated during welding, for example, borax cleans the surface of Cu_2O and prevents further oxidation of the fused metal. Explain why borax is effective at cleaning the surface and preventing surface oxidation.
2. Extensive research is being conducted into using GaAs as a material for computer memory chips. It has been found, for example, that chips made from GaAs are up to 10 times faster than those made from silicon. Propose an explanation for this increase in speed.
3. Cement that has a high content of alumina (Al_2O_3) is particularly resistant to corrosion, so it is used for structures that must be resistant to seawater and acidic conditions. Why is this material so effective under these service conditions? Failure occurs under prolonged exposure to a hot, wet environment. Why?
4. Aluminum is light and ductile. If you were considering using aluminum rather than steel as a structural material for building a high-speed ferry, what disadvantages would you need to consider in using aluminum for these service conditions?
5. Life on Earth is based on carbon. A possible explanation is that no other element in the periodic table forms compounds that are so diverse in their chemistry and physical properties. Discuss the chemistry of carbon with regard to

a. types of bonding.

b. the states of matter of carbon compounds.

c. the properties of elemental C.

d. the reactivity of elemental C and its compounds.

Then compare B, Al, Si, N, and P with C in terms of these properties.

6. After a traffic accident in which a tanker truck carrying liquid nitrogen overturned, a reporter at the scene warned of a danger to residents in the vicinity of the accident because nitrogen would react with hydrocarbons in the asphalt to produce ammonia gas. Comment on the credibility of this statement.
7. Nitrogen forms a hydride called hydrazoic acid (HN_3), which is a colorless, highly toxic, explosive substance that boils at 37°C. The thermal decomposition of one of its salts—NaN_3—is used to inflate automotive air bags. The N_3^- ion is isoelectronic with CO_2.

a. Draw the Lewis electron structure of the N_3^- anion.

b. Write a balanced chemical equation for the thermal decomposition of NaN_3.

c. Based on your answer to part (b), propose an explanation for why many people have suffered skin burns when their air bags exploded.

8. Hydrazine (N_2H_4), a rocket fuel, is a colorless, oily liquid with a melting point of 1.4°C, and it is a powerful reducing agent. The physical properties of hydrazine presumably reflect the presence of multiple hydrogen-bond acceptors and donors within a single molecule. Explain the basis for this statement.
9. Because the N–C bond is almost as strong as the N–H bond, organic analogues of ammonia, hydrazine, and hydroxylamine are stable and numerous. Conceptually at least, they are formed by the successive replacement of H atoms by alkyl or aryl groups. Methylhydrazine and dimethylhydrazine, for example, were used as fuels in the US*Apollo* space program. They react spontaneously and vigorously with liquid N_2O_4, thus eliminating the need for an ignition source. Write balanced chemical equations for these reactions and calculate $\Delta G°$ for each reaction.
10. In an effort to remove a troublesome stain from a sink, a member of the cleaning staff of a commercial building first used bleach on the stain and then decided to neutralize the bleach with ammonia. What happened? Why?
11. A slow reaction that occurs on the ocean floor is the conversion of carbonate to bicarbonate, which absorbs CO_2. Write a balanced chemical equation for this reaction. Silicate sediments play an important role in controlling the pH of seawater. Given the reaction, propose a chemical explanation for this.

12. Marketing surveys have shown that customers prefer to buy a bright red steak rather than a dull gray one. It is known that NO combines with myoglobin to form a bright red NO complex. What would you add to beef during processing to ensure that this reaction occurs and yields the desired appearance?
13. Covalent azides are used as detonators and explosives. Ionic azides, in contrast, are usually much more stable and are used in dyestuffs. Why is there such a difference between these two types of compounds? The N_3^- ion is considered a pseudohalide. Why?
14. The heads of modern "strike anywhere" matches contain a mixture of a nonvolatile phosphorus sulfide (P_4S_3) and an oxidizing agent ($KClO_3$), which is ignited by friction when the match is struck against a rough object. Safety matches separate the oxidant and the reductant by putting $KClO_3$ in the head and a paste containing nonvolatile red phosphorus on the match box or cover. Write a balanced chemical equation for the reaction that occurs when a match is rubbed against the abrasive end of a matchbox.
15. Paris green was a common pigment in paints and wallpaper of the Napoleonic era. It is a mixed acetate/arsenite salt of copper with the formula $Cu_2(OAc)_2(AsO_3)$. In damp conditions, certain fungi are able to convert arsenite salts to volatile, toxic organoarsenic compounds. Shortly after his exile in 1815 to the remote island of St. Helena in the southern Atlantic Ocean, Napoleon died. As a forensic scientist investigating the cause of Napoleon's mysterious death, you notice that the walls of his enclosed bedchamber are covered in green wallpaper. What chemical clues would you look for to determine the cause of his death?
16. Selenium, an element essential to humans, appears to function biologically in an enzyme that destroys peroxides. Why is selenium especially suited for this purpose? Would sulfur or tellurium be as effective? Why or why not?
17. One way to distinguish between fool's gold (FeS_2, or iron pyrite) and real gold is to heat the sample over a fire. If your sample of "gold" were actually fool's gold, what would happen?
18. Calcium hypochlorite is sold as swimming pool bleach. It is formed by the hydrolysis of Cl_2O, which gives only one product, followed by neutralization with lime [$Ca(OH)_2$]. Write balanced chemical equations for these reactions.
19. There is much interest in the superheavy elements beyond $Z = 111$ because of their potentially unique properties. Predict the valence electron configurations, preferred oxidation states, and products of the reaction with aqueous acid for elements 113 and 115.

20. Zeolites have become increasingly important in chemical engineering. They can be used as desiccants because the dehydrated zeolite absorbs small molecules, such as water. To be retained by the zeolite frame, a molecule must satisfy two conditions. What are they? Why can linear CO_2 and tetrahedral CH_4 not be held by a typical zeolite, even though they can penetrate it easily?

ANSWERS

1.

2.

3.

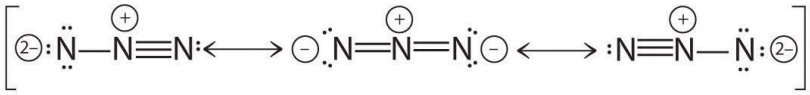
4.

5.

6.

7.

a. Three resonance structures for the azide ion may be reasonably drawn:



b. $a.\quad 2NaN3(s)\text{-} \rightarrow D2Na(s)\ +3N2(g)$

c. One of the products of the decomposition of sodium azide is elemental sodium, which is highly reactive and can ignite in the presence of water and air.

8.

9.

10.

11.

12.

13.

14.

15. Examine samples of Napoleon's hair and/or fingernails from museums or collections to determine arsenic concentrations.

16.

17. Upon heating, pyrite will react with oxygen to form SO_2(g), which has a pungent smell.

18.

19. Element 113: $5f^{14}6d^{10}7s^{2}7p^{1}$, +1, $E^{+}(aq)$; element 115: $5f^{14}6d^{10}7s^{2}7p^{3}$, +3, $E^{3+}(aq)$

Chapter 23
The *d*-Block Elements

Chapter 21 "Periodic Trends and the " and Chapter 22 "The " described the chemistry of the *s*-block and *p*-block elements. In this chapter, we survey the chemistry of the *d*-block elements, which are also called the *transition metals*. We again use valence electron configurations and periodic trends, as well as the principles of chemical bonding, thermodynamics, and kinetics, as tools to describe the properties and reactivity of these elements. Because all the *d*-block elements are metals, they do not have the extreme variability in chemistry that we saw among the elements of the *p*block. Instead, these elements exhibit significant horizontal and vertical similarities in chemistry, and all have a common set of characteristic properties due to partially filled*d* subshells.

Alloys and compounds of the *d*-block elements are important components of the materials the modern world depends on for its continuing technological development, while most of the first-row transition metals are essential for life. This chapter introduces some of the key industrial and biological roles of these elements. You will learn, for example, why copper, silver, and gold have been used for coins and jewelry since ancient times, how Cr^{3+}impurities can be responsible for the characteristic colors of both rubies and emeralds, why an iron oxide was used in primitive compasses, why insects have greenish-blue blood, and why cobalt is an essential component of vitamin B_{12}.

23.1 General Trends among the Transition Metals

LEARNING OBJECTIVE

1. To understand the trends in properties and reactivity of the *d*-block elements.

The transition metals, groups 3–12 in the periodic table, are generally characterized by partially filled *d* subshells in the free elements or their cations. (Although the metals of group 12 do not have partially filled *d* shells, their chemistry is similar in many ways to that of the preceding groups, and we therefore include them in our discussion.) Unlike the *s*-block and *p*-block elements, the transition metals exhibit significant horizontal similarities in chemistry in addition to their vertical similarities.

Electronic Structure and Reactivity of the Transition Metals

The valence electron configurations of the first-row transition metals are given in Table 23.1 "Valence Electron Configurations of the First-Row Transition Metals". As we go across the row from left to right, electrons are added to the 3*d* subshell to neutralize the increase in the positive charge of the nucleus as the atomic number increases. With two important exceptions, the 3*d* subshell is filled as expected based

on the aufbau principle and Hund's rule. Unexpectedly, however, chromium has a $4s^1 3d^5$ electron configuration rather than the $4s^2 3d^4$ configuration predicted by the aufbau principle, and copper is $4s^1 3d^{10}$ rather than $4s^2 3d^9$. In Chapter 7 "The Periodic Table and Periodic Trends", we attributed these anomalies to the extra stability associated with half-filled subshells. Because the *ns* and $(n - 1)d$ subshells in these elements are similar in energy, even relatively small effects are enough to produce apparently anomalous electron configurations.

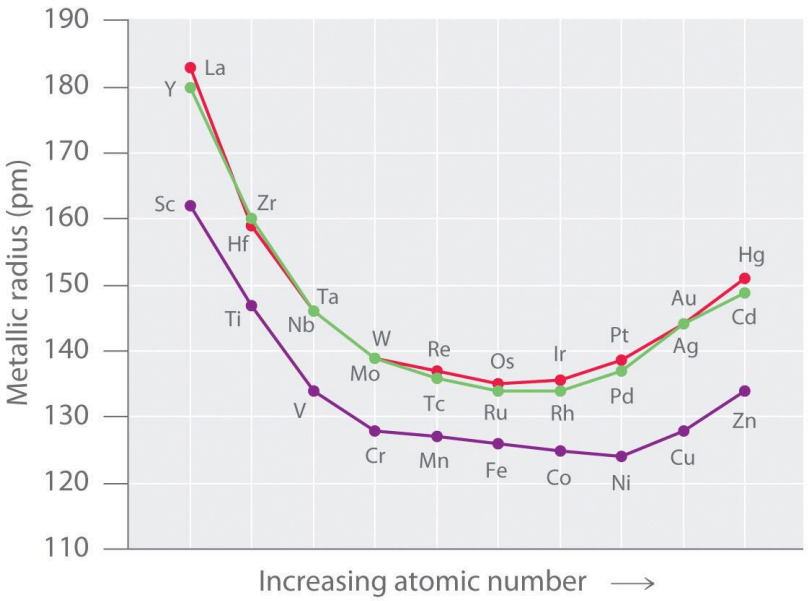
Table 23.1 Valence Electron Configurations of the First-Row Transition Metals

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$4s^2 3d^1$	$4s^2 3d^2$	$4s^2 3d^3$	$4s^1 3d^5$	$4s^2 3d^5$	$4s^2 3d^6$	$4s^2 3d^7$	$4s^2 3d^8$	$4s^1 3d^{10}$	$4s^2 3d^{10}$

In the second-row transition metals, electron–electron repulsions within the 4*d*subshell cause additional irregularities in electron configurations that are not easily predicted. For example, Nb and Tc, with atomic numbers 41 and 43, both have a half-filled 5*s* subshell, with $5s^1 4d^4$ and $5s^1 4d^6$ valence electron configurations, respectively. Further complications occur among the third-row transition metals, in which the 4*f*, 5*d*, and 6*s* orbitals are extremely close in energy. Although La has a $6s^2 5d^1$ valence electron configuration, the valence electron configuration of the next element—Ce—is $6s^2 5d^0 4f^2$. From this point through element 71, added electrons enter the 4*f* subshell, giving rise to the 14 elements known as the lanthanides. After the 4*f* subshell is filled, the 5*d* subshell is populated, producing the third row of the transition metals. Next comes the seventh period, where the actinides have three subshells (7*s*, 6*d*, and 5*f*) that are so similar in energy that their electron configurations are even more unpredictable.

As we saw in the *s*-block and *p*-block elements, the size of neutral atoms of the *d*-block elements gradually decreases from left to right across a row, due to an increase in the effective nuclear charge (Z_{eff}) with increasing atomic number. In addition, the atomic radius increases down a group, just as it does in the *s* and *p* blocks. Because of the*lanthanide contraction*, however, the increase in size between the 3*d* and 4*d* metals is much greater than between the 4*d* and 5*d* metals (Figure 23.1 "The Metallic Radii of the First-, Second-, and Third-Row Transition Metals"). (For more information on the lanthanides, see Chapter 7 "The Periodic Table and Periodic Trends", Section 7.3 "Energetics of Ion Formation".) The effects of the lanthanide contraction are also observed in ionic radii, which explains why, for example, there is only a slight increase in radius from Mo^{3+} to W^{3+}.

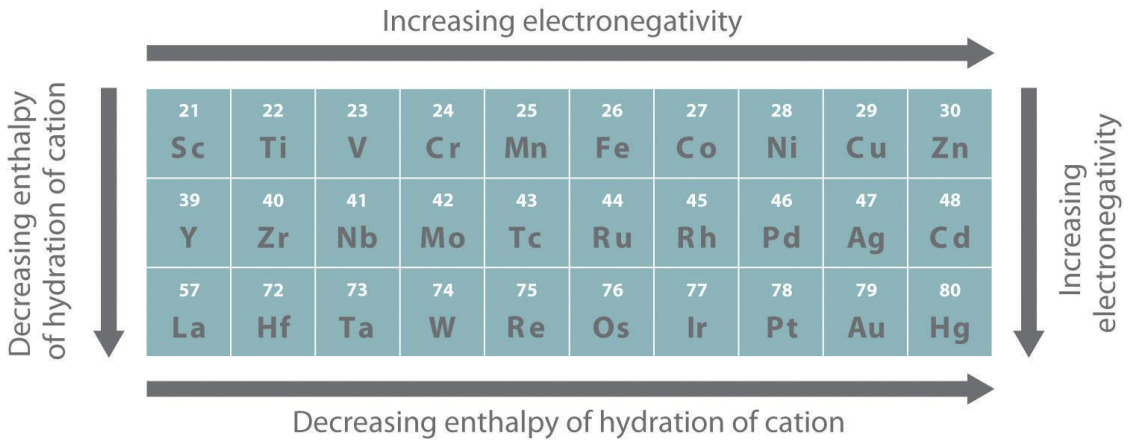
Figure 23.1 *The Metallic Radii of the First-, Second-, and Third-Row Transition Metals*



Because of the lanthanide contraction, the second- and third-row transition metals are very similar in size.

As you learned in Chapter 7 "The Periodic Table and Periodic Trends", electrons in $(n - 1)d$ and $(n - 2)f$ subshells are only moderately effective at shielding the nuclear charge; as a result, the effective nuclear charge experienced by valence electrons in the *d*-block and *f*-block elements does not change greatly as the nuclear charge increases across a row. Consequently, the ionization energies of these elements increase very slowly across a given row (Figure 7.10 "A Plot of Periodic Variation of First Ionization Energy with Atomic Number for the First Six Rows of the Periodic Table"). In addition, as we go from the top left to the bottom right corner of the *d* block, electronegativities generally increase, densities and electrical and thermal conductivities increase, and enthalpies of hydration of the metal cations decrease in magnitude, as summarized inFigure 23.2 "Some Trends in Properties of the Transition Metals". Consistent with this trend, the transition metals become steadily less reactive and more “noble” in character from left to right across a row. The relatively high ionization energies and electronegativities and relatively low enthalpies of hydration are all major factors in the noble character of metals such as Pt and Au.

Figure 23.2 *Some Trends in Properties of the Transition Metals*



The electronegativity of the elements increases, and the hydration energies of the metal cations decrease in magnitude from left to right and from top to bottom of the dblock. As a result, the metals in the lower right corner of the d block are so unreactive that they are often called the "noble metals."

Trends in Transition Metal Oxidation States

The similarity in ionization energies and the relatively small increase in successive ionization energies lead to the formation of metal ions with the same charge for many of the transition metals. This in turn results in extensive horizontal similarities in chemistry, which are most noticeable for the first-row transition metals and for the lanthanides and actinides. Thus all the first-row transition metals except Sc form stable compounds that contain the 2+ ion, and, due to the small difference between the second and third ionization energies for these elements, all except Zn also form stable compounds that contain the 3+ ion. The relatively small increase in successive ionization energies causes most of the transition metals to exhibit multiple oxidation states separated by a single electron. Manganese, for example, forms compounds in every oxidation state between −3 and +7. Because of the slow but steady increase in ionization potentials across a row, high oxidation states become progressively less stable for the elements on the right side of the *d* block. The occurrence of multiple oxidation states separated by a single electron causes many, if not most, compounds of the transition metals to be paramagnetic, with one to five unpaired electrons. This behavior is in sharp contrast to that of the *p*-block elements, where the occurrence of two oxidation states separated by two electrons is common, which makes virtually all compounds of the *p*-block elements diamagnetic.

Note the Pattern

Due to a small increase in successive ionization energies, most of the transition metals have multiple oxidation states separated by a single electron.

Note the Pattern:

Most compounds of transition metals are paramagnetic, whereas virtually all compounds of the *p*-block elements are diamagnetic.

The electronegativities of the first-row transition metals increase smoothly from Sc ($\chi = 1.4$) to Cu ($\chi = 1.9$). Thus Sc is a rather active metal, whereas Cu is much less reactive. The steady increase in electronegativity is also reflected in the standard reduction potentials: thus E° for the reaction $M^{2+}(aq) + 2e^- \rightarrow M^0(s)$ becomes progressively less negative from Ti ($E^\circ = -1.63$ V) to Cu ($E^\circ = +0.34$ V). Exceptions to the overall trends are rather common, however, and in many cases, they are attributable to the stability associated with filled and half-filled subshells. For example, the $4s^2 3d^{10}$ electron configuration of zinc results in its strong tendency to form the stable Zn^{2+} ion, with a $3d^{10}$ electron configuration, whereas Cu^+, which also has a $3d^{10}$ electron configuration, is the only stable monocation formed by a first-row transition metal. Similarly, with a half-filled subshell, Mn^{2+} ($3d^5$) is much more difficult to oxidize than Fe^{2+} ($3d^6$). The chemistry of manganese is therefore primarily that of the Mn^{2+} ion, whereas both the Fe^{2+} and Fe^{3+} ions are important in the chemistry of iron.

The transition metals form cations by the initial loss of the *ns* electrons of the metal, even though the *ns* orbital is *lower* in energy than the $(n - 1)d$ subshell in the neutral atoms. This apparent contradiction is due to the small difference in energy between the*ns* and $(n - 1)d$ orbitals, together with screening effects. The loss of one or more electrons reverses the relative energies of the *ns* and $(n - 1)d$ subshells, making the latter lower in energy. Consequently, *all transition-metal cations possess* d^n *valence electron configurations*, as shown in Table 23.2 for the 2+ ions of the first-row transition metals.

Note the Pattern

All transition-metal cations have d^n electron configurations; the *ns* electrons are*always* lost *before* the $(n - 1)d$ electrons.

Table 23.2 *d*-Electron Configurations of the Dications of the First-Row Transition Metals

Ti^{2+}	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}

The most common oxidation states of the first-row transition metals are shown in Table 23.3 "Common Oxidation States of the First-Row Transition Metals*". The second- and third-row transition metals behave similarly but with three important differences:

1. The maximum oxidation states observed for the second- and third-row transition metals in groups 3–8 increase from +3 for Y and La to +8 for Ru and Os, corresponding to the formal loss of all *ns* and $(n - 1)d$ valence electrons. As we go farther to the right, the maximum oxidation state decreases steadily, reaching +2 for the elements of group 12 (Zn, Cd, and Hg), which corresponds to a filled $(n - 1)d$ subshell.
2. Within a group, higher oxidation states become more stable down the group. For example, the chromate ion ($[CrO_4]^{2-}$) is a powerful oxidant, whereas the tungstate ion ($[WO_4]^{2-}$) is extremely stable and has essentially no tendency to act as an oxidant.
3. Cations of the second- and third-row transition metals in lower oxidation states (+2 and +3) are much more easily oxidized than the corresponding ions of the first-row transition metals. For example, the most stable compounds of chromium are those of Cr(III), but the corresponding Mo(III) and W(III) compounds are highly reactive. In fact, they are often *pyrophoric*, bursting into flames on contact with atmospheric oxygen. As we shall see, the heavier elements in each group form stable compounds in higher oxidation states that have no analogues with the lightest member of the group.

Note the Pattern

The highest possible oxidation state, corresponding to the formal loss of all valence electrons, becomes increasingly less stable as we go from group 3 to group 8, and it is never observed in later groups.

Note the Pattern

In the transition metals, the stability of higher oxidation states increases down a column.

Table 23.3 Common Oxidation States of the First-Row Transition Metals*

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
electronic structure	$s^2 d^1$	$s^2 d^2$	$s^2 d^3$	$s^1 d^5$	$s^2 d^5$	$s^2 d^6$	$s^2 d^7$	$s^2 d^8$	$s^1 d^{10}$	$s^2 d^{10}$
oxidation states				I					I	
		II	II	II	II	II	II	II	II	II
	III	III	III	III	III	III	III	III	III	
		IV	IV	IV	IV	IV	IV	IV		

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
			V	V	V	V	V			
				VI	VI	VI				
					VII					
***The convention of using roman numerals to indicate the oxidation states of a metal is used here.**										

Binary transition-metal compounds, such as the oxides and sulfides, are usually written with idealized stoichiometries, such as FeO or FeS, but these compounds are usually cation deficient and almost never contain a 1:1 cation:anion ratio. Thus a substance such as ferrous oxide is actually a nonstoichiometric compound with a range of compositions.

The acid–base character of transition-metal oxides depends strongly on the oxidation state of the metal and its ionic radius. Oxides of metals in lower oxidation states (less than or equal to +3) have significant ionic character and tend to be basic. Conversely, oxides of metals in higher oxidation states are more covalent and tend to be acidic, often dissolving in strong base to form oxoanions.

EXAMPLE 1

Two of the group 8 metals (Fe, Ru, and Os) form stable oxides in the +8 oxidation state. Identify these metals; predict the stoichiometry of the oxides; describe the general physical and chemical properties, type of bonding, and physical state of the oxides; and decide whether they are acidic or basic oxides.

Given: group 8 metals

Asked for: identity of metals and expected properties of oxides in +8 oxidation state

Strategy:

Refer to the trends outlined in Figure 23.1 "The Metallic Radii of the First-, Second-, and Third-Row Transition Metals", Figure 23.2 "Some Trends in Properties of the Transition Metals", Table 23.1 "Valence Electron Configurations of the First-Row Transition Metals", Table 23.2, and Table 23.3 "Common Oxidation States of the First-Row Transition Metals*" to identify the metals. Decide whether their oxides are covalent or ionic in character, and, based on this, predict the general physical and chemical properties of the oxides.

Solution:

The +8 oxidation state corresponds to a stoichiometry of MO_4. Because the heavier transition metals tend to be stable in higher oxidation states, we expect Ru and Os to form the most stable tetroxides. Because

oxides of metals in high oxidation states are generally covalent compounds, RuO_4 and OsO_4 should be volatile solids or liquids that consist of discrete MO_4 molecules, which the valence-shell electron-pair repulsion (VSEPR) model predicts to be tetrahedral. Finally, because oxides of transition metals in high oxidation states are usually acidic, RuO_4 and OsO_4 should dissolve in strong aqueous base to form oxoanions.

Exercise

Predict the identity and stoichiometry of the stable group 9 bromide in which the metal has the lowest oxidation state and describe its chemical and physical properties.

Answer: Because the lightest element in the group is most likely to form stable compounds in lower oxidation states, the bromide will be $CoBr_2$. We predict that $CoBr_2$ will be an ionic solid with a relatively high melting point and that it will dissolve in water to give the $Co^{2+}(aq)$ ion.

Summary

The transition metals are characterized by partially filled *d* subshells in the free elements and cations. The *ns* and $(n - 1)d$ subshells have similar energies, so small influences can produce electron configurations that do not conform to the general order in which the subshells are filled. In the second- and third-row transition metals, such irregularities can be difficult to predict, particularly for the third row, which has 4*f*, 5*d*, and 6*s* orbitals that are very close in energy. The increase in atomic radius is greater between the 3*d* and 4*d* metals than between the 4*d* and 5*d* metals because of the lanthanide contraction. Ionization energies and electronegativities increase slowly across a row, as do densities and electrical and thermal conductivities, whereas enthalpies of hydration decrease. Anomalies can be explained by the increased stabilization of half-filled and filled subshells. Transition-metal cations are formed by the initial loss of *ns* electrons, and many metals can form cations in several oxidation states. Higher oxidation states become progressively less stable across a row and more stable down a column. Oxides of small, highly charged metal ions tend to be acidic, whereas oxides of metals with a low charge-to-radius ratio are basic.

KEY TAKEAWAYS

- Transition metals are characterized by the existence of multiple oxidation states separated by a single electron.

- Most transition-metal compounds are paramagnetic, whereas virtually all compounds of the *p*-block elements are diamagnetic.

CONCEPTUAL PROBLEMS

1. The transition metals show significant horizontal similarities in chemistry in addition to their vertical similarities, whereas the same cannot be said of the *s*-block and *p*-block elements. Explain why this is so.
2. The energy of the *d* subshell does not change appreciably in a given period. Why? What effect does this have on the ionization potentials of the transition metals? on their electronegativities?
3. Standard reduction potentials vary across the first-row transition metals. What effect does this have on the chemical reactivity of the first-row transition metals? Which two elements in this period are more active than would be expected? Why?
4. Many transition metals are paramagnetic (have unpaired electrons). How does this affect electrical and thermal conductivities across the rows?
5. What is the lanthanide contraction? What effect does it have on the radii of the transition metals of a given group? What effect does it have on the chemistry of the elements in a group?
6. Why are the atomic volumes of the transition elements low compared with the elements of groups 1 and 2? Ir has the highest density of any element in the periodic table (22.65 g/cm^3). Why?
7. Of the elements Ti, Ni, Cu, and Cd, which do you predict has the highest electrical conductivity? Why?
8. The chemistry of As is most similar to the chemistry of which transition metal? Where in the periodic table do you find elements with chemistry similar to that of Ge? Explain your answers.
9. The coinage metals (group 11) have significant noble character. In fact, they are less reactive than the elements of group 12. Explain why this is so, referring specifically to their reactivity with mineral acids, electronegativity, and ionization energies. Why are the group 12 elements more reactive?

STRUCTURE AND REACTIVITY

1. Give the valence electron configurations of the 2+ ion for each first-row transition element. Which two ions do you expect to have the most negative $E°$ value? Why?
2. Arrange Ru^{3+}, Cu^{2+}, Zn, Ti^{4+}, Cr^{3+}, and Ni^{2+} in order of increasing radius.
3. Arrange Pt^{4+}, Hg^{2+}, Fe^{2+}, Zr^{4+}, and Fe^{3+} in order of decreasing radius.
4. Of Ti^{2+}, V^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}, which divalent ion has the smallest ionic radius? Explain your reasoning.

ANSWERS

1. Ti^{2+}, $3d^2$; V^{2+}, $3d^3$; Cr^{2+}, $3d^4$; Mn^{2+}, $3d^5$; Fe^{2+}, $3d^6$; Co^{2+}, $3d^7$; Ni^{2+}, $3d^8$; Cu^{2+}, $3d^9$; Zn^{2+}, $3d^{10}$. Because Z_{eff} increases from left to right, Ti^{2+} and V^{2+} will have the most negative reduction potentials (be most difficult to reduce).
2.
3. $Hg^{2+} > Fe^{2+} > Zr^{4+} > Fe^{3+} > Pt^{4+}$

23.2 A Brief Survey of Transition-Metal Chemistry

LEARNING OBJECTIVE

1. To use periodic trends to understand the chemistry of the transition metals.

We turn now to a brief survey of the chemistry of the transition metals, beginning with group 3. As we shall see, the two heaviest members of each group usually exhibit substantial similarities in chemical behavior and are quite different from the lightest member.

Groups 3, 4, and 5

Group 3 (Sc, Y, La, and Ac)

As shown in Table 23.4 "Some Properties of the Elements of Groups 3, 4, and 5", the observed trends in the properties of the group 3 elements are similar to those of groups 1 and 2. Due to their $ns^2(n - 1)d^1$ valence electron configurations, the chemistry of all four elements is dominated by the +3 oxidation state formed by losing all three valence electrons. As expected based on periodic trends, these elements are highly electropositive metals and powerful reductants, with La (and Ac) being the most reactive. In keeping with their highly electropositive character, the group 3 metals react with water to produce the metal hydroxide and hydrogen gas:

Equation 23.1

$$2M(s) + 6H_2O(l) \rightarrow 2M(OH)_3(s) + 3H_2(g)$$

Note the Pattern

The chemistry of the group 3 metals is almost exclusively that of the M^{3+} ion; the elements are powerful reductants.

Moreover, all dissolve readily in aqueous acid to produce hydrogen gas and a solution of the hydrated metal ion: $M^{3+}(aq)$.

Table 23.4 Some Properties of the Elements of Groups 3, 4, and 5

The group 3 metals react with nonmetals to form compounds that are primarily ionic in character. For example, reacting group 3 metals with the halogens produces the corresponding trihalides: MX_3. The trifluorides are insoluble in water because of their high lattice energies, but the other trihalides are very soluble in water and behave like typical ionic metal halides. All group 3 elements react with air to form an oxide coating, and all burn in oxygen to form the so-called *sesquioxides* (M_2O_3), which react with H2O or CO_2 to form the corresponding hydroxides or carbonates, respectively. Commercial uses of the group 3 metals are limited, but "mischmetal," a mixture of lanthanides containing about 40% La, is used as an additive to improve the properties of steel and make flints for cigarette lighters.

Group 4 (Ti, Zr, and Hf)

Because the elements of group 4 have a high affinity for oxygen, all three metals occur naturally as oxide ores that contain the metal in the +4 oxidation state resulting from losing all four $ns^2(n-1)d^2$ valence electrons. They are isolated by initial conversion to the tetrachlorides, as shown for Ti:

Equation 23.2

$$2FeTiO_3(s) + 6C(s) + 7Cl_2(g) \rightarrow 2TiCl_4(g) + 2FeCl_3(g) + 6CO(g)$$

followed by reduction of the tetrachlorides with an active metal such as Mg.

Note the Pattern

The chemistry of the group 4 metals is dominated by the +4 oxidation state. Only Ti has an extensive chemistry in lower oxidation states.

In contrast to the elements of group 3, the group 4 elements have important applications. Titanium (melting point = 1668°C) is often used as a replacement for aluminum (melting point = 660°C) in applications that require high temperatures or corrosion resistance. For example, friction with the air heats the skin of supersonic aircraft operating above Mach 2.2 to temperatures near the melting point of aluminum; consequently, titanium is used instead of aluminum in many aerospace applications. The corrosion resistance of titanium is increasingly exploited in architectural applications, as shown in the chapter-opening photo. Metallic zirconium is used in UO_2-containing fuel rods in nuclear reactors, while hafnium is used in the control rods that modulate the output of high-power nuclear reactors, such as those in nuclear submarines.

Consistent with the periodic trends shown in Figure 23.2 "Some Trends in Properties of the Transition Metals", the group 4 metals become denser, higher melting, and more electropositive down the column (Table 23.4 "Some Properties of the Elements of Groups 3, 4, and 5"). Unexpectedly, however, the atomic

radius of Hf is slightly *smaller* than that of Zr due to the lanthanide contraction. Because of their $ns^2(n-1)d^2$ valence electron configurations, the +4 oxidation state is by far the most important for all three metals. Only titanium exhibits a significant chemistry in the +2 and +3 oxidation states, although compounds of Ti^{2+} are usually powerful reductants. In fact, the $Ti^{2+}(aq)$ ion is such a strong reductant that it rapidly reduces water to form hydrogen gas.

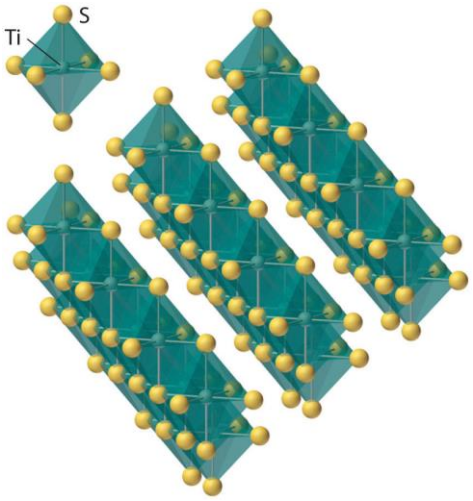
Reaction of the group 4 metals with excess halogen forms the corresponding tetrahalides (MX_4), although titanium, the lightest element in the group, also forms dihalides and trihalides (X is not F). The covalent character of the titanium halides increases as the oxidation state of the metal increases because of increasing polarization of the anions by the cation as its charge-to-radius ratio increases. Thus $TiCl_2$ is an ionic salt, whereas $TiCl_4$ is a volatile liquid that contains tetrahedral molecules. All three metals react with excess oxygen or the heavier chalcogens (Y) to form the corresponding dioxides (MO_2) and dichalcogenides (MY_2). Industrially, TiO_2, which is used as a white pigment in paints, is prepared by reacting $TiCl_4$ with oxygen at high temperatures:

Equation 23.3

$$TiCl_4(g) + O_2(g) \rightarrow TiO_2(s) + 2Cl_2(g)$$

The group 4 dichalcogenides have unusual layered structures with no M–Y bonds holding adjacent sheets together, which makes them similar in some ways to graphite (Figure 23.3 "The Layered Structure of TiS"). The group 4 metals also react with hydrogen, nitrogen, carbon, and boron to form hydrides (such as TiH_2), nitrides (such as TiN), carbides (such as TiC), and borides (such as TiB_2), all of which are hard, high-melting solids. Many of these binary compounds are nonstoichiometric and exhibit metallic conductivity.

Figure 23.3 *The Layered Structure of TiS_2*



Each titanium atom is surrounded by an octahedral arrangement of six sulfur atoms that are shared to form extended layers of atoms. Because the layers are held together by only van der Waals forces between adjacent sulfur atoms, rather than covalent bonds, the layers slide past one another relatively easily when a mechanical stress is applied.

Group 5 (V, Nb, and Ta)

Like the group 4 elements, all group 5 metals are normally found in nature as oxide ores that contain the metals in their highest oxidation state (+5). Because of the lanthanide contraction, the chemistry of Nb and Ta is so similar that these elements are usually found in the same ores.

Three-fourths of the vanadium produced annually is used in the production of steel alloys for springs and high-speed cutting tools. Adding a small amount of vanadium to steel results in the formation of small grains of V_4C_3, which greatly increase the strength and resilience of the metal, especially at high temperatures. The other major use of vanadium is as V_2O_5, an important catalyst for the industrial conversion of $SO_2$to SO_3 in the contact process for the production of sulfuric acid. (For more information on sulfuric acid production, see Chapter 2 "Molecules, Ions, and Chemical Formulas",Section 2.6 "Industrially Important Chemicals".) In contrast, Nb and Ta have only limited applications, and they are therefore produced in relatively small amounts. Although niobium is used as an additive in certain stainless steels, its primary application is in superconducting wires such as Nb_3Zr and Nb_3Ge, which are used in superconducting magnets for the magnetic resonance imaging of soft tissues. Because tantalum is highly resistant to corrosion, it is used as a liner for chemical reactors, in missile parts, and as a biologically compatible material in screws and pins for repairing fractured bones.

Note the Pattern

The chemistry of the two heaviest group 5 metals (Nb and Ta) is dominated by the +5 oxidation state. The chemistry of the lightest element (V) is dominated by lower oxidation states, especially +4.

As indicated in Table 23.4 "Some Properties of the Elements of Groups 3, 4, and 5", the trends in properties of the group 5 metals are similar to those of group 4. Only vanadium, the lightest element, has any tendency to form compounds in oxidation states lower than +5. For example, vanadium is the only element in the group that forms stable halides in the lowest oxidation state (+2). All three metals react with excess oxygen, however, to produce the corresponding oxides in the +5 oxidation state (M_2O_5), in which polarization of the oxide ions by the high-oxidation-state metal is so extensive that the compounds are primarily covalent in character. Vanadium–oxygen species provide a classic example of the effect of increasing metal oxidation state on the protonation state of a coordinated water molecule: vanadium(II) in water exists as the violet hydrated ion $[V(H_2O)_6]^{2+}$; the blue-green $[V(H_2O)_6]^{3+}$ ion is acidic, dissociating to form small amounts of the $[V(H_2O)_5(OH)]^{2+}$ ion and a proton; and in water, vanadium(IV) forms the blue vanadyl ion $[(H_2O)_4VO]^{2+}$, which contains a formal V=O bond (Figure 23.4 "Aqueous Solutions of Vanadium Ions in Oxidation States of +2 to +5"). Consistent with its covalent character, V_2O_5 is acidic, dissolving in base to give the vanadate ion ($[VO_4]^{3-}$), whereas both Nb_2O_5 and Ta_2O_5 are comparatively inert. Oxides of these metals in lower oxidation states tend to be nonstoichiometric.

Although group 5 metals react with the heavier chalcogens to form a complex set of binary chalcogenides, the most important are the dichalcogenides (MY_2), whose layered structures are similar to those of the group 4 dichalcogenides. The elements of group 5 also form binary nitrides, carbides, borides, and hydrides, whose stoichiometries and properties are similar to those of the corresponding group 4 compounds. One such compound, tantalum carbide (TiC), has the highest melting point of any compound known (3738°C); it is used for the cutting edges of high-speed machine tools.

Groups 6 and 7

Group 6 (Cr, Mo, and W)

As an illustration of the trend toward increasing polarizability as we go from left to right across the *d*block, in group 6 we first encounter a metal (Mo) that occurs naturally as a sulfide ore rather than as an oxide. Molybdenite (MoS_2) is a soft black mineral that can be used for writing, like PbS and graphite. Because of this similarity, people long assumed that these substances were all the same. In fact, the name *molybdenum* is derived from the Greek *molybdos*, meaning “lead.” More than 90% of the

molybdenum produced annually is used to make steels for cutting tools, which retain their sharp edge even when red hot. In addition, molybdenum is the only second- or third-row transition element that is essential for humans. The major chromium ore is chromite ($FeCr_2O_4$), which is oxidized to the soluble $[CrO_4]^{2-}$ ion under basic conditions and reduced successively to Cr_2O_3 and Cr with carbon and aluminum, respectively. Pure chromium can be obtained by dissolving Cr_2O_3 in sulfuric acid followed by electrolytic reduction; a similar process is used for electroplating metal objects to give them a bright, shiny, protective surface layer. Pure tungsten is obtained by first converting tungsten ores to WO_3, which is then reduced with hydrogen to give the metal.

Consistent with periodic trends, the group 6 metals are slightly less electropositive than those of the three preceding groups, and the two heaviest metals are essentially the same size because of the lanthanide contraction (Table 23.5 "Some Properties of the Elements of Groups 6 and 7"). All three elements have a total of six valence electrons, resulting in a maximum oxidation state of +6. Due to extensive polarization of the anions, compounds in the +6 oxidation state are highly covalent. As in groups 4 and 5, the lightest element exhibits variable oxidation states, ranging from Cr^{2+}, which is a powerful reductant, to CrO_3, a red solid that is a powerful oxidant. For Mo and W, the highest oxidation state (+6) is by far the most important, although compounds in the +4 and +5 oxidation states are known.

Note the Pattern

The metals become increasing polarizable across the *d* block.

Table 23.5 Some Properties of the Elements of Groups 6 and 7

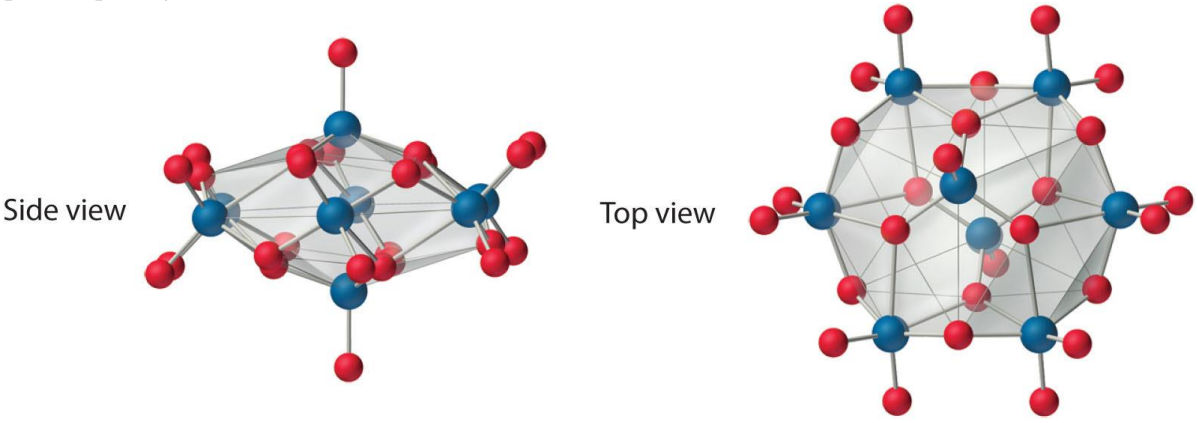
Group	Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	Density($g/cm3$)
6	Cr	24	$4s^1 3d^5$	1.66	128	1907	7.15
	Mo	42	$5s^1 4d^5$	2.16	139	2623	10.20
	W	74	$6s^2 5d^4 4f^{14}$	1.70	139	3422	19.30
7	Mn	25	$4s^2 3d^5$	1.55	127	1246	7.30
	Tc	43	$5s^2 4d^5$	2.10	136	2157	11.50
	Re	75	$6s^2 5d^5 4f^{14}$	1.90	137	3186	20.80

Note the Pattern

The chemistry of the two heaviest group 6 metals (Mo and W) is dominated by the +6 oxidation state. The chemistry of the lightest element (Cr) is dominated by lower oxidation states.

As observed in previous groups, the group 6 halides become more covalent as the oxidation state of the metal increases: their volatility increases, and their melting points decrease. Recall that as the electronegativity of the halogens decreases from F to I, they are less able to stabilize high oxidation states; consequently, the maximum oxidation state of the corresponding metal halides decreases. Thus all three metals form hexafluorides, but CrF_6 is unstable at temperatures above −100°C, whereas $MoF_6$and WF_6 are stable. Consistent with the trend toward increased stability of the highest oxidation state for the second- and third-row elements, the other halogens can oxidize chromium to only the trihalides, CrX_3 (X is Cl, Br, or I), while molybdenum forms $MoCl_5$, $MoBr_4$, and MoI_3, and tungsten gives WCl_6, WBr_5, and WI_4.

Both Mo and W react with oxygen to form the covalent trioxides (MoO_3 and WO_3), but Cr reacts to form only the so-called sesquioxide (Cr_2O_3). Chromium will form CrO_3, which is a highly toxic compound that can react explosively with organic materials. All the trioxides are acidic, dissolving in base to form the corresponding oxoanions ($[MO_4]^{2-}$). Consistent with periodic trends, the sesquioxide of the lightest element in the group (Cr_2O_3) is amphoteric. The aqueous chemistry of molybdate and tungstate is complex, and at low pH they form a series of polymeric anions called*isopolymetallates*, such as the $[Mo_8O_{26}]^{4-}$ ion, whose structure is as follows:



An isopolymolybdate cluster. *The $[Mo_8O_{26}]^{4-}$ ion, shown here in both side and top views, is typical of the oxygen-bridged clusters formed by Mo(VI) and W(VI) in aqueous solution.*

Reacting molybdenum or tungsten with heavier chalcogens gives binary chalcogenide phases, most of which are nonstoichiometric and electrically conducting. One of the most stable is MoS_2; it has a layered structure similar to that of TiS_2 (Figure 23.3 "The Layered Structure of TiS"), in which the layers are held together by only weak van der Waals forces, which allows them to slide past one another rather easily. Consequently, both MoS_2 and WS_2 are used as lubricants in a variety of applications, including automobile

engines. Because tungsten itself has an extraordinarily high melting point (3380°C), lubricants described as containing "liquid tungsten" actually contain a suspension of very small WS_2 particles.

As in groups 4 and 5, the elements of group 6 form binary nitrides, carbides, and borides whose stoichiometries and properties are similar to those of the preceding groups. Tungsten carbide (WC), one of the hardest compounds known, is used to make the tips of drill bits.

Group 7 (Mn, Tc, and Re)

Continuing across the periodic table, we encounter the group 7 elements (Table 23.5 "Some Properties of the Elements of Groups 6 and 7"). One group 7 metal (Mn) is usually combined with iron in an alloy called *ferromanganese*, which has been used since 1856 to improve the mechanical properties of steel by scavenging sulfur and oxygen impurities to form MnS and MnO. Technetium is named after the Greek*technikos*, meaning "artificial," because all its isotopes are radioactive. One isotope,^{99m}Tc (*m* for metastable), has become an important biomedical tool for imaging internal organs. (For more information on biomedical imaging, see Chapter 20 "Nuclear Chemistry", Section 20.5 "Applied Nuclear Chemistry".) Because of its scarcity, Re is one of the most expensive elements, and its applications are limited. It is, however, used in a bimetallic Pt/Re catalyst for refining high-octane gasoline.

All three group 7 elements have seven valence electrons and can form compounds in the +7 oxidation state. Once again, the lightest element exhibits multiple oxidation states. Compounds of Mn in oxidation states ranging from −3 to +7 are known, with the most common being +2 and +4 (Figure 23.5 "Compounds of Manganese in Oxidation States +2 to +7"). In contrast, compounds of Tc and Re in the +2 oxidation state are quite rare. Because the electronegativity of Mn is anomalously low, elemental manganese is unusually reactive. In contrast, the chemistry of Tc is similar to that of Re because of their similar size and electronegativity, again a result of the lanthanide contraction. Due to the stability of the half-filled $3d^5$ electron configuration, the aqueous Mn^{3+} ion, with a $3d^4$ valence electron configuration, is a potent oxidant that is able to oxidize water. It is difficult to generalize about other oxidation states for Tc and Re because their stability depends dramatically on the nature of the compound.

Consistent with higher oxidation states being more stable for the heavier transition metals, reacting Mn with F_2 gives only MnF_3, a high-melting, red-purple solid, whereas Re reacts with F_2 to give ReF_7, a volatile, low-melting, yellow solid. Again, reaction with the less oxidizing, heavier halogens produces halides in lower oxidation states. Thus reaction with Cl_2, a weaker oxidant than F_2, gives $MnCl_2$ and $ReCl_6$.

Reaction of Mn with oxygen forms only Mn_3O_4, a mixed-valent compound that contains two Mn(II) and one Mn(III) per formula unit and is similar in both stoichiometry and structure to magnetite (Fe_3O_4). In contrast, Tc and Re form high-valent oxides, the so-called *heptoxides*(M_2O_7), consistent with the increased stability of higher oxidation states for the second and third rows of transition metals. Under forced conditions, manganese will form Mn_2O_7, an unstable, explosive, green liquid. Also consistent with this trend, the permanganate ion $[MnO_4]^{2-}$ is a potent oxidant, whereas $[TcO_4]^-$ and $[ReO_4]^-$ are much more stable. Both Tc and Re form disulfides and diselenides with layered structures analogous to that of MoS_2, as well as more complex*heptasulfides* (M_2S_7). As is typical of the transition metals, the group 7 metals form binary nitrides, carbides, and borides that are generally stable at high temperatures and exhibit metallic properties.

Note the Pattern

The chemistry of the group 7 metals (Mn, Tc, and Re) is dominated by lower oxidation states. Compounds in the maximum possible oxidation state (+7) are readily reduced.

Groups 8, 9, and 10

In many older versions of the periodic table, groups 8, 9, and 10 were combined in a single group (group VIII) because the elements of these three groups exhibit many horizontal similarities in their chemistry, in addition to the similarities within each column. In part, these horizontal similarities are due to the fact that the ionization potentials of the elements, which increase slowly but steadily across the *d* block, have now become so large that the oxidation state corresponding to the formal loss of all valence electrons is encountered only rarely (group 8) or not at all (groups 9 and 10). As a result, the chemistry of all three groups is dominated by intermediate oxidation states, especially +2 and +3 for the first-row metals (Fe, Co, and Ni). The heavier elements of these three groups are called *precious metals* because they are rather rare in nature and mostly chemically inert.

Note the Pattern

The chemistry of groups 8, 9, and 10 is dominated by intermediate oxidation states such as +2 and +3.

Group 8 (Fe, Ru, and Os)

The chemistry of group 8 is dominated by iron, whose high abundance in Earth's crust is due to the extremely high stability of its nucleus. Ruthenium and osmium, on the other hand, are extremely rare elements, with terrestrial abundances of only about 0.1 ppb and 5 ppb, respectively, and they were not

discovered until the 19th century. Because of the high melting point of iron (1538°C), early humans could not use it for tools or weapons. The advanced techniques needed to work iron were first developed by the Hittite civilization in Asia Minor sometime before 2000 BC, and they remained a closely guarded secret that gave the Hittites military supremacy for almost a millennium. With the collapse of the Hittite civilization around 1200 BC, the technology became widely distributed, however, leading to the Iron Age.

Group 9 (Co, Rh, and Ir)

Cobalt is one of the least abundant of the first-row transition metals. Its oxide ores, however, have been used in glass and pottery for thousands of years to produce the brilliant color known as “cobalt blue,” and its compounds are consumed in large quantities in the paint and ceramics industries. The heavier elements of group 9 are also rare, with terrestrial abundances of less than 1 ppb; they are generally found in combination with the heavier elements of groups 8 and 10 in Ni–Cu–S ores.

Group 10 (Ni, Pd, and Pt)

Nickel silicates are easily processed; consequently, nickel has been known and used since antiquity. In fact, a 75:25 Cu:Ni alloy was used for more than 2000 years to mint “silver” coins, and the modern US nickel uses the same alloy. In contrast to nickel, palladium and platinum are rare (their terrestrial abundance is about 10–15 ppb), but they are at least an order of magnitude more abundant than the heavier elements of groups 8 and 9. Platinum and palladium are used in jewelry, the former as the pure element and the latter as the Pd/Au alloy known as *white gold*.

Some properties of the elements in groups 8–10 are summarized in Table 23.6 "Some Properties of the Elements of Groups 8, 9, and 10". As in earlier groups, similarities in size and electronegativity between the two heaviest members of each group result in similarities in chemistry. We are now at the point in the *d* block where there is no longer a clear correlation between the valence electron configuration and the preferred oxidation state. For example, all the elements of group 8 have eight valence electrons, but only Ru and Os have any tendency to form compounds in the +8 oxidation state, and those compounds are powerful oxidants. The predominant oxidation states for all three group 8 metals are +2 and +3. Although the elements of group 9 possess a total of nine valence electrons, the +9 oxidation state is unknown for these elements, and the most common oxidation states in the group are +3 and +1. Finally, the elements of group 10 all have 10 valence electrons, but all three elements are normally found in the +2 oxidation

state formed by losing the ns^2 valence electrons. In addition, Pd and Pt form numerous compounds and complexes in the +4 oxidation state.

Table 23.6 Some Properties of the Elements of Groups 8, 9, and 10

Group	Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	Density($g/cm3$)
	Fe	26	$4s^2 3d^6$	1.83	126	1538	7.87
	Ru	44	$5s^1 4d^7$	2.20	134	2334	12.10
8	Os	76	$6s^2 5d^6 4f^{14}$	2.20	135	3033	22.59
	Co	27	$4s^2 3d^7$	1.88	125	1495	8.86
	Rh	45	$5s^1 4d^8$	2.28	134	1964	12.40
9	Ir	77	$6s^2 5d^7 4f^{14}$	2.20	136	2446	22.50
	Ni	28	$4s^2 3d^8$	1.91	124	1455	8.90
	Pd	46	$4d^{10}$	2.20	137	1555	12.00
10	Pt	78	$6s^2 5d^8 4f^{14}$	2.20	139	1768	21.50

We stated that higher oxidation states become less stable as we go across the *d*-block elements and more stable as we go down a group. Thus Fe and Co form trifluorides, but Ni forms only the difluoride NiF_2. In contrast to Fe, Ru and Os form a series of fluorides up to RuF_6 and OsF_7. The hexafluorides of Rh and Ir are extraordinarily powerful oxidants, and Pt is the only element in group 10 that forms a hexafluoride. Similar trends are observed among the oxides. For example, Fe forms only FeO, Fe_2O_3, and the mixed-valent Fe_3O_4 (magnetite), all of which are nonstoichiometric. In contrast, Ru and Os form the dioxides (MO_2) and the highly toxic, volatile, yellow tetroxides, which contain formal M=O bonds. As expected for compounds of metals in such high oxidation states, the latter are potent oxidants. The tendency of the metals to form the higher oxides decreases rapidly as we go farther across the *d* block.

Note the Pattern

Higher oxidation states become less stable across the *d*-block, but more stable down a group.

Reactivity with the heavier chalcogens is rather complex. Thus the oxidation state of Fe, Ru, Os, Co, and Ni in their disulfides is +2 because of the presence of the disulfide ion (S_2^{2-}), but the disulfides of Rh, Ir, Pd, and Pt contain the metal in the +4 oxidation state together with sulfide ions (S^{2-}). This combination of highly charged cations and easily polarized anions results in substances that are not simple ionic compounds and have significant covalent character.

The groups 8–10 metals form a range of binary nitrides, carbides, and borides. By far the most important of these is cementite (Fe_3C), which is used to strengthen steel. At high temperatures, Fe_3C is soluble in iron, but slow cooling causes the phases to separate and form particles of cementite, which gives a metal that retains much of its strength but is significantly less brittle than pure iron. Palladium is unusual in that it forms a binary hydride with the approximate composition $PdH_{0.5}$. Because the H atoms in the metal lattice are highly mobile, thin sheets of Pd are highly permeable to H_2 but essentially impermeable to all other gases, including He. Consequently, diffusion of H_2 through Pd is an effective method for separating hydrogen from other gases.

Groups 11 and 12

Group 11 (Cu, Ag, and Au)

The coinage metals—copper, silver, and gold—occur naturally (like the gold nugget shown here); consequently, these were probably the first metals used by ancient humans. For example, decorative gold artifacts dating from the late Stone Age are known, and some gold Egyptian coins are more than 5000 yr old. Copper is almost as ancient, with objects dating to about 5000 BC. Bronze, an alloy of copper and tin that is harder than either of its constituent metals, was used before 3000 BC, giving rise to the Bronze Age. Deposits of silver are much less common than deposits of gold or copper, yet by 3000 BC, methods had been developed for recovering silver from its ores, which allowed silver coins to be widely used in ancient times.

Deposits of gold and copper are widespread and numerous, and for many centuries it was relatively easy to obtain large amounts of the pure elements. For example, a single gold nugget discovered in Australia in 1869 weighed more than 150 lb. Because the demand for these elements has outstripped their availability, methods have been developed to recover them economically from even very low-grade ores (as low as 1% Cu content for copper) by operating on a vast scale, as shown in the photo of an open-pit copper mine. Copper is used primarily to manufacture electric wires, but large quantities are also used to produce bronze, brass, and alloys for coins. Much of the silver made today is obtained as a by-product of the manufacture of other metals, especially Cu, Pb, and Zn. In addition to its use in jewelry and silverware, silver is used in Ag/Zn and Ag/Cd button batteries. (For more information on button batteries, see Chapter 19 "Electrochemistry", Section 19.5 "Commercial Galvanic Cells".) Gold is typically found either as tiny particles of the pure metal or as gold telluride ($AuTe_2$). It is used as a currency reserve, in

jewelry, in the electronics industry for corrosion-free contacts, and, in very thin layers, as a reflective window coating that minimizes heat transfer.

Some properties of the coinage metals are listed in Table 23.7 "Some Properties of the Elements of Groups 11 and 12". The electronegativity of gold ($\chi = 2.40$) is close to that of the nonmetals sulfur and iodine, which suggests that the chemistry of gold should be somewhat unusual for a metal. The coinage metals have the highest electrical and thermal conductivities of all the metals, and they are also the most ductile and malleable. With an $ns^1(n-1)d^{10}$ valence electron configuration, the chemistry of these three elements is dominated by the +1 oxidation state due to losing the single *ns* electron. Higher oxidation states are also known, however: +2 is common for Cu and, to a lesser extent, Ag, and +3 for Au because of the relatively low values of the second and (for Au) third ionization energies. All three elements have significant electron affinities due to the half-filled *ns* orbital in the neutral atoms. As a result, gold reacts with powerful reductants like Cs and solutions of the alkali metals in liquid ammonia to produce the gold *anion* Au^- with a $6s^25d^{10}$ valence electron configuration.

Table 23.7 Some Properties of the Elements of Groups 11 and 12

Group	Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	Density$(g/cm3)$
	Cu	29	$4s^13d^{10}$	1.90	128	1085	8.96
	Ag	47	$5s^14d^{10}$	1.93	144	962	10.50
11	Au	79	$6s^15d^{10}4f^{14}$	2.40	144	1064	19.30
	Zn	30	$4s^23d^{10}$	1.65	134	420	7.13
	Cd	48	$5s^24d^{10}$	1.69	149	321	8.69
12	Hg	80	$6s^25d^{10}4f^{14}$	1.90	151	−38.8	13.53

All group 11 elements are relatively unreactive, and their reactivity decreases from Cu to Au. Hence they are noble metals that are particularly well suited for use in coins and jewelry. Copper reacts with O_2 at high temperatures to produce Cu_2O and with sulfur to form Cu_2S. Neither silver nor gold reacts directly with oxygen, although oxides of these elements can be prepared by other routes. Silver reacts with sulfur compounds to form the black Ag_2S coating known as tarnish. Gold is the only metal that does not react with sulfur; it also does not react with nitrogen, carbon, or boron. All the coinage metals do, however, react with oxidizing acids. Thus both Cu and Ag dissolve in $HNO_3$and in hot concentrated H_2SO_4, while Au

dissolves in the 3:1 $HCl:HNO_3$ mixture known as *aqua regia*. Furthermore, all three metals dissolve in basic cyanide solutions in the presence of oxygen to form very stable $[M(CN)_2]^-$ ions, a reaction that is used to separate gold from its ores. (For more information about gold processing, see Chapter 4 "Reactions in Aqueous Solution", Section 4.3 "Stoichiometry of Reactions in Solution".)

Note the Pattern

Although the most important oxidation state for group 11 is +1, the elements are relatively unreactive, with reactivity decreasing from Cu to Au.

All the monohalides except CuF and AuF are known (including AgF). Once again, iodine is unable to stabilize the higher oxidation states (Au^{3+} and Cu^{2+}). Thus all the copper(II) halides except the iodide are known, but the only dihalide of silver is AgF_2. In contrast, all the gold trihalides (AuX_3) are known, again except the triiodide. No binary nitrides, borides, or carbides are known for the group 11 elements.

Group 12 (Zn, Cd, and Hg)

We next encounter the group 12 elements. Because none of the elements in group 12 has a partially filled $(n - 1)d$ subshell, they are not, strictly speaking, transition metals. Nonetheless, much of their chemistry is similar to that of the elements that immediately precede them in the *d* block. The group 12 metals are similar in abundance to those of group 11, and they are almost always found in combination with sulfur. Because zinc and cadmium are chemically similar, virtually all zinc ores contain significant amounts of cadmium. All three metals are commercially important, although the use of Cd is restricted because of its toxicity. Zinc is used for corrosion protection, in batteries, to make brass, and, in the form of ZnO, in the production of rubber and paints. (For more information on corrosion, see Chapter 19 "Electrochemistry", Section 19.6 "Corrosion".) Cadmium is used as the cathode in rechargeable NiCad batteries. Large amounts of mercury are used in the production of chlorine and NaOH by the chloralkali process, while smaller amounts are consumed in mercury-vapor streetlights and mercury batteries. (For more information on the uses of mercury, see Chapter 19 "Electrochemistry", Section 19.5 "Commercial Galvanic Cells".)

As shown in Table 23.7 "Some Properties of the Elements of Groups 11 and 12", the group 12 metals are significantly more electropositive than the elements of group 11, and they therefore have less noble character. They also have much lower melting and boiling points than the preceding transition metals. In contrast to trends in the preceding groups, Zn and Cd are similar to each other, but very different from the

heaviest element (Hg). In particular, Zn and Cd are rather active metals, whereas mercury is not. Because mercury, the only metal that is a liquid at room temperature, can dissolve many metals by forming amalgams, medieval alchemists especially valued it when trying to transmute base metals to gold and silver. All three elements in group 12 have $ns^2(n-1)d^{10}$ valence electron configurations; consequently, the +2 oxidation state, corresponding to losing the two *ns* electrons, dominates their chemistry. In addition, mercury forms a series of compounds in the +1 oxidation state that contain the diatomic mercurous ion Hg_2^{2+}.

Note the Pattern

The most important oxidation state for group 12 is +2; the metals are significantly more electropositive than the group 11 elements, so they are less noble.

All the possible group 12 dihalides (MX_2) are known, and they range from ionic (the fluorides) to highly covalent (such as $HgCl_2$). The highly covalent character of many mercuric and mercurous halides is surprising given the large size of the cations, and this has been attributed to the existence of an easily distorted $5d^{10}$ subshell. Zinc and cadmium react with oxygen to form amphoteric MO, whereas mercury forms HgO only within a narrow temperature range (350–400°C). Whereas zinc and cadmium dissolve in mineral acids such as HCl with the evolution of hydrogen, mercury dissolves only in oxidizing acids such as HNO_3 and H_2SO_4. All three metals react with sulfur and the other chalcogens to form the binary chalcogenides; mercury also has an extraordinarily high affinity for sulfur.

EXAMPLE 2

For each reaction, explain why the indicated products form.

a. $TiCl_4(l) + 2H_2O(l) \rightarrow TiO_2(s) + 4HCl(aq)$

b. $WO_3(s) + 3C(s) + 3Cl_2(g) \text{ - } \rightarrow \text{D } WCl_6(s) + 3CO(g)$

$Sc_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2[Sc(OH)_4]^-(aq)$

b. $2KMnO_4(aq) + 2H_2SO_4(l) \rightarrow Mn_2O_7(l) + 2KHSO_4(soln) + H_2O(soln)$

c. $4CrCl_2(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Cr^{3+}(aq) + 8Cl^-(aq) + 2H_2O(l)$

Given: balanced chemical equation

Asked for: why the indicated products form

Strategy:

Refer to the periodic trends in this section, Figure 23.1 "The Metallic Radii of the First-, Second-, and Third-Row Transition Metals", Figure 23.2 "Some Trends in Properties of the Transition Metals", Figure 7.11 "First Ionization Energies of the ", Table 23.1 "Valence Electron Configurations of the First-Row Transition Metals", Table 23.2,Table 23.3 "Common Oxidation States of the First-Row Transition Metals*", Table 23.4 "Some Properties of the Elements of Groups 3, 4, and 5", Table 23.5 "Some Properties of the Elements of Groups 6 and 7", Table 23.6 "Some Properties of the Elements of Groups 8, 9, and 10", and Table 23.7 "Some Properties of the Elements of Groups 11 and 12" to explain why these products form.

Solution:

a. The most stable oxidation state for Ti is +4, and neither reactant is a particularly strong oxidant or reductant; hence a redox reaction is unlikely. Similarly, neither reactant is a particularly strong acid or base, so an acid–base reaction is unlikely. Because $TiCl_4$ contains Ti in a relatively high oxidation state (+4), however, it is likely to be rather covalent in character, with reactivity similar to that of a semimetal halide such as $SiCl_4$. Covalent halides tend to hydrolyze in water to produce the hydrohalic acid and either the oxide of the other element or a species analogous to an oxoacid.

b. This reaction involves the oxide of a group 6 metal in its highest oxidation state (WO_3) and two elements, one of which is a reductant (C) and the other an oxidant (Cl_2). Consequently, some sort of redox reaction will occur. Carbon can certainly react with chlorine to form CCl_4, and WO_3 is a potential source of oxygen atoms that can react with carbon to produce CO, which is very stable. If CO is one of the products, then it seems likely that the other product will contain the metal and chlorine. The most likely combination is WCl_6 (leaving the oxidation state of the metal unchanged).

c. One of the reactants is a strong base (OH^-), so an acid–base reaction is likely if the other reactant is acidic. Because oxides like Sc_2O_3, in which the metal is in an intermediate oxidation state, are often amphoteric, we expect Sc_2O_3 to dissolve in base to form a soluble hydroxide complex.

d. Concentrated sulfuric acid is both an oxidant and a strong acid that tends to protonate and dehydrate other substances. The permanganate ion already contains manganese in its highest possible oxidation state (+7), so it cannot be oxidized further. A redox

reaction is impossible, which leaves an acid–base reaction as the most likely alternative. Sulfuric acid is likely to protonate the terminal oxygen atoms of permanganate, allowing them to be lost as water.

e. Molecular oxygen is an oxidant, so a redox reaction is likely if the other reactant can be oxidized. Because chromous chloride contains chromium in its lowest accessible oxidation state, a redox reaction will occur in which Cr^{2+} ions are oxidized and O_2 is reduced. In the presence of protons, the reduction product of O_2 is water, so we need to determine only the identity of the oxidation product of Cr^{2+}. Chromium forms compounds in two common higher oxidation states: the Cr^{3+} ion, which is the most stable, and the $[Cr_2O_7]^{2-}$ ion, which is a more powerful oxidant than O_2. We therefore predict that the reaction will form $Cr^{3+}(aq)$ and water.

Exercise

Predict the products of each reactions and then balance each chemical equation.

a. $Cr^{2+}(aq) + Fe^{3+}(aq) \text{ - } \rightarrow H +$

b. $Na_2Cr_2O_7(aq) + H_2SO_4(l) \rightarrow$

a. $FeBr_2(aq) + O_2(g) \text{ - } \rightarrow H +$

b. $VBr_4(l) + H_2O(l) \rightarrow$

$ZrO_2(s) + C(s) + Cl_2(g) \text{ - } \rightarrow$ D

Answer:

a. a. $Cr^{2+}(aq) + Fe^{3+}(aq) \text{ - } \rightarrow H + Cr^{3+}(aq) + Fe^{2+}(aq)$

$Na_2Cr_2O_7(aq) + 2H_2SO_4(l) \rightarrow 2NaHSO_4(soln) + H_2O(soln) + 2CrO_3(s)$

b. $4FeBr_2(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Fe^{3+}(aq) + 2H_2O(l) + 8Br^-(aq)$

c. $VBr_4(l) + H_2O(l) \rightarrow VO^{2+}(aq) + 4Br^-(aq) + 2H^+(aq)$

$ZrO_2(s) + 2C(s) + 2Cl_2(g) \text{ - } \rightarrow$ D $ZrCl_4(s) + 2CO(g)$

Summary

The group 3 transition metals are highly electropositive metals and powerful reductants. They react with nonmetals to form compounds that are largely ionic and with oxygen to form sesquioxides (M_2O_3). The group 4 metals also have a high affinity for oxygen. In their reactions with halogens, the covalent character of the halides increases as the oxidation state of the metal increases because the high charge-to-

radius ratio causes extensive polarization of the anions. The dichalcogenides have layered structures similar to graphite, and the hydrides, nitrides, carbides, and borides are all hard, high-melting-point solids with metallic conductivity. The group 5 metals also have a high affinity for oxygen. Consistent with periodic trends, only the lightest (vanadium) has any tendency to form compounds in oxidation states lower than +5. The oxides are sufficiently polarized to make them covalent in character. These elements also form layered chalcogenides, as well as nitrides, carbides, borides, and hydrides that are similar to those of the group 4 elements. As the metals become more polarizable across the row, their affinity for oxygen decreases. The group 6 metals are less electropositive and have a maximum oxidation state of +6, making their compounds in high oxidation states largely covalent in character. As the oxidizing strength of the halogen decreases, the maximum oxidation state of the metal also decreases. All three trioxides are acidic, but Cr_2O_3 is amphoteric. The chalcogenides of the group 6 metals are generally nonstoichiometric and electrically conducting, and these elements also form nitrides, carbides, and borides that are similar to those in the preceding groups. The metals of group 7 have a maximum oxidation state of +7, but the lightest element, manganese, exhibits an extensive chemistry in lower oxidation states. As with the group 6 metals, reaction with less oxidizing halogens produces metals in lower oxidation states, and disulfides and diselenides of Tc and Re have layered structures. The group 7 metals also form nitrides, carbides, and borides that are stable at high temperatures and have metallic properties. In groups 8, 9, and 10, the ionization potentials of the elements are so high that the oxidation state corresponding to the formal loss of all valence electrons is encountered rarely (group 8) or not at all (groups 9 and 10). Compounds of group 8 metals in their highest oxidation state are powerful oxidants. The reaction of metals in groups 8, 9, and 10 with the chalcogens is complex, and these elements form a range of binary nitrides, carbides, and borides. The coinage metals (group 11) have the highest electrical and thermal conductivities and are the most ductile and malleable of the metals. Although they are relatively unreactive, they form halides but not nitrides, borides, or carbides. The group 12 elements, whose chemistry is dominated by the +2 oxidation state, are almost always found in nature combined with sulfur. Mercury is the only metal that is a liquid at room temperature, and it dissolves many metals to form amalgams. The group 12 halides range from ionic to covalent. These elements form chalcogenides and have a high affinity for soft ligands.

KEY TAKEAWAY

- The elements tend to become more polarizable going across the *d* block and higher oxidation states become less stable; higher oxidation states become more stable going down a group.

CONCEPTUAL PROBLEMS

1. The valence electron configuration of Sc is $4s^2 3d^1$, yet it does not lose the d^1 electron to form 1+ ion. Why?
2. Give the ground-state electron configuration for Mn, Mn^{2+}, Au, Au^{3+}, Mo, and Mo^{5+}.
3. A great deal of research is being conducted on the use of titanium alloys as materials for transportation applications (airplanes, ships, automobiles, etc.). Why is Ti particularly suited to this purpose? What is the primary disadvantage that needs to be overcome?
4. Both Ti and Ta are used for bioimplants because they are highly resistant to corrosion. Their uses also extend to other applications where corrosion must be avoided. Why are these metals so corrosion resistant?
5. Give two reasons why Zr is used to make the casing for UO_2 fuel in water-cooled nuclear reactors.
6. Why is chromium added to steel to form stainless steel? What other elements might also be effective additives for this purpose? Why did you select these elements?
7. Tungsten is commonly used as the filament in electric light bulbs. Why is tungsten particularly suited to this purpose?
8. Palladium metal is used to purify H_2 by removing other gases. Why is Pd so permeable to H_2?
9. Give the valence electron configuration for Sc, Fe, Re, Ag, Zr, Co, V, Pr, Hg, Cr, Ni, Ce, Cu, and Tb.
10. The Hg–Hg bond is much stronger than the Cd–Cd bond, reversing the trend found among the other transition-metal groups. Explain this anomaly.
11. Which of the transition metals are most likely to form compounds in the +6 oxidation state? Why?

STRUCTURE AND REACTIVITY

1. Do you expect $TiCl_4$, $TiCl_3$, $TiCl_2$, and Ti to be oxidized, reduced, or hydrolyzed by water? Explain your reasoning.
2. The atomic radii of vanadium, niobium, and tantalum are 134 pm, 146 pm, and 146 pm, respectively. Why does the radius increase from vanadium to niobium but not from niobium to tantalum?
3. The most stable oxidation state for the metals of groups 3, 4, and 5 is the highest oxidation state possible. In contrast, for nearly all the metals of groups 8, 9, and 10, intermediate oxidation states are most stable. Why?

4. Most of the transition metals can form compounds in multiple oxidation states. Ru, for example, can form compounds in the +8, +6, +4, +3, +2, and −2 oxidation states. Give the valence electron configuration of Ru in each oxidation state. Why does Ru exhibit so many oxidation states? Which ones are the most stable? Why?
5. Predict the maximum oxidation states of Cu, Cr, Mo, Rh, Zr, Y, Ir, Hg, and Fe.
6. In the +4 oxidation state all three group 7 metals form the dioxides (MO_2). Which of the three metals do you expect to form the most stable dioxide? Why?
7. Of $[Fe(H_2O)_6]^+$, $OsBr_7$, CoF_4, PtF_6, FeI_3, $[Ni(H_2O)_6]^{2+}$, OsO_4, IrO_4, NiO, RhS_2, and PtH, which do not exist? Why?
8. The chemistry of gold is somewhat anomalous for a metal. With which elements does it form the Au^- ion? Does it form a stable sulfide?
9. Of Os^{4+}, Pt^{10+}, Cr^{6+}, Ir^{9+}, Ru^{8+}, Re^{7+}, and Ni^{10+}, which are not likely to exist? Why?
10. Of Ag_2S, Cu_2S, AuI_3, CuF, AuF, AgN, and AuO, which are not likely to exist?
11. There is evidence that the Au^- ion exists. What would be its electron configuration? The compound CsAu has been isolated; it does not exhibit a metallic luster and does not conduct electricity. Is this compound an alloy? What type of bonding is involved? Explain your answers.
12. Of Hg_2Cl_2, ZnO, HgF_2, $Cs_2[ZnCl_5]$, and HgNa, which are not likely to exist?
13. Mercurous oxide (Hg_2O) and mercurous hydroxide $[Hg_2(OH)_2]$ have never been prepared. Why not? What products are formed if a solution of aqueous sodium hydroxide is added to an aqueous solution of mercurous nitrate $[Hg_2(NO_3)_2]$?
14. Arrange Fe_2O_3, TiO_2, V_2O_5, MoO_3, Mn_2O_7, and OsO_4 in order of increasing basicity.
15. Mercurous sulfide has never been prepared. What products are formed when H_2S gas is bubbled through an aqueous solution of mercurous nitrate?
16. Arrange Sc_2O_3, VO, V_2O_5, Cr_2O_3, Fe_2O_3, Fe_3O_4, and ZnO in order of increasing acidity.
17. Arrange Sc_2O_3, V_2O_5, CrO_3, Mn_2O_7, MnO_2, and VO_2 in order of increasing basicity.
18. Predict the products of each reaction and then balance each chemical equation.

a. Ti + excess Cl_2, heated
b. V_2O_5 in aqueous base
c. $K_2Cr_2O_7 + H_2SO_4$
d. $RuBr_2 + O_2$, in water
e. $[CrO_4]^{2-}$ in aqueous acid

f. Hg^{2+} + Hg, in aqueous acid

19. Predict the products of each reaction and then balance each chemical equation.

a. AgBr + *h*v

b. W + excess Cl_2, heated

c. CuO + H_2, heated

d. Fe_2O_3 in aqueous acid

e. $RhCl_3$ + NH_3, in water

f. Fe^{2+} + $[MnO_4]^-$, in water

20. What do you predict to be the coordination number of Pt^{2+}, Au^+, Fe^{3+}, and Os^{2+}?

21. Of La, Sc, Cr, and Hf, which is most likely to form stable compounds in the +4 oxidation state? Why?

22. Give the most common oxidation state for Y, W, Ru, Ag, Hg, Zn, Cr, Nb, and Ti.

23. Give the most common oxidation state for Os, Cd, Hf, V, Ac, Ni, Mn, Pt, and Fe.

24. Give the highest oxidation state observed for Zr, Fe, Re, Hg, Ni, La, and Mo.

25. Give the highest oxidation state observed for Ag, Co, Os, Au, W, and Mn.

26. Arrange La, Cs, Y, Pt, Cd, Mo, Fe, Co, and Ir in order of increasing first ionization energy.

27. Briefly explain the following trends within the transition metals.

a. Transition-metal fluorides usually have higher oxidation states than their iodides.

b. For a given metal, the lowest-oxidation-state oxide is basic and the highest-oxidation-state oxide is acidic.

c. Halides of the transition metals become more covalent with increasing oxidation state and are more prone to hydrolysis.

28. Propose a method to prepare each of the following compounds: $TiCl_4[(CH_3)_2O]_2$, Na_2TiO_3, V_2O_5, and $Na_2Cr_2O_7$.

29. Of the group 5 elements, which

a. has the greatest tendency to form ions in the lower oxidation states?

b. has the greatest tendency to form a polymeric fluoride?

c. does not form an MX_2 species?

d. forms the most basic oxide?

e. has the greatest tendency to form complexes with coordination numbers higher than 6?

ANSWERS

1.
2.
3.
4.
5.
6.
7.
8.
9. Pt^{10+}, Ir^{9+}, and Ni^{10+}. Because ionization energies increase from left to right across the *d* block, by the time you reach group 9, it is impossible to form compounds in the oxidation state that corresponds to loss of all the valence electrons.

23.2 A Brief Survey of Transition-Metal Chemistry

LEARNING OBJECTIVE

1. To use periodic trends to understand the chemistry of the transition metals.

We turn now to a brief survey of the chemistry of the transition metals, beginning with group 3. As we shall see, the two heaviest members of each group usually exhibit substantial similarities in chemical behavior and are quite different from the lightest member.

Groups 3, 4, and 5

Group 3 (Sc, Y, La, and Ac)

As shown in Table 23.4 "Some Properties of the Elements of Groups 3, 4, and 5", the observed trends in the properties of the group 3 elements are similar to those of groups 1 and 2. Due to their $ns^2(n - 1)d^1$ valence electron configurations, the chemistry of all four elements is dominated by the +3 oxidation state formed by losing all three valence electrons. As expected based on periodic trends, these elements are highly electropositive metals and powerful reductants, with La (and Ac) being the most reactive. In keeping with their highly electropositive character, the group 3 metals react with water to produce the metal hydroxide and hydrogen gas:

Equation 23.1

$$2M(s) + 6H_2O(l) \rightarrow 2M(OH)_3(s) + 3H_2(g)$$

Note the Pattern

The chemistry of the group 3 metals is almost exclusively that of the M^{3+} ion; the elements are powerful reductants.

Moreover, all dissolve readily in aqueous acid to produce hydrogen gas and a solution of the hydrated metal ion: $M^{3+}(aq)$.

Table 23.4 Some Properties of the Elements of Groups 3, 4, and 5

Group	Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	$Density(g/cm3)$
3	Sc	21	$4s^2 3d^1$	1.36	162	1541	2.99
	Y	39	$5s^2 4d^1$	1.22	180	1522	4.47
	La	57	$6s^2 5d^1$	1.10	183	918	6.15
	Ac	89	$7s^2 6d^1$	1.10	188	1051	10.07
4	Ti	22	$4s^2 3d^2$	1.54	147	1668	4.51
	Zr	40	$5s^2 4d^2$	1.33	160	1855	6.52
	Hf	72	$6s^2 5d^2 4f^{14}$	1.30	159	2233	13.31
5	V	23	$4s^2 3d^3$	1.63	134	1910	6.00
	Nb	41	$5s^2 4d^3$	1.60	146	2477	8.57
	Ta	73	$6s^2 5d^3 4f^{14}$	1.50	146	3017	16.65

The group 3 metals react with nonmetals to form compounds that are primarily ionic in character. For example, reacting group 3 metals with the halogens produces the corresponding trihalides: MX_3. The trifluorides are insoluble in water because of their high lattice energies, but the other trihalides are very soluble in water and behave like typical ionic metal halides. All group 3 elements react with air to form an oxide coating, and all burn in oxygen to form the so-called *sesquioxides* (M_2O_3), which react with H2O or CO_2 to form the corresponding hydroxides or carbonates, respectively. Commercial uses of the group 3 metals are limited, but "mischmetal," a mixture of lanthanides containing about 40% La, is used as an additive to improve the properties of steel and make flints for cigarette lighters.

Group 4 (Ti, Zr, and Hf)

Because the elements of group 4 have a high affinity for oxygen, all three metals occur naturally as oxide ores that contain the metal in the +4 oxidation state resulting from losing all four $ns^2(n-1)d^2$ valence electrons. They are isolated by initial conversion to the tetrachlorides, as shown for Ti:

Equation 23.2

$2FeTiO_3(s) + 6C(s) + 7Cl_2(g) \rightarrow 2TiCl_4(g) + 2FeCl_3(g) + 6CO(g)$

followed by reduction of the tetrachlorides with an active metal such as Mg.

Note the Pattern

The chemistry of the group 4 metals is dominated by the +4 oxidation state. Only Ti has an extensive chemistry in lower oxidation states.

In contrast to the elements of group 3, the group 4 elements have important applications. Titanium (melting point = 1668°C) is often used as a replacement for aluminum (melting point = 660°C) in applications that require high temperatures or corrosion resistance. For example, friction with the air heats the skin of supersonic aircraft operating above Mach 2.2 to temperatures near the melting point of aluminum; consequently, titanium is used instead of aluminum in many aerospace applications. The corrosion resistance of titanium is increasingly exploited in architectural applications, as shown in the chapter-opening photo. Metallic zirconium is used in UO_2-containing fuel rods in nuclear reactors, while hafnium is used in the control rods that modulate the output of high-power nuclear reactors, such as those in nuclear submarines.

Consistent with the periodic trends shown in Figure 23.2 "Some Trends in Properties of the Transition Metals", the group 4 metals become denser, higher melting, and more electropositive down the column (Table 23.4 "Some Properties of the Elements of Groups 3, 4, and 5"). Unexpectedly, however, the atomic radius of Hf is slightly*smaller* than that of Zr due to the lanthanide contraction. Because of their $ns^2(n - 1)d^2$valence electron configurations, the +4 oxidation state is by far the most important for all three metals. Only titanium exhibits a significant chemistry in the +2 and +3 oxidation states, although compounds of Ti^{2+} are usually powerful reductants. In fact, the $Ti^{2+}(aq)$ ion is such a strong reductant that it rapidly reduces water to form hydrogen gas.

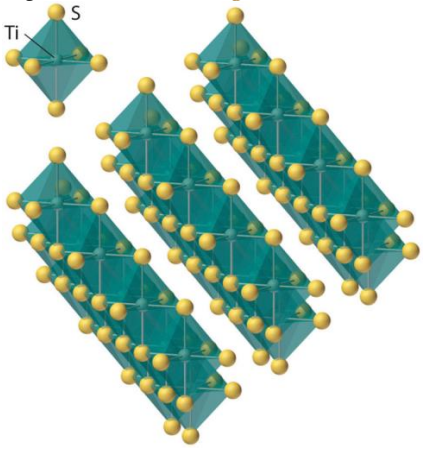
Reaction of the group 4 metals with excess halogen forms the corresponding tetrahalides (MX_4), although titanium, the lightest element in the group, also forms dihalides and trihalides (X is not F). The covalent character of the titanium halides increases as the oxidation state of the metal increases because of increasing polarization of the anions by the cation as its charge-to-radius ratio increases. Thus $TiCl_2$ is an ionic salt, whereas $TiCl_4$ is a volatile liquid that contains tetrahedral molecules. All three metals react with excess oxygen or the heavier chalcogens (Y) to form the corresponding dioxides (MO_2) and dichalcogenides (MY_2). Industrially, TiO_2, which is used as a white pigment in paints, is prepared by reacting $TiCl_4$ with oxygen at high temperatures:

Equation 23.3

$TiCl_4(g) + O_2(g) \rightarrow TiO_2(s) + 2Cl_2(g)$

The group 4 dichalcogenides have unusual layered structures with no M–Y bonds holding adjacent sheets together, which makes them similar in some ways to graphite (Figure 23.3 "The Layered Structure of TiS"). The group 4 metals also react with hydrogen, nitrogen, carbon, and boron to form hydrides (such as TiH_2), nitrides (such as TiN), carbides (such as TiC), and borides (such as TiB_2), all of which are hard, high-melting solids. Many of these binary compounds are nonstoichiometric and exhibit metallic conductivity.

Figure 23.3 The Layered Structure of TiS_2



Each titanium atom is surrounded by an octahedral arrangement of six sulfur atoms that are shared to form extended layers of atoms. Because the layers are held together by only van der Waals forces between adjacent sulfur atoms, rather than covalent bonds, the layers slide past one another relatively easily when a mechanical stress is applied.

Group 5 (V, Nb, and Ta)

Like the group 4 elements, all group 5 metals are normally found in nature as oxide ores that contain the metals in their highest oxidation state (+5). Because of the lanthanide contraction, the chemistry of Nb and Ta is so similar that these elements are usually found in the same ores.

Three-fourths of the vanadium produced annually is used in the production of steel alloys for springs and high-speed cutting tools. Adding a small amount of vanadium to steel results in the formation of small grains of V_4C_3, which greatly increase the strength and resilience of the metal, especially at high temperatures. The other major use of vanadium is as V_2O_5, an important catalyst for the industrial conversion of $SO_2$to SO_3 in the contact process for the production of sulfuric acid. (For more information

on sulfuric acid production, see Chapter 2 "Molecules, Ions, and Chemical Formulas",Section 2.6 "Industrially Important Chemicals".) In contrast, Nb and Ta have only limited applications, and they are therefore produced in relatively small amounts. Although niobium is used as an additive in certain stainless steels, its primary application is in superconducting wires such as Nb_3Zr and Nb_3Ge, which are used in superconducting magnets for the magnetic resonance imaging of soft tissues. Because tantalum is highly resistant to corrosion, it is used as a liner for chemical reactors, in missile parts, and as a biologically compatible material in screws and pins for repairing fractured bones.

Note the Pattern

The chemistry of the two heaviest group 5 metals (Nb and Ta) is dominated by the +5 oxidation state. The chemistry of the lightest element (V) is dominated by lower oxidation states, especially +4.

As indicated in Table 23.4 "Some Properties of the Elements of Groups 3, 4, and 5", the trends in properties of the group 5 metals are similar to those of group 4. Only vanadium, the lightest element, has any tendency to form compounds in oxidation states lower than +5. For example, vanadium is the only element in the group that forms stable halides in the lowest oxidation state (+2). All three metals react with excess oxygen, however, to produce the corresponding oxides in the +5 oxidation state (M_2O_5), in which polarization of the oxide ions by the high-oxidation-state metal is so extensive that the compounds are primarily covalent in character. Vanadium–oxygen species provide a classic example of the effect of increasing metal oxidation state on the protonation state of a coordinated water molecule: vanadium(II) in water exists as the violet hydrated ion $[V(H_2O)_6]^{2+}$; the blue-green $[V(H_2O)_6]^{3+}$ ion is acidic, dissociating to form small amounts of the $[V(H_2O)_5(OH)]^{2+}$ ion and a proton; and in water, vanadium(IV) forms the blue vanadyl ion $[(H_2O)_4VO]^{2+}$, which contains a formal V=O bond (Figure 23.4 "Aqueous Solutions of Vanadium Ions in Oxidation States of +2 to +5"). Consistent with its covalent character, V_2O_5 is acidic, dissolving in base to give the vanadate ion ($[VO_4]^{3-}$), whereas both Nb_2O_5 and Ta_2O_5 are comparatively inert. Oxides of these metals in lower oxidation states tend to be nonstoichiometric.

Figure 23.4 *Aqueous Solutions of Vanadium Ions in Oxidation States of +2 to +5*

Although group 5 metals react with the heavier chalcogens to form a complex set of binary chalcogenides, the most important are the dichalcogenides (MY_2), whose layered structures are similar to those of the group 4 dichalcogenides. The elements of group 5 also form binary nitrides, carbides, borides, and hydrides, whose stoichiometries and properties are similar to those of the corresponding group 4

compounds. One such compound, tantalum carbide (TiC), has the highest melting point of any compound known (3738°C); it is used for the cutting edges of high-speed machine tools.

Groups 6 and 7

Group 6 (Cr, Mo, and W)

As an illustration of the trend toward increasing polarizability as we go from left to right across the *d*block, in group 6 we first encounter a metal (Mo) that occurs naturally as a sulfide ore rather than as an oxide. Molybdenite (MoS_2) is a soft black mineral that can be used for writing, like PbS and graphite. Because of this similarity, people long assumed that these substances were all the same. In fact, the name *molybdenum* is derived from the Greek *molybdos*, meaning "lead." More than 90% of the molybdenum produced annually is used to make steels for cutting tools, which retain their sharp edge even when red hot. In addition, molybdenum is the only second- or third-row transition element that is essential for humans. The major chromium ore is chromite ($FeCr_2O_4$), which is oxidized to the soluble $[CrO_4]^{2-}$ ion under basic conditions and reduced successively to Cr_2O_3 and Cr with carbon and aluminum, respectively. Pure chromium can be obtained by dissolving Cr_2O_3 in sulfuric acid followed by electrolytic reduction; a similar process is used for electroplating metal objects to give them a bright, shiny, protective surface layer. Pure tungsten is obtained by first converting tungsten ores to WO_3, which is then reduced with hydrogen to give the metal.

Consistent with periodic trends, the group 6 metals are slightly less electropositive than those of the three preceding groups, and the two heaviest metals are essentially the same size because of the lanthanide contraction (Table 23.5 "Some Properties of the Elements of Groups 6 and 7"). All three elements have a total of six valence electrons, resulting in a maximum oxidation state of +6. Due to extensive polarization of the anions, compounds in the +6 oxidation state are highly covalent. As in groups 4 and 5, the lightest element exhibits variable oxidation states, ranging from Cr^{2+}, which is a powerful reductant, to CrO_3, a red solid that is a powerful oxidant. For Mo and W, the highest oxidation state (+6) is by far the most important, although compounds in the +4 and +5 oxidation states are known.

Note the Pattern

The metals become increasing polarizable across the *d* block.

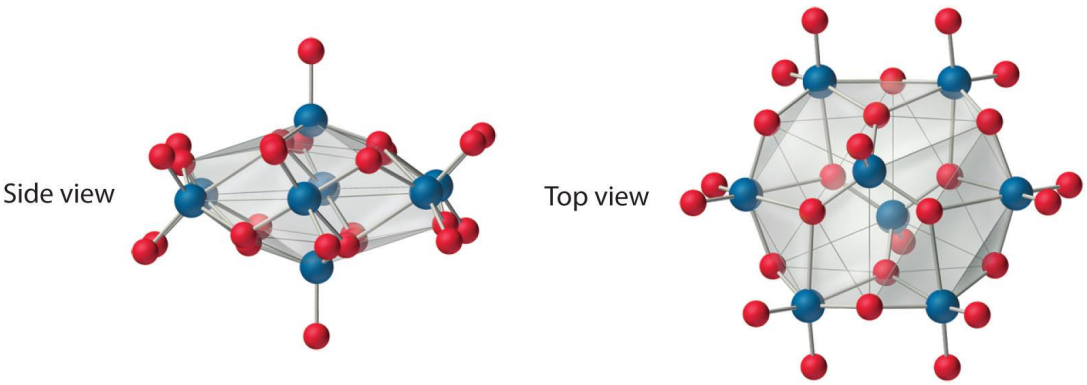
Table 23.5 Some Properties of the Elements of Groups 6 and 7

Group	Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	$Density(g/cm3)$
	Cr	24	$4s^1 3d^5$	1.66	128	1907	7.15
	Mo	42	$5s^1 4d^5$	2.16	139	2623	10.20
6	W	74	$6s^2 5d^4 4f^{14}$	1.70	139	3422	19.30
	Mn	25	$4s^2 3d^5$	1.55	127	1246	7.30
	Tc	43	$5s^2 4d^5$	2.10	136	2157	11.50
7	Re	75	$6s^2 5d^5 4f^{14}$	1.90	137	3186	20.80

Note the Pattern

The chemistry of the two heaviest group 6 metals (Mo and W) is dominated by the +6 oxidation state. The chemistry of the lightest element (Cr) is dominated by lower oxidation states.

As observed in previous groups, the group 6 halides become more covalent as the oxidation state of the metal increases: their volatility increases, and their melting points decrease. Recall that as the electronegativity of the halogens decreases from F to I, they are less able to stabilize high oxidation states; consequently, the maximum oxidation state of the corresponding metal halides decreases. Thus all three metals form hexafluorides, but CrF_6 is unstable at temperatures above −100°C, whereas $MoF_6$and WF_6 are stable. Consistent with the trend toward increased stability of the highest oxidation state for the second- and third-row elements, the other halogens can oxidize chromium to only the trihalides, CrX_3 (X is Cl, Br, or I), while molybdenum forms $MoCl_5$, $MoBr_4$, and MoI_3, and tungsten gives WCl_6, WBr_5, and WI_4.
Both Mo and W react with oxygen to form the covalent trioxides (MoO_3 and WO_3), but Cr reacts to form only the so-called sesquioxide (Cr_2O_3). Chromium will form CrO_3, which is a highly toxic compound that can react explosively with organic materials. All the trioxides are acidic, dissolving in base to form the corresponding oxoanions ($[MO_4]^{2-}$). Consistent with periodic trends, the sesquioxide of the lightest element in the group (Cr_2O_3) is amphoteric. The aqueous chemistry of molybdate and tungstate is complex, and at low pH they form a series of polymeric anions called*isopolymetallates*, such as the $[Mo_8O_{26}]^{4-}$ ion, whose structure is as follows:



An isopolymolybdate cluster. *The $[Mo_8O_{26}]^{4-}$ ion, shown here in both side and top views, is typical of the oxygen-bridged clusters formed by Mo(VI) and W(VI) in aqueous solution.*

Reacting molybdenum or tungsten with heavier chalcogens gives binary chalcogenide phases, most of which are nonstoichiometric and electrically conducting. One of the most stable is MoS_2; it has a layered structure similar to that of TiS_2 (Figure 23.3 "The Layered Structure of TiS"), in which the layers are held together by only weak van der Waals forces, which allows them to slide past one another rather easily. Consequently, both MoS_2 and WS_2 are used as lubricants in a variety of applications, including automobile engines. Because tungsten itself has an extraordinarily high melting point (3380°C), lubricants described as containing "liquid tungsten" actually contain a suspension of very small WS_2 particles.

As in groups 4 and 5, the elements of group 6 form binary nitrides, carbides, and borides whose stoichiometries and properties are similar to those of the preceding groups. Tungsten carbide (WC), one of the hardest compounds known, is used to make the tips of drill bits.

Group 7 (Mn, Tc, and Re)

Continuing across the periodic table, we encounter the group 7 elements (Table 23.5 "Some Properties of the Elements of Groups 6 and 7"). One group 7 metal (Mn) is usually combined with iron in an alloy called *ferromanganese*, which has been used since 1856 to improve the mechanical properties of steel by scavenging sulfur and oxygen impurities to form MnS and MnO. Technetium is named after the Greek*technikos*, meaning "artificial," because all its isotopes are radioactive. One isotope,^{99m}Tc (*m* for metastable), has become an important biomedical tool for imaging internal organs. (For more information on biomedical imaging, see Chapter 20 "Nuclear Chemistry", Section 20.5 "Applied Nuclear Chemistry".) Because of its scarcity, Re is one of the most expensive elements, and its applications are limited. It is, however, used in a bimetallic Pt/Re catalyst for refining high-octane gasoline.

All three group 7 elements have seven valence electrons and can form compounds in the +7 oxidation state. Once again, the lightest element exhibits multiple oxidation states. Compounds of Mn in oxidation states ranging from −3 to +7 are known, with the most common being +2 and +4 (Figure 23.5 "Compounds of Manganese in Oxidation States +2 to +7"). In contrast, compounds of Tc and Re in the +2 oxidation state are quite rare. Because the electronegativity of Mn is anomalously low, elemental manganese is unusually reactive. In contrast, the chemistry of Tc is similar to that of Re because of their similar size and electronegativity, again a result of the lanthanide contraction. Due to the stability of the half-filled $3d^5$ electron configuration, the aqueous Mn^{3+} ion, with a $3d^4$ valence electron configuration, is a potent oxidant that is able to oxidize water. It is difficult to generalize about other oxidation states for Tc and Re because their stability depends dramatically on the nature of the compound.

Figure 23.5Compounds of Manganese in Oxidation States +2 to +7

Consistent with higher oxidation states being more stable for the heavier transition metals, reacting Mn with F_2 gives only MnF_3, a high-melting, red-purple solid, whereas Re reacts with F_2 to give ReF_7, a volatile, low-melting, yellow solid. Again, reaction with the less oxidizing, heavier halogens produces halides in lower oxidation states. Thus reaction with Cl_2, a weaker oxidant than F_2, gives $MnCl_2$ and $ReCl_6$. Reaction of Mn with oxygen forms only Mn_3O_4, a mixed-valent compound that contains two Mn(II) and one Mn(III) per formula unit and is similar in both stoichiometry and structure to magnetite (Fe_3O_4). In contrast, Tc and Re form high-valent oxides, the so-called *heptoxides*(M_2O_7), consistent with the increased stability of higher oxidation states for the second and third rows of transition metals. Under forced conditions, manganese will form Mn_2O_7, an unstable, explosive, green liquid. Also consistent with this trend, the permanganate ion $[MnO_4]^{2-}$ is a potent oxidant, whereas $[TcO_4]^-$ and $[ReO_4]^-$ are much more stable. Both Tc and Re form disulfides and diselenides with layered structures analogous to that of MoS_2, as well as more complex*heptasulfides* (M_2S_7). As is typical of the transition metals, the group 7 metals form binary nitrides, carbides, and borides that are generally stable at high temperatures and exhibit metallic properties.

Note the Pattern

The chemistry of the group 7 metals (Mn, Tc, and Re) is dominated by lower oxidation states. Compounds in the maximum possible oxidation state (+7) are readily reduced.

Groups 8, 9, and 10

In many older versions of the periodic table, groups 8, 9, and 10 were combined in a single group (group VIII) because the elements of these three groups exhibit many horizontal similarities in their chemistry, in addition to the similarities within each column. In part, these horizontal similarities are due to the fact that the ionization potentials of the elements, which increase slowly but steadily across the *d* block, have now become so large that the oxidation state corresponding to the formal loss of all valence electrons is encountered only rarely (group 8) or not at all (groups 9 and 10). As a result, the chemistry of all three groups is dominated by intermediate oxidation states, especially +2 and +3 for the first-row metals (Fe, Co, and Ni). The heavier elements of these three groups are called *precious metals* because they are rather rare in nature and mostly chemically inert.

Note the Pattern

The chemistry of groups 8, 9, and 10 is dominated by intermediate oxidation states such as +2 and +3.

Group 8 (Fe, Ru, and Os)

The chemistry of group 8 is dominated by iron, whose high abundance in Earth's crust is due to the extremely high stability of its nucleus. Ruthenium and osmium, on the other hand, are extremely rare elements, with terrestrial abundances of only about 0.1 ppb and 5 ppb, respectively, and they were not discovered until the 19th century. Because of the high melting point of iron (1538°C), early humans could not use it for tools or weapons. The advanced techniques needed to work iron were first developed by the Hittite civilization in Asia Minor sometime before 2000 BC, and they remained a closely guarded secret that gave the Hittites military supremacy for almost a millennium. With the collapse of the Hittite civilization around 1200 BC, the technology became widely distributed, however, leading to the Iron Age.

Group 9 (Co, Rh, and Ir)

Cobalt is one of the least abundant of the first-row transition metals. Its oxide ores, however, have been used in glass and pottery for thousands of years to produce the brilliant color known as "cobalt blue," and its compounds are consumed in large quantities in the paint and ceramics industries. The heavier elements of group 9 are also rare, with terrestrial abundances of less than 1 ppb; they are generally found in combination with the heavier elements of groups 8 and 10 in Ni–Cu–S ores.

Group 10 (Ni, Pd, and Pt)

Nickel silicates are easily processed; consequently, nickel has been known and used since antiquity. In fact, a 75:25 Cu:Ni alloy was used for more than 2000 years to mint "silver" coins, and the modern US

nickel uses the same alloy. In contrast to nickel, palladium and platinum are rare (their terrestrial abundance is about 10–15 ppb), but they are at least an order of magnitude more abundant than the heavier elements of groups 8 and 9. Platinum and palladium are used in jewelry, the former as the pure element and the latter as the Pd/Au alloy known as

Trends in Group 8, 9, and 10

Some properties of the elements in groups 8–10 are summarized in Table 23.6 "Some Properties of the Elements of Groups 8, 9, and 10". As in earlier groups, similarities in size and electronegativity between the two heaviest members of each group result in similarities in chemistry. We are now at the point in the *d* block where there is no longer a clear correlation between the valence electron configuration and the preferred oxidation state. For example, all the elements of group 8 have eight valence electrons, but only Ru and Os have any tendency to form compounds in the +8 oxidation state, and those compounds are powerful oxidants. The predominant oxidation states for all three group 8 metals are +2 and +3. Although the elements of group 9 possess a total of nine valence electrons, the +9 oxidation state is unknown for these elements, and the most common oxidation states in the group are +3 and +1. Finally, the elements of group 10 all have 10 valence electrons, but all three elements are normally found in the +2 oxidation state formed by losing the ns^2 valence electrons. In addition, Pd and Pt form numerous compounds and complexes in the +4 oxidation state.

Table 23.6 Some Properties of the Elements of Groups 8, 9, and 10

Group	Element	*Z*	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	Density (g/cm3)
8	Fe	26	$4s^2 3d^6$	1.83	126	1538	7.87
	Ru	44	$5s^1 4d^7$	2.20	134	2334	12.10
	Os	76	$6s^2 5d^6 4f^{14}$	2.20	135	3033	22.59
9	Co	27	$4s^2 3d^7$	1.88	125	1495	8.86
	Rh	45	$5s^1 4d^8$	2.28	134	1964	12.40
	Ir	77	$6s^2 5d^7 4f^{14}$	2.20	136	2446	22.50
10	Ni	28	$4s^2 3d^8$	1.91	124	1455	8.90
	Pd	46	$4d^{10}$	2.20	137	1555	12.00
	Pt	78	$6s^2 5d^8 4f^{14}$	2.20	139	1768	21.50

We stated that higher oxidation states become less stable as we go across the *d*-block elements and more stable as we go down a group. Thus Fe and Co form trifluorides, but Ni forms only the difluoride NiF_2. In contrast to Fe, Ru and Os form a series of fluorides up to RuF_6 and OsF_7. The hexafluorides of Rh and Ir are extraordinarily powerful oxidants, and Pt is the only element in group 10 that forms a hexafluoride. Similar trends are observed among the oxides. For example, Fe forms only FeO, Fe_2O_3, and the mixed-valent Fe_3O_4 (magnetite), all of which are nonstoichiometric. In contrast, Ru and Os form the dioxides (MO_2) and the highly toxic, volatile, yellow tetroxides, which contain formal M=O bonds. As expected for compounds of metals in such high oxidation states, the latter are potent oxidants. The tendency of the metals to form the higher oxides decreases rapidly as we go farther across the *d* block.

Note the Pattern

Higher oxidation states become less stable across the *d*-block, but more stable down a group.

Reactivity with the heavier chalcogens is rather complex. Thus the oxidation state of Fe, Ru, Os, Co, and Ni in their disulfides is +2 because of the presence of the disulfide ion (S_2^{2-}), but the disulfides of Rh, Ir, Pd, and Pt contain the metal in the +4 oxidation state together with sulfide ions (S^{2-}). This combination of highly charged cations and easily polarized anions results in substances that are not simple ionic compounds and have significant covalent character.

The groups 8–10 metals form a range of binary nitrides, carbides, and borides. By far the most important of these is cementite (Fe_3C), which is used to strengthen steel. At high temperatures, Fe_3C is soluble in iron, but slow cooling causes the phases to separate and form particles of cementite, which gives a metal that retains much of its strength but is significantly less brittle than pure iron. Palladium is unusual in that it forms a binary hydride with the approximate composition $PdH_{0.5}$. Because the H atoms in the metal lattice are highly mobile, thin sheets of Pd are highly permeable to H_2 but essentially impermeable to all other gases, including He. Consequently, diffusion of H_2 through Pd is an effective method for separating hydrogen from other gases.

Groups 11 and 12

Group 11 (Cu, Ag, and Au)

The coinage metals—copper, silver, and gold—occur naturally (like the gold nugget shown here); consequently, these were probably the first metals used by ancient humans. For example, decorative gold artifacts dating from the late Stone Age are known, and some gold Egyptian coins are more than 5000 yr

old. Copper is almost as ancient, with objects dating to about 5000 BC. Bronze, an alloy of copper and tin that is harder than either of its constituent metals, was used before 3000 BC, giving rise to the Bronze Age. Deposits of silver are much less common than deposits of gold or copper, yet by 3000 BC, methods had been developed for recovering silver from its ores, which allowed silver coins to be widely used in ancient times.

Deposits of gold and copper are widespread and numerous, and for many centuries it was relatively easy to obtain large amounts of the pure elements. For example, a single gold nugget discovered in Australia in 1869 weighed more than 150 lb. Because the demand for these elements has outstripped their availability, methods have been developed to recover them economically from even very low-grade ores (as low as 1% Cu content for copper) by operating on a vast scale, as shown in the photo of an open-pit copper mine. Copper is used primarily to manufacture electric wires, but large quantities are also used to produce bronze, brass, and alloys for coins. Much of the silver made today is obtained as a by-product of the manufacture of other metals, especially Cu, Pb, and Zn. In addition to its use in jewelry and silverware, silver is used in Ag/Zn and Ag/Cd button batteries. (For more information on button batteries, see Chapter 19 "Electrochemistry", Section 19.5 "Commercial Galvanic Cells".) Gold is typically found either as tiny particles of the pure metal or as gold telluride ($AuTe_2$). It is used as a currency reserve, in jewelry, in the electronics industry for corrosion-free contacts, and, in very thin layers, as a reflective window coating that minimizes heat transfer.

Some properties of the coinage metals are listed in Table 23.7 "Some Properties of the Elements of Groups 11 and 12". The electronegativity of gold ($\chi = 2.40$) is close to that of the nonmetals sulfur and iodine, which suggests that the chemistry of gold should be somewhat unusual for a metal. The coinage metals have the highest electrical and thermal conductivities of all the metals, and they are also the most ductile and malleable. With an $ns^1(n - 1)d^{10}$ valence electron configuration, the chemistry of these three elements is dominated by the +1 oxidation state due to losing the single *ns* electron. Higher oxidation states are also known, however: +2 is common for Cu and, to a lesser extent, Ag, and +3 for Au because of the relatively low values of the second and (for Au) third ionization energies. All three elements have significant electron affinities due to the half-filled *ns* orbital in the neutral atoms. As a result, gold reacts with powerful reductants like Cs and solutions of the alkali metals in liquid ammonia to produce the gold *anion* Au^- with a $6s^25d^{10}$ valence electron configuration.

Table 23.7 Some Properties of the Elements of Groups 11 and 12

All group 11 elements are relatively unreactive, and their reactivity decreases from Cu to Au. Hence they are noble metals that are particularly well suited for use in coins and jewelry. Copper reacts with O_2 at high temperatures to produce Cu_2O and with sulfur to form Cu_2S. Neither silver nor gold reacts directly with oxygen, although oxides of these elements can be prepared by other routes. Silver reacts with sulfur compounds to form the black Ag_2S coating known as tarnish. Gold is the only metal that does not react with sulfur; it also does not react with nitrogen, carbon, or boron. All the coinage metals do, however, react with oxidizing acids. Thus both Cu and Ag dissolve in $HNO_3$and in hot concentrated H_2SO_4, while Au dissolves in the 3:1 HCl:HNO_3 mixture known as *aqua regia*. Furthermore, all three metals dissolve in basic cyanide solutions in the presence of oxygen to form very stable $[M(CN)_2]^-$ ions, a reaction that is used to separate gold from its ores. (For more information about gold processing, see Chapter 4 "Reactions in Aqueous Solution", Section 4.3 "Stoichiometry of Reactions in Solution".)

Note the Pattern

Although the most important oxidation state for group 11 is +1, the elements are relatively unreactive, with reactivity decreasing from Cu to Au.

All the monohalides except CuF and AuF are known (including AgF). Once again, iodine is unable to stabilize the higher oxidation states (Au^{3+} and Cu^{2+}). Thus all the copper(II) halides except the iodide are known, but the only dihalide of silver is AgF_2. In contrast, all the gold trihalides (AuX_3) are known, again except the triiodide. No binary nitrides, borides, or carbides are known for the group 11 elements.

Group 12 (Zn, Cd, and Hg)

We next encounter the group 12 elements. Because none of the elements in group 12 has a partially filled $(n - 1)d$ subshell, they are not, strictly speaking, transition metals. Nonetheless, much of their chemistry is similar to that of the elements that immediately precede them in the *d* block. The group 12 metals are similar in abundance to those of group 11, and they are almost always found in combination with sulfur. Because zinc and cadmium are chemically similar, virtually all zinc ores contain significant amounts of cadmium. All three metals are commercially important, although the use of Cd is restricted because of its toxicity. Zinc is used for corrosion protection, in batteries, to make brass, and, in the form of ZnO, in the production of rubber and paints. (For more information on corrosion, see Chapter 19 "Electrochemistry", Section 19.6 "Corrosion".) Cadmium is used as the cathode in rechargeable NiCad

batteries. Large amounts of mercury are used in the production of chlorine and NaOH by the chloralkali process, while smaller amounts are consumed in mercury-vapor streetlights and mercury batteries. (For more information on the uses of mercury, see Chapter 19 "Electrochemistry", Section 19.5 "Commercial Galvanic Cells".)

As shown in Table 23.7 "Some Properties of the Elements of Groups 11 and 12", the group 12 metals are significantly more electropositive than the elements of group 11, and they therefore have less noble character. They also have much lower melting and boiling points than the preceding transition metals. In contrast to trends in the preceding groups, Zn and Cd are similar to each other, but very different from the heaviest element (Hg). In particular, Zn and Cd are rather active metals, whereas mercury is not. Because mercury, the only metal that is a liquid at room temperature, can dissolve many metals by forming amalgams, medieval alchemists especially valued it when trying to transmute base metals to gold and silver. All three elements in group 12 have $ns^2(n-1)d^{10}$ valence electron configurations; consequently, the +2 oxidation state, corresponding to losing the two *ns* electrons, dominates their chemistry. In addition, mercury forms a series of compounds in the +1 oxidation state that contain the diatomic mercurous ion Hg_2^{2+}.

Note the Pattern

The most important oxidation state for group 12 is +2; the metals are significantly more electropositive than the group 11 elements, so they are less noble.

All the possible group 12 dihalides (MX_2) are known, and they range from ionic (the fluorides) to highly covalent (such as $HgCl_2$). The highly covalent character of many mercuric and mercurous halides is surprising given the large size of the cations, and this has been attributed to the existence of an easily distorted $5d^{10}$ subshell. Zinc and cadmium react with oxygen to form amphoteric MO, whereas mercury forms HgO only within a narrow temperature range (350–400°C). Whereas zinc and cadmium dissolve in mineral acids such as HCl with the evolution of hydrogen, mercury dissolves only in oxidizing acids such as HNO_3 and H_2SO_4. All three metals react with sulfur and the other chalcogens to form the binary chalcogenides; mercury also has an extraordinarily high affinity for sulfur.

EXAMPLE 2

For each reaction, explain why the indicated products form.

a. $TiCl_4(l) + 2H_2O(l) \rightarrow TiO_2(s) + 4HCl(aq)$

b. a. $WO_3(s) + 3C(s) + 3Cl_2(g) - \rightarrow D\, WCl_6(s) + 3CO(g)$ $Sc_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2[Sc(OH)_4]^-(aq)$

c. $2KMnO_4(aq) + 2H_2SO_4(l) \rightarrow Mn_2O_7(l) + 2KHSO_4(soln) + H_2O(soln)$

d. $4CrCl_2(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Cr^{3+}(aq) + 8Cl^-(aq) + 2H_2O(l)$

Given: balanced chemical equation

Asked for: why the indicated products form

Strategy:

Refer to the periodic trends in this section, Figure 23.1 "The Metallic Radii of the First-, Second-, and Third-Row Transition Metals", Figure 23.2 "Some Trends in Properties of the Transition Metals", Figure 7.11 "First Ionization Energies of the ", Table 23.1 "Valence Electron Configurations of the First-Row Transition Metals", Table 23.2,Table 23.3 "Common Oxidation States of the First-Row Transition Metals*", Table 23.4 "Some Properties of the Elements of Groups 3, 4, and 5", Table 23.5 "Some Properties of the Elements of Groups 6 and 7", Table 23.6 "Some Properties of the Elements of Groups 8, 9, and 10", and Table 23.7 "Some Properties of the Elements of Groups 11 and 12" to explain why these products form.

Solution:

a. The most stable oxidation state for Ti is +4, and neither reactant is a particularly strong oxidant or reductant; hence a redox reaction is unlikely. Similarly, neither reactant is a particularly strong acid or base, so an acid–base reaction is unlikely. Because $TiCl_4$ contains Ti in a relatively high oxidation state (+4), however, it is likely to be rather covalent in character, with reactivity similar to that of a semimetal halide such as $SiCl_4$. Covalent halides tend to hydrolyze in water to produce the hydrohalic acid and either the oxide of the other element or a species analogous to an oxoacid.

b. This reaction involves the oxide of a group 6 metal in its highest oxidation state (WO_3) and two elements, one of which is a reductant (C) and the other an oxidant (Cl_2). Consequently, some sort of redox reaction will occur. Carbon can certainly react with chlorine to form CCl_4, and WO_3 is a potential source of oxygen atoms that can react with carbon to produce CO, which is very stable. If CO is one of the products, then it seems likely that the other product will contain the metal and

chlorine. The most likely combination is WCl_6 (leaving the oxidation state of the metal unchanged).

c. One of the reactants is a strong base (OH^-), so an acid–base reaction is likely if the other reactant is acidic. Because oxides like Sc_2O_3, in which the metal is in an intermediate oxidation state, are often amphoteric, we expect Sc_2O_3 to dissolve in base to form a soluble hydroxide complex.

d. Concentrated sulfuric acid is both an oxidant and a strong acid that tends to protonate and dehydrate other substances. The permanganate ion already contains manganese in its highest possible oxidation state (+7), so it cannot be oxidized further. A redox reaction is impossible, which leaves an acid–base reaction as the most likely alternative. Sulfuric acid is likely to protonate the terminal oxygen atoms of permanganate, allowing them to be lost as water.

e. Molecular oxygen is an oxidant, so a redox reaction is likely if the other reactant can be oxidized. Because chromous chloride contains chromium in its lowest accessible oxidation state, a redox reaction will occur in which Cr^{2+} ions are oxidized and O_2 is reduced. In the presence of protons, the reduction product of O_2 is water, so we need to determine only the identity of the oxidation product of Cr^{2+}. Chromium forms compounds in two common higher oxidation states: the Cr^{3+} ion, which is the most stable, and the $[Cr_2O_7]^{2-}$ ion, which is a more powerful oxidant than O_2. We therefore predict that the reaction will form $Cr^{3+}(aq)$ and water.

Exercise

Predict the products of each reactions and then balance each chemical equation.

a. $Cr^{2+}(aq) + Fe^{3+}(aq) \text{ - } \rightarrow$

b. $Na_2Cr_2O_7(aq) + H_2SO_4(l) \rightarrow$

c. $FeBr_2(aq) + O_2(g) \text{ - } \rightarrow H +$

d. $VBr_4(l) + H_2O(l) \rightarrow$

$ZrO_2(s) + C(s) + Cl_2(g) \text{ - } \rightarrow$ D

Answer:

a. $Cr^{2+}(aq) + Fe^{3+}(aq) \rightarrow H + Cr^{3+}(aq) + Fe^{2+}(aq)$

b. $Na_2Cr_2O_7(aq) + 2H_2SO_4(l) \rightarrow 2NaHSO_4(soln) + H_2O(soln) + 2CrO_3(s)$

c. $4FeBr_2(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Fe^{3+}(aq) + 2H_2O(l) + 8Br^-(aq)$

d. $VBr_4(l) + H_2O(l) \rightarrow VO^{2+}(aq) + 4Br^-(aq) + 2H^+(aq)$

$ZrO_2(s) + 2C(s) + 2Cl_2(g) \rightarrow D\ ZrCl_4(s) + 2CO(g)$

Summary

The group 3 transition metals are highly electropositive metals and powerful reductants. They react with nonmetals to form compounds that are largely ionic and with oxygen to form sesquioxides (M_2O_3). The group 4 metals also have a high affinity for oxygen. In their reactions with halogens, the covalent character of the halides increases as the oxidation state of the metal increases because the high charge-to-radius ratio causes extensive polarization of the anions. The dichalcogenides have layered structures similar to graphite, and the hydrides, nitrides, carbides, and borides are all hard, high-melting-point solids with metallic conductivity. The group 5 metals also have a high affinity for oxygen. Consistent with periodic trends, only the lightest (vanadium) has any tendency to form compounds in oxidation states lower than +5. The oxides are sufficiently polarized to make them covalent in character. These elements also form layered chalcogenides, as well as nitrides, carbides, borides, and hydrides that are similar to those of the group 4 elements. As the metals become more polarizable across the row, their affinity for oxygen decreases. The group 6 metals are less electropositive and have a maximum oxidation state of +6, making their compounds in high oxidation states largely covalent in character. As the oxidizing strength of the halogen decreases, the maximum oxidation state of the metal also decreases. All three trioxides are acidic, but Cr_2O_3 is amphoteric. The chalcogenides of the group 6 metals are generally nonstoichiometric and electrically conducting, and these elements also form nitrides, carbides, and borides that are similar to those in the preceding groups. The metals of group 7 have a maximum oxidation state of +7, but the lightest element, manganese, exhibits an extensive chemistry in lower oxidation states. As with the group 6 metals, reaction with less oxidizing halogens produces metals in lower oxidation states, and disulfides and diselenides of Tc and Re have layered structures. The group 7 metals also form nitrides, carbides, and borides that are stable at high temperatures and have metallic properties. In groups 8, 9, and 10, the ionization potentials of the elements are so high that the oxidation state corresponding to the formal loss of all valence electrons is encountered rarely (group 8) or not at all (groups 9 and 10). Compounds of

group 8 metals in their highest oxidation state are powerful oxidants. The reaction of metals in groups 8, 9, and 10 with the chalcogens is complex, and these elements form a range of binary nitrides, carbides, and borides. The coinage metals (group 11) have the highest electrical and thermal conductivities and are the most ductile and malleable of the metals. Although they are relatively unreactive, they form halides but not nitrides, borides, or carbides. The group 12 elements, whose chemistry is dominated by the +2 oxidation state, are almost always found in nature combined with sulfur. Mercury is the only metal that is a liquid at room temperature, and it dissolves many metals to form amalgams. The group 12 halides range from ionic to covalent. These elements form chalcogenides and have a high affinity for soft ligands.

KEY TAKEAWAY

- The elements tend to become more polarizable going across the *d* block and higher oxidation states become less stable; higher oxidation states become more stable going down a group.

CONCEPTUAL PROBLEMS

1. The valence electron configuration of Sc is $4s^2 3d^1$, yet it does not lose the d^1 electron to form 1+ ion. Why?
2. Give the ground-state electron configuration for Mn, Mn^{2+}, Au, Au^{3+}, Mo, and Mo^{5+}.
3. A great deal of research is being conducted on the use of titanium alloys as materials for transportation applications (airplanes, ships, automobiles, etc.). Why is Ti particularly suited to this purpose? What is the primary disadvantage that needs to be overcome?
4. Both Ti and Ta are used for bioimplants because they are highly resistant to corrosion. Their uses also extend to other applications where corrosion must be avoided. Why are these metals so corrosion resistant?
5. Give two reasons why Zr is used to make the casing for UO_2 fuel in water-cooled nuclear reactors.
6. Why is chromium added to steel to form stainless steel? What other elements might also be effective additives for this purpose? Why did you select these elements?
7. Tungsten is commonly used as the filament in electric light bulbs. Why is tungsten particularly suited to this purpose?
8. Palladium metal is used to purify H_2 by removing other gases. Why is Pd so permeable to H_2?
9. Give the valence electron configuration for Sc, Fe, Re, Ag, Zr, Co, V, Pr, Hg, Cr, Ni, Ce, Cu, and Tb.
10. The Hg–Hg bond is much stronger than the Cd–Cd bond, reversing the trend found among the other transition-metal groups. Explain this anomaly.

11. Which of the transition metals are most likely to form compounds in the +6 oxidation state? Why?

STRUCTURE AND REACTIVITY

1. Do you expect $TiCl_4$, $TiCl_3$, $TiCl_2$, and Ti to be oxidized, reduced, or hydrolyzed by water? Explain your reasoning.
2. The atomic radii of vanadium, niobium, and tantalum are 134 pm, 146 pm, and 146 pm, respectively. Why does the radius increase from vanadium to niobium but not from niobium to tantalum?
3. The most stable oxidation state for the metals of groups 3, 4, and 5 is the highest oxidation state possible. In contrast, for nearly all the metals of groups 8, 9, and 10, intermediate oxidation states are most stable. Why?
4. Most of the transition metals can form compounds in multiple oxidation states. Ru, for example, can form compounds in the +8, +6, +4, +3, +2, and −2 oxidation states. Give the valence electron configuration of Ru in each oxidation state. Why does Ru exhibit so many oxidation states? Which ones are the most stable? Why?
5. Predict the maximum oxidation states of Cu, Cr, Mo, Rh, Zr, Y, Ir, Hg, and Fe.
6. In the +4 oxidation state all three group 7 metals form the dioxides (MO_2). Which of the three metals do you expect to form the most stable dioxide? Why?
7. Of $[Fe(H_2O)_6]^+$, $OsBr_7$, CoF_4, PtF_6, FeI_3, $[Ni(H_2O)_6]^{2+}$, OsO_4, IrO_4, NiO, RhS_2, and PtH, which do not exist? Why?
8. The chemistry of gold is somewhat anomalous for a metal. With which elements does it form the Au^- ion? Does it form a stable sulfide?
9. Of Os^{4+}, Pt^{10+}, Cr^{6+}, Ir^{9+}, Ru^{8+}, Re^{7+}, and Ni^{10+}, which are not likely to exist? Why?
10. Of Ag_2S, Cu_2S, AuI_3, CuF, AuF, AgN, and AuO, which are not likely to exist?

ANSWER

1.
2.
3.
4.
5.
6.
7.
8.

9. Pt^{10+}, Ir^{9+}, and Ni^{10+}. Because ionization energies increase from left to right across the *d* block, by the time you reach group 9, it is impossible to form compounds in the oxidation state that corresponds to loss of all the valence electrons.

23.3 Metallurgy

LEARNING OBJECTIVE

1. To understand how metals are extracted from their ores.

Very few of the transition metals are found in nature as free metals. Consequently, almost all metallic elements must be isolated from metal oxide or metal sulfide ores. Metallurgy is the set of processes by which metals are extracted from their ores and converted to more useful forms.

Metallurgy consists of three general steps: (1) mining the ore, (2) separating and concentrating the metal or the metal-containing compound, and (3) reducing the ore to the metal. Additional processes are sometimes required to improve the mechanical properties of the metal or increase its purity. Many ores contain relatively low concentrations of the desired metal; for example, copper ores that contain even 1% Cu by mass are considered commercially useful. After an ore has been mined, the first step in processing is usually to crush it because the rate of chemical reactions increases dramatically with increased surface area. Next, one of three general strategies is used to separate and concentrate the compound(s) of interest: *settling* and *flotation*, which are based on differences in density between the desired compound and impurities; *pyrometallurgy*, which uses chemical reduction at high temperatures; and *hydrometallurgy*, which employs chemical or electrochemical reduction of an aqueous solution of the metal. Other methods that take advantage of unusual physical or chemical properties of a particular compound may also be used. For example, crystals of magnetite (Fe_3O_4) are tiny but rather powerful magnets; in fact, magnetite (also known as *lodestone*) was used to make the first compasses in China during the first century BC. If a crushed ore that contains magnetite is passed through a powerful magnet, the Fe_3O_4 particles are attracted to the poles of the magnet, allowing them to be easily separated from other minerals.

Note the Pattern

Metallurgy depends on the separation of a metal compound from its ore and reduction to the metal at high temperature (pyrometallurgy) or in aqueous solution (hydrometallurgy).

Settling and flotation have been used for thousands of years to separate particles of dense metals such as gold, using the technique known as *panning*, in which a sample of gravel or sand is swirled in water in a shallow metal pan. Because the density of gold (19.3 g/cm^3) is so much greater than that of most silicate minerals (about 2.5 g/cm^3), silicate particles settle more slowly and can be poured off with the water, leaving dense gold particles on the bottom of the pan. Conversely, in flotation, the compound of interest is made to float on top of a solution. Blowing air through a suspension of the crude ore in a mixture of water and an organic liquid, such as pine tar, produces a "froth" that contains tiny particles of hydrophobic solids, such as metal sulfides, while more hydrophilic oxide minerals remain suspended in the aqueous phase (Figure 23.6 "Froth Flotation"). To make the separation more efficient, small amounts of an anionic sulfur-containing compound, such as $Na^+C_2H_5OCS_2^-$, are added; the additive binds to the sulfur-rich surface of the metal sulfide particles and makes the metal sulfide particles even more hydrophobic. The resulting froth is highly enriched in the desired metal sulfide(s), which can be removed simply by skimming. This method works even for compounds as dense as PbS (7.5 g/cm^3).

(a) When air is blown through a mixture of a finely ground metal sulfide ore and water, the more hydrophobic metal sulfides form a froth that can be easily removed, allowing them to be separated from more hydrophilic metal oxides and silicates. (b) A froth containing precious metal sulfides is formed as a by-product during the production of metallic nickel. (c) An anionic sulfur additive with hydrophobic "tails" can be used to enhance the hydrophobic character of metal sulfide particles, which causes them to be attracted to the air/water interface in the foam.

Pyrometallurgy

In pyrometallurgy, an ore is heated with a reductant to obtain the metal. Theoretically, it should be possible to obtain virtually any metal from its ore by using coke, an inexpensive form of crude carbon, as the reductant. An example of such a reaction is as follows:

Equation 23.4

$$CaO(s) + C(s) \rightarrow \text{D}Ca(l) + CO(g)$$

Unfortunately, many of the early transition metals, such as Ti, react with carbon to form stable binary carbides. Consequently, more expensive reductants, such as hydrogen, aluminum, magnesium, or calcium, must be used to obtain these metals. Many metals that occur naturally as sulfides can be obtained by heating the sulfide in air, as shown for lead in the following equation:

Equation 23.5

$$PbS(s) + O2(g) \rightarrow DPb(l) + SO2(g)$$

The reaction is driven to completion by the formation of SO_2, a stable gas.

Pyrometallurgy is also used in the iron and steel industries. The overall reaction for the production of iron in a blast furnace is as follows:

Equation 23.6

$$Fe2O3(s) + 3C(s) \rightarrow D2Fe(l) + 3CO(g)$$

The actual reductant is CO, which reduces Fe_2O_3 to give Fe(l) and CO_2(g); the CO_2 is then reduced back to CO by reaction with excess carbon. As the ore, lime, and coke drop into the furnace (Figure 23.7 "A Blast Furnace for Converting Iron Oxides to Iron Metal"), any silicate minerals in the ore react with the lime to produce a low-melting mixture of calcium silicates called *slag*, which floats on top of the molten iron. Molten iron is then allowed to run out the bottom of the furnace, leaving the slag behind. Originally, the iron was collected in pools called *pigs*, which is the origin of the name*pig iron*.

Iron that is obtained directly from a blast furnace has an undesirably low melting point (about 1100°C instead of 1539°C) because it contains a large amount of dissolved carbon. It contains other impurities (such as Si, S, P, and Mn from contaminants in the iron ore that were also reduced during processing) that must be removed because they make iron brittle and unsuitable for most structural applications. In the Bessemer process, oxygen is blown through the molten pig iron to remove the impurities by selective oxidation because these impurities are more readily oxidized than iron (Figure 23.8 "A Basic Oxygen Furnace for Converting Crude Iron to Steel"). In the final stage of this process, small amounts of other metals are added at specific temperatures to produce steel with the desired combination of properties.

Hydrometallurgy

The most selective methods for separating metals from their ores are based on the formation of metal complexes. For example, gold is often found as tiny flakes of the metal, usually in association with quartz or pyrite deposits. In those circumstances, gold is typically extracted by using *cyanide leaching*, which forms a stable gold–cyanide complex—$[Au(CN)_2]^-$:

Equation 23.7

$$4Au(s) + 8NaCN(aq) + O_2(g) + 2H_2O(l) \rightarrow 4Na[Au(CN)_2](aq) + 4NaOH(aq)$$

Virtually pure gold can be obtained by adding powdered zinc to the solution:

Equation 23.8

$$Zn(s) + 2[Au(CN)_2]^-(aq) \rightarrow [Zn(CN)_4]^{2-}(aq) + 2Au(s)$$

A related method, which is used to separate Co^{3+}, Ni^{2+}, and Cu^{+} from Fe, Mn, and Ti, is based on the formation of stable, soluble ammonia complexes of ions of the late transition metals.

EXAMPLE 3

Suppose you are working in the chemistry laboratory of a mining company that has discovered a new source of tungsten ore containing about 5% WS_2 in a granite matrix (granite is a complex aluminosilicate mineral). You have been asked to outline an economical procedure for isolating WS_2 from the ore and then converting it to elemental tungsten in as few steps as possible. What would you recommend?

Given: composition of ore

Asked for: procedure to isolate metal sulfide

Strategy:

Determine which method would be most effective for separating the metal sulfide from the ore. Then determine the best method for reducing the metal to the pure element.

Solution:

You need to separate and concentrate the WS_2, convert it to a suitable form so it can be reduced to the metal (if necessary), and then carry out the reduction. Because the new ore is a binary metal sulfide, you could take advantage of the hydrophilic nature of most metal sulfides to separate WS_2 by froth flotation. Then, because most metal sulfides cannot be reduced directly to the metal using carbon, you will probably need to convert WS_2 to an oxide for subsequent reduction. One point to consider is whether the oxide can be reduced using carbon because many transition metals react with carbon to form stable carbides. Here is one possible procedure for producing tungsten from this new ore:

1. Grind the ore and separate WS_2 from the silicate matrix by flotation.
2. Convert the crude WS_2 to an oxide by roasting in air (because W is in group 6, you anticipate that roasting will yield WO_3, the oxide in the highest possible oxidation state). The reaction will also produce SO_2, which will have to be removed by scrubbing the exhaust gases to minimize environmental pollution.

3. Reduce the oxide with hydrogen gas at high temperature to avoid carbide formation:

$$WO3(s) +3H2(g)- \rightarrow DW(s) +3H2O(g)$$

Exercise

Propose an economical procedure for converting a silicate mineral deposit containing $BaCO_3$ to the pure Ba metal.

Answer:

1. Dissolve the sample containing barium carbonate in HCl(aq) to give Ba^{2+}(aq), which will allow the insoluble silicate minerals to be removed by filtration.
2. Precipitate the barium from solution as $BaCO_3$ by adding solid Na_2CO_3.
3. Dissolve the solid $BaCO_3$ in concentrated HCl and remove the water by evaporation to obtain anhydrous $BaCl_2$.
4. Reduce molten $BaCl_2$ to the metal by electrolysis.

Summary

The conversion of metals from their ores to more useful forms is called**metallurgy**, which consists of three general steps: mining, separation and concentration, and reduction. Settling and flotation are separation methods based on differences in density, whereas pyrometallurgy is based on a chemical reduction at elevated temperatures, and hydrometallurgy uses chemical or electrochemical reduction of an aqueous solution. In pyrometallurgy, a reductant must be used that does not form stable compounds with the metal of interest. In hydrometallurgy, metals are separated via the formation of metal complexes.

KEY TAKEAWAY

- A metal is separated from its ore and then isolated by using pyrometallurgy or hydrometallurgy or by taking advantage of unusual chemical or physical properties of a particular compound.

CONCEPTUAL PROBLEMS

1. Coke is a plentiful and inexpensive reductant that is used to isolate metals from their ores. Of Cr, Co, W, Cu, Ni, Os, Fe, Mn, La, and Hf, which cannot be isolated using this reductant? Why?
2. Hydrometallurgy is the preferred method for separating late transition metals from their ores. What types of ligands are most effective in this process?

ANSWER

1. Coke cannot be used as a reductant for metals that form stable carbides, such as the early transition metals (La, Hf, and W).

2.

STRUCTURE AND REACTIVITY

1. Tantalum and niobium are frequently found together in ores. These elements can be separated from other metals present by treatment with a solution of HF. Explain why this is an effective separation technique.
2. A commercially important ore of chromium is chromite ($FeCr_2O_4$), which is an analogue of magnetite (Fe_3O_4). Based on what you know about the oxidation states of iron in magnetite, predict the oxidation states of the metal ions in chromite.
3. Pure vanadium is obtained by reducing VCl_4 with H_2 or Mg or by reducing V_2O_5 with Ca. Write a balanced chemical equation for each reaction. Why is carbon not used for the reduction?
4. Manganese is an important additive in steel because of its reactivity with oxygen and sulfur, both of which contribute to brittleness. Predict the products of reacting Mn with these species.
5. The diagram of a blast furnace in Figure 23.7 "A Blast Furnace for Converting Iron Oxides to Iron Metal" illustrates several important features of the reduction of Fe_2O_3 to iron. Write a balanced chemical equation for each step of the process described in the figure and give the overall equation for the conversion. Oxygen is blown through the final product to remove impurities. Why does this step not simply reverse the process and produce iron oxides?
6. Metallic Zr is produced by the Kroll method, which uses Na as the reductant. Write a balanced chemical equation for each reaction involved in this process. The product is frequently contaminated with Hf. Propose a feasible method for separating the two elements.
7. The compound Cr_2O_3 is important commercially; among other things, it is used as a pigment in paint and as a catalyst for the manufacture of butadiene. Write a balanced chemical equation to show how you would produce this compound from

a. chromium metal.

b. ammonium dichromate.

c. $CrCl_3$ in a basic solution.

ANSWER

1.

2.

3.

$$VCl4(l) + 2H2(g) VCl4(l) + 2Mg(s) V2O5(s) + 5Ca(s) - \rightarrow DV(s) + 4HCl(g)$$

$$- \rightarrow DV(s) + 2MgCl2(g) - \rightarrow D2V(s) + 5CaO(s)$$

Carbon cannot be used as a reductant because vanadium forms stable carbides, such as VC and VC_2.

23.4 Coordination Compounds

LEARNING OBJECTIVES

1. To know the most common structures observed for metal complexes.
2. To predict the relative stabilities of metal complexes with different ligands.

One of the most important properties of metallic elements is their ability to act as Lewis acids that form complexes with a variety of Lewis bases. A metal complex consists of a central metal atom or ion that is bonded to one or more ligands (from the Latin*ligare*, meaning “to bind”), which are ions or molecules that contain one or more pairs of electrons that can be shared with the metal. Metal complexes can be neutral, such as $Co(NH_3)_3Cl_3$; positively charged, such as $[Nd(H_2O)_9]^{3+}$; or negatively charged, such as $[UF_8]^{4-}$. Electrically charged metal complexes are sometimes called complex ions.

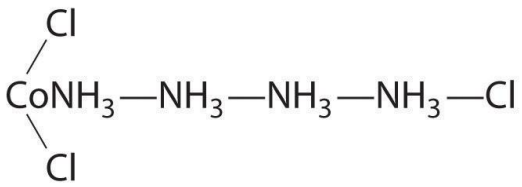
A coordination compound contains one or more metal complexes.

Coordination compounds are important for at least three reasons. First, most of the elements in the periodic table are metals, and almost all metals form complexes, so metal complexes are a feature of the chemistry of more than half the elements. Second, many industrial catalysts are metal complexes, and such catalysts are steadily becoming more important as a way to control reactivity. For example, a mixture of a titanium complex and an organometallic compound of aluminum is the catalyst used to produce most of the polyethylene and polypropylene “plastic” items we use every day. Finally, transition-metal complexes are essential in biochemistry. Examples include hemoglobin, an iron complex that transports oxygen in our blood; cytochromes, iron complexes that transfer electrons in our cells; and complexes of Fe, Zn, Cu, and Mo that are crucial components of certain enzymes, the catalysts for all biological reactions. Metal complexes are so important in biology that we consider the topic separately in Section 23.6 "Transition Metals in Biology".

History of the Coordination Compounds

Coordination compounds have been known and used since antiquity; probably the oldest is the deep blue pigment called Prussian blue: $KFe_2(CN)_6$. The chemical nature of these substances, however, was unclear for a number of reasons. For example, many compounds called "double salts" were known, such as $AlF_3 \cdot 3KF$, $Fe(CN)_2 \cdot 4KCN$, and $ZnCl_2 \cdot 2CsCl$, which were combinations of simple salts in fixed and apparently arbitrary ratios. Why should $AlF_3 \cdot 3KF$ exist but not $AlF_3 \cdot 4KF$ or $AlF_3 \cdot 2KF$? And why should a 3:1 KF:AlF_3 mixture have different chemical and physical properties than either of its components? Similarly, *adducts* of metal salts with neutral molecules such as ammonia were also known—for example, $CoCl_3 \cdot 6NH_3$, which was first prepared sometime before 1798. Like the double salts, the compositions of these adducts exhibited fixed and apparently arbitrary ratios of the components. For example, $CoCl_3 \cdot 6NH_3$, $CoCl_3 \cdot 5NH_3$, $CoCl_3 \cdot 4NH_3$, and $CoCl_3 \cdot 3NH_3$ were all known and had very different properties, but despite all attempts, chemists could not prepare $CoCl_3 \cdot 2NH_3$ or $CoCl_3 \cdot NH_3$.

Although the chemical *composition* of such compounds was readily established by existing analytical methods, their chemical *nature* was puzzling and highly controversial. The major problem was that what we now call *valence* (i.e., the oxidation state) and *coordination number* were thought to be identical. As a result, highly implausible (to modern eyes at least) structures were proposed for such compounds, including the "Chattanooga choo-choo" model for $CoCl_3 \cdot 4NH_3$ shown here.



$CoCl_3 \cdot 4NH_3$

The modern theory of coordination chemistry is based largely on the work of Alfred Werner (1866–1919; Nobel Prize in Chemistry in 1913). In a series of careful experiments carried out in the late 1880s and early 1890s, he examined the properties of several series of metal halide complexes with ammonia. For example, five different "adducts" of ammonia with $PtCl_4$ were known at the time: $PtCl_4 \cdot nNH_3$ (n = 2–6). Some of Werner's original data on these compounds are shown in Table 23.8 "Werner's Data on Complexes of Ammonia with PtCl". The electrical conductivity of aqueous solutions of these compounds was roughly proportional to the number of ions formed per mole, while the number of chloride ions that could be precipitated as AgCl after adding $Ag^+(aq)$ was a measure of the number of "free" chloride ions

present. For example, Werner's data on $PtCl_4 \cdot 6NH_3$ in Table 23.8 "Werner's Data on Complexes of Ammonia with PtCl" showed that all the chloride ions were present as free chloride. In contrast, $PtCl_4 \cdot 2NH_3$ was a neutral molecule that contained no free chloride ions.

Alfred Werner (1866–1919)

Werner, the son of a factory worker, was born in Alsace. He developed an interest in chemistry at an early age, and he did his first independent research experiments at age 18. While doing his military service in southern Germany, he attended a series of chemistry lectures, and he subsequently received his PhD at the University of Zurich in Switzerland, where he was appointed professor of chemistry at age 29. He won the Nobel Prize in Chemistry in 1913 for his work on coordination compounds, which he performed as a graduate student and first presented at age 26. Apparently, Werner was so obsessed with solving the riddle of the structure of coordination compounds that his brain continued to work on the problem even while he was asleep. In 1891, when he was only 25, he woke up in the middle of the night and, in only a few hours, had laid the foundation for modern coordination chemistry.

Table 23.8 Werner's Data on Complexes of Ammonia with $PtCl_4$

Complex	Conductivity (ohm^{-1})	Number of Ions per Formula Unit	Number of Cl^- Ions Precipitated by Ag^+
$PtCl_4 \cdot 6NH_3$	523	5	4
$PtCl_4 \cdot 5NH_3$	404	4	3
$PtCl_4 \cdot 4NH_3$	299	3	2
$PtCl_4 \cdot 3NH_3$	97	2	1
$PtCl_4 \cdot 2NH_3$	0	0	0

These data led Werner to postulate that metal ions have two different kinds of valence: (1) a *primary valence* (oxidation state) that corresponds to the positive charge on the metal ion and (2) a *secondary valence* (coordination number) that is the total number of ligands bound to the metal ion. If Pt had a primary valence of 4 and a secondary valence of 6, Werner could explain the properties of the $PtCl_4 \cdot NH_3$ adducts by the following reactions, where the metal complex is enclosed in square brackets:

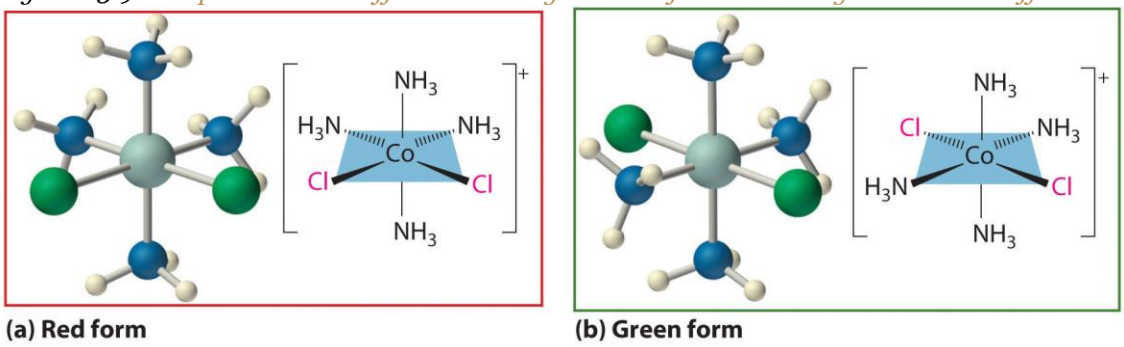
Equation 23.9

$$[Pt(NH3)6]Cl4[Pt(NH3)5Cl]Cl3[Pt(NH3)4Cl2]Cl2[Pt(NH3)3Cl3]Cl$$
$$[Pt(NH3)2Cl4]\rightarrow\left[Pt(NH3)6\right]4+(aq)+4Cl-(aq)\rightarrow[Pt(NH3$$
$$5Cl]3+(aq)+3Cl-(aq)\rightarrow[Pt(NH3)4Cl2]2+(aq)+2Cl-(aq)$$
$$\rightarrow[Pt(NH3)3Cl3]+(aq)+Cl-(aq)\rightarrow[Pt(NH3)2Cl4]0(aq)$$

Further work showed that the two missing members of the series—$[Pt(NH_3)Cl_5]^-$ and $[PtCl_6]^{2-}$—could be prepared as their mono- and dipotassium salts, respectively. Similar studies established coordination numbers of 6 for Co^{3+} and Cr^{3+} and 4 for $Pt^{2+}$and Pd^{2+}.

Werner's studies on the analogous Co^{3+} complexes also allowed him to propose a structural model for metal complexes with a coordination number of 6. Thus he found that $[Co(NH_3)_6]Cl_3$ (yellow) and $[Co(NH_3)_5Cl]Cl_2$ (purple) were 1:3 and 1:2 electrolytes. Unexpectedly, however, two different $[Co(NH_3)_4Cl_2]Cl$ compounds were known: one was red, and the other was green (part (a) in Figure 23.9 "Complexes with Different Arrangements of the Same Ligands Have Different Properties"). Because both compounds had the same chemical composition and the same number of groups of the same kind attached to the same metal, there had to be something different about the*arrangement* of the ligands around the metal ion. Werner's key insight was that the six ligands in $[Co(NH_3)_4Cl_2]Cl$ had to be arranged at the vertices of an octahedron because that was the only structure consistent with the existence of two, and only two, arrangements of ligands (part (b) in Figure 23.9 "Complexes with Different Arrangements of the Same Ligands Have Different Properties"). His conclusion was corroborated by the existence of only two different forms of the next compound in the series: $Co(NH_3)_3Cl_3$.

Figure 23.9 Complexes with Different Arrangements of the Same Ligands Have Different Properties



The $[Co(NH_3)_4Cl_2]^+$ ion can have two different arrangements of the ligands, which results in different colors: if the two Cl^- ligands are next to each other, the complex is red (a), but if they are opposite each other, the complex is green (b).

EXAMPLE 4

In Werner's time, many complexes of the general formula MA_4B_2 were known, but no more than two different compounds with the same composition had been prepared for any metal. To confirm Werner's reasoning, calculate the maximum number of different structures that are possible for six-coordinate

MA_4B_2 complexes with each of the three most symmetrical possible structures: a hexagon, a trigonal prism, and an octahedron. What does the fact that no more than two forms of any MA_4B_2 complex were known tell you about the three-dimensional structures of these complexes?

Given: three possible structures and the number of different forms known for MA_4B_2complexes

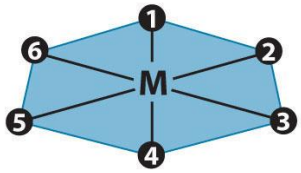
Asked for: number of different arrangements of ligands for MA_4B_2 complex for each structure

Strategy:

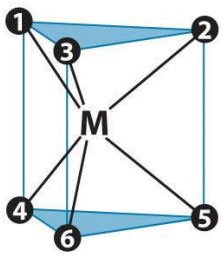
Sketch each structure, place a B ligand at one vertex, and see how many different positions are available for the second B ligand.

Solution:

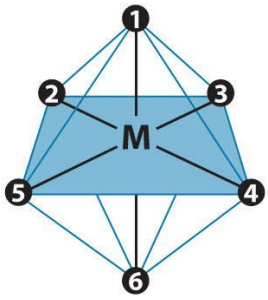
The three regular six-coordinate structures are shown here, with each coordination position numbered so that we can keep track of the different arrangements of ligands. For each structure, all vertices are equivalent. We begin with a symmetrical MA_6complex and simply replace two of the A ligands in each structure to give an MA_4B_2complex:



Hexagon



Trigonal prism



Octahedron

For the hexagon, we place the first B ligand at position 1. There are now three possible places for the second B ligand: at position 2 (or 6), position 3 (or 5), or position 4. These are the only possible arrangements. The (1, 2) and (1, 6) arrangements are chemically identical because the two B ligands are adjacent to each other. The (1, 3) and (1, 5) arrangements are also identical because in both cases the two B ligands are separated by an A ligand.

Turning to the trigonal prism, we place the first B ligand at position 1. Again, there are three possible choices for the second B ligand: at position 2 or 3 on the same triangular face, position 4 (on the other triangular face but adjacent to 1), or position 5 or 6 (on the other triangular face but not adjacent to 1). The (1, 2) and (1, 3) arrangements are chemically identical, as are the (1, 5) and (1, 6) arrangements.

In the octahedron, however, if we place the first B ligand at position 1, then we have only two choices for the second B ligand: at position 2 (or 3 or 4 or 5) or position 6. In the latter, the two B ligands are at opposite vertices of the octahedron, with the metal lying directly between them. Although there are four possible arrangements for the former, they are chemically identical because in all cases the two B ligands are adjacent to each other.

The number of possible MA_4B_2 arrangements for the three geometries is thus: hexagon, 3; trigonal prism, 3; and octahedron, 2. The fact that only two different forms were known for all MA_4B_2 complexes that had been prepared suggested that the correct structure was the octahedron but did not prove it. For some reason one of the three arrangements possible for the other two structures could have been less stable or harder to prepare and had simply not yet been synthesized. When combined with analogous results for other types of complexes (e.g., MA_3B_3), however, the data were best explained by an octahedral structure for six-coordinate metal complexes.

Exercise

Determine the maximum number of structures that are possible for a four-coordinate MA_2B_2 complex with either a square planar or a tetrahedral symmetrical structure.

Answer: square planar, 2; tetrahedral, 1

Structures of Metal Complexes

The coordination numbers of metal ions in metal complexes can range from 2 to at least 9. In general, the differences in energy between different arrangements of ligands are greatest for complexes with low coordination numbers and decrease as the coordination number increases. Usually only one or two structures are possible for complexes with low coordination numbers, whereas several different energetically equivalent structures are possible for complexes with high coordination numbers ($n > 6$). The following presents the most commonly encountered structures for coordination numbers 2–9. Many of these structures should be familiar to you from our discussion of the valence-shell electron-pair repulsion (VSEPR) model in Chapter 9 "Molecular Geometry and Covalent Bonding Models" because they correspond to the lowest-energy arrangements of n electron pairs around a central atom.

Note the Pattern

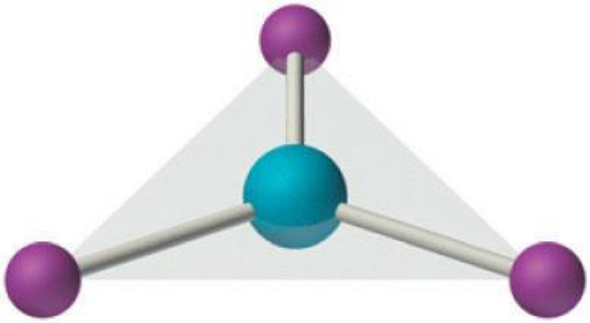
Compounds with low coordination numbers exhibit the greatest differences in energy between different arrangements of ligands.

Coordination Number 2

Linear ML_2

Although it is rare for most metals, this coordination number is surprisingly common for d^{10} metal ions, especially Cu^+, Ag^+, Au^+, and Hg^{2+}. An example is the $[Au(CN)_2]^-$ ion, which is used to extract gold from its ores, as described in Section 23.3 "Metallurgy". As expected based on VSEPR considerations, these complexes have the linear L–M–L structure shown here.

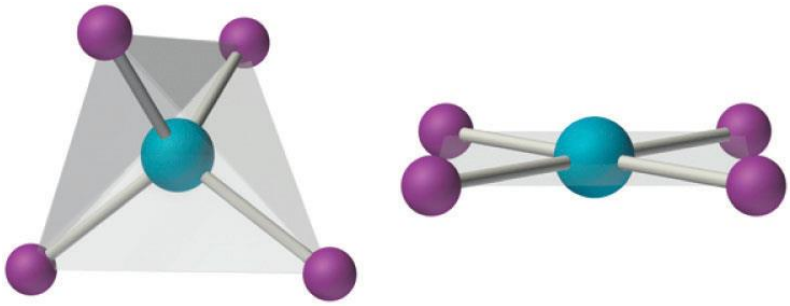
Coordination Number 3



Trigonal planar ML_3

Although it is also rare, this coordination number is encountered with d^{10} metal ions such as Cu^+ and Hg^{2+}. Among the few known examples is the HgI_3^- ion. Three-coordinate complexes almost always have the trigonal planar structure expected from the VSEPR model.

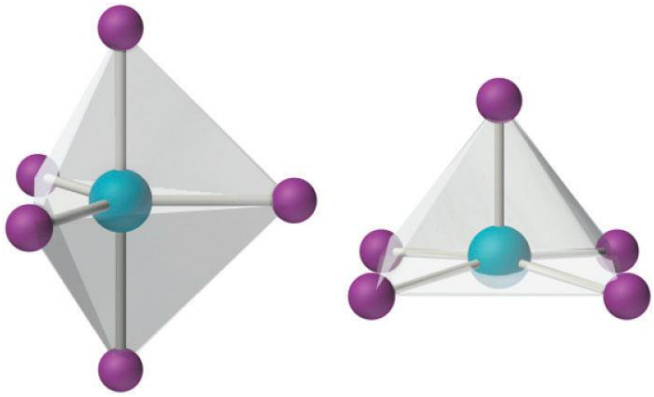
Coordination Number 4



Tetrahedral and square planar ML_4

Two common structures are observed for four-coordinate metal complexes: tetrahedral and square planar. The tetrahedral structure is observed for all four-coordinate complexes of nontransition metals, such as $[BeF_4]^{2-}$, and d^{10} ions, such as $[ZnCl_4]^{2-}$. It is also found for four-coordinate complexes of the first-row transition metals, especially those with halide ligands (e.g., $[FeCl_4]^-$ and $[FeCl_4]^{2-}$). In contrast, square planar structures are routinely observed for four-coordinate complexes of second- and third-row transition metals with d^8 electron configurations, such as Rh^+ and Pd^{2+}, and they are also encountered in some complexes of Ni^{2+} and Cu^{2+}.

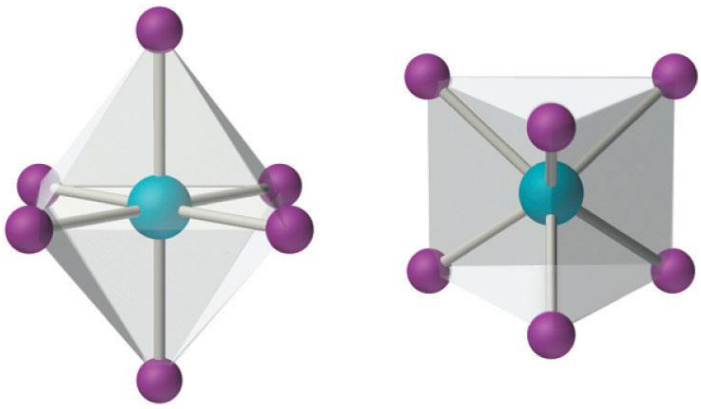
Coordination Number 5



Trigonal bipyramidal and square pyramidal ML_5

This coordination number is less common than 4 and 6, but it is still found frequently in two different structures: trigonal bipyramidal and square pyramidal. Because the energies of these structures are usually rather similar for most ligands, many five-coordinate complexes have distorted structures that lie somewhere between the two extremes.

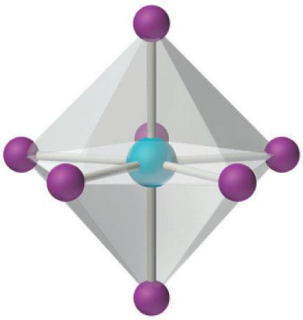
Coordination Number 6



Octahedral and trigonal prismatic ML_6

This coordination number is by far the most common. The six ligands are almost always at the vertices of an octahedron or a distorted octahedron. The only other six-coordinate structure is the trigonal prism, which is very uncommon in simple metal complexes.

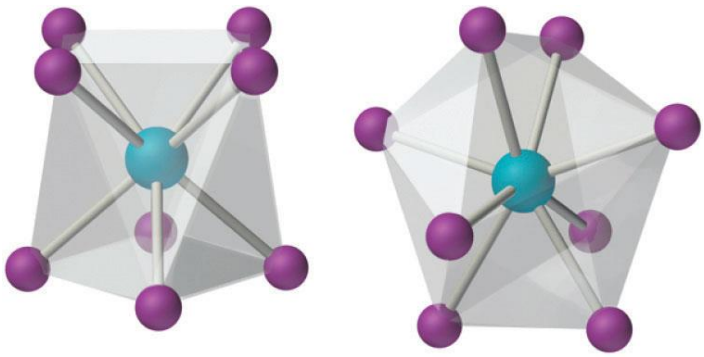
Coordination Number 7



Pentagonal bipyramidal ML_7

This relatively uncommon coordination number is generally encountered for only large metals (such as the second- and third-row transition metals, lanthanides, and actinides). At least three different structures are known, two of which are derived from an octahedron or a trigonal prism by adding a ligand to one face of the polyhedron to give a “capped” octahedron or trigonal prism. By far the most common, however, is the pentagonal bipyramid.

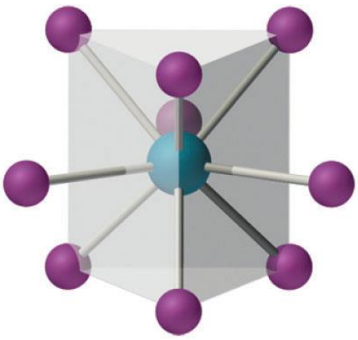
Coordination Number 8



Square antiprismatic and trigonal dodecahedral ML_8

This coordination number is relatively common for larger metal ions. The simplest structure is the cube, which is rare because it does not minimize interligand repulsive interactions. Common structures are the square antiprism and the dodecahedron, both of which can be generated from the cube.

Coordination Number 9



Tricapped trigonal prismatic ML_9

This coordination number is found in larger metal ions, and the most common structure is the tricapped trigonal prism, as in $[Nd(H_2O)_9]^{3+}$.

Stability of Metal Complexes

The thermodynamic stability of a metal complex depends greatly on the properties of the ligand and the metal ion and on the type of bonding. Recall that the metal–ligand interaction is an example of a Lewis acid–base interaction. Lewis bases can be divided into two categories: hard bases, which contain small, relatively nonpolarizable donor atoms (such as N, O, and F), and soft bases, which contain larger, relatively polarizable donor atoms (such as P, S, and Cl). Metal ions with the highest affinities for hard

bases are hard acids, whereas metal ions with the highest affinity for soft bases are soft acids. Some examples of hard and soft acids and bases are given inTable 23.9 "Examples of Hard and Soft Acids and Bases". Notice that hard acids are usually cations of electropositive metals; consequently, they are relatively nonpolarizable and have higher charge-to-radius ratios. Conversely, soft acids tend to be cations of less electropositive metals; consequently, they have lower charge-to-radius ratios and are more polarizable. Chemists can predict the relative stabilities of complexes formed by the *d*-block metals with a remarkable degree of accuracy by using a simple rule: *hard acids prefer to bind to hard bases, and soft acids prefer to bind to soft bases*.

Table 23.9 Examples of Hard and Soft Acids and Bases

	Acids	Bases
hard	H^+	NH_3, RNH_2, N_2H_4
	Li^+, Na^+, K^+	H_2O, ROH, R_2O
	Be^{2+}, Mg^{2+}, Ca^{2+}, VO^{2+}	OH^-, F^-, Cl^-, $CH_3CO_2^-$
	Al^{3+}, Sc^{3+}, Cr^{3+}	CO_3^{2-}
	Ti^{4+}	PO_4^{3-}
soft	BF_3, Al_2Cl_6, CO_2, SO_3	
	Cu^+, Ag^+, Au^+, Tl^+, Hg_2^{2+}	H^-
	Pd^{2+}, Pt^{2+}, Hg^{2+}	CN^-, SCN^-, I^-, RS^-
	$GaCl_3$, $GaBr_3$, GaI_3	CO, R_2S

Because the interaction between hard acids and hard bases is primarily electrostatic in nature, the stability of complexes involving hard acids and hard bases increases as the positive charge on the metal ion increases and as its radius decreases. For example, the complex of Al^{3+} (r = 53.5 pm) with four fluoride ligands (AlF_4^-) is about 10^8 times more stable than InF_4^-, the corresponding fluoride complex of In^{3+} (r = 80 pm). In general, the stability of complexes of divalent first-row transition metals with a given ligand varies inversely with the radius of the metal ion, as shown in the following series:[1]

$$complex\ stability \propto ionic\ radius\ (pm)\ Mn2+83 < Fe2+78 < Co2+74.5 < Ni2+69 < Cu2+73 > Zn2+74$$

Because a hard metal interacts with a base in much the same way as a proton, by binding to a lone pair of electrons on the base, the stability of complexes of hard acids with hard bases increases as the ligand becomes more basic. For example, because ammonia is a stronger base than water, metal ions bind

preferentially to ammonia. Consequently, adding ammonia to aqueous solutions of many of the first-row transition-metal cations results in the formation of the corresponding ammonia complexes.

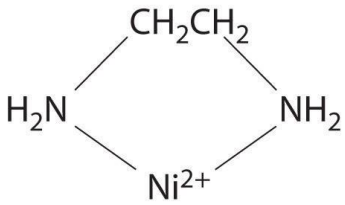
In contrast, the interaction between soft metals (such as the second- and third-row transition metals and Cu^+) and soft bases is largely covalent in nature. Most soft-metal ions have a filled or nearly filled *d* subshell, which suggests that metal-to-ligand π bonding is important. Complexes of soft metals with soft bases are therefore much more stable than would be predicted based on electrostatic arguments.

Note the Pattern

Hard acids prefer to bind to hard bases, and soft acids prefer to bind to soft bases.

The hard acid–hard base/soft acid–soft base concept also allows us to understand why metals are found in nature in different kinds of ores. Recall from Section 23.2 "A Brief Survey of Transition-Metal Chemistry" that most of the first-row transition metals are isolated from oxide ores but that copper and zinc tend to occur naturally in sulfide ores. This is consistent with the increase in the soft character of the metals across the first row of the transition metals from left to right. Recall also that most of the second- and third-row transition metals occur in nature as sulfide ores, consistent with their greater soft character.

Ligands like chloride, water, and ammonia are said to be *monodentate* (one-toothed, from the Greek *mono*, meaning "one," and the Latin *dent-*, meaning "tooth"): they are attached to the metal via only a single atom. Ligands can, however, be *bidentate* (two-toothed, from the Greek *di*, meaning "two"), *tridentate* (three-toothed, from the Greek*tri*, meaning "three"), or, in general, *polydentate* (many-toothed, from the Greek *poly*, meaning "many"), indicating that they are attached to the metal at two, three, or several sites, respectively. Ethylenediamine ($H_2NCH_2CH_2NH_2$, often abbreviated as en) and diethylenetriamine ($H_2NCH_2CH_2NHCH_2CH_2NH_2$, often abbreviated as dien) are examples of a bidentate and a tridentate ligand, respectively, because each nitrogen atom has a lone pair that can be shared with a metal ion. When a bidentate ligand such as ethylenediamine binds to a metal such as Ni^{2+}, a five-membered ring is formed. A metal-containing ring like that shown is called a *chelate* ring (from the Greek *chele*, meaning "claw"). Correspondingly, a polydentate ligand is a *chelating agent*, and complexes that contain polydentate ligands are called *chelate complexes*.



A chelate complex

Experimentally, it is observed that metal complexes of polydentate ligands are significantly more stable than the corresponding complexes of chemically similar monodentate ligands; this increase in stability is called the **chelate effect**. For example, the complex of Ni^{2+} with three ethylenediamine ligands, $[Ni(en)_3]^{2+}$, should be chemically similar to the Ni^{2+} complex with six ammonia ligands, $[Ni(NH_3)_6]^{2+}$. In fact, the equilibrium constant for the formation of $[Ni(en)_3]^{2+}$ is almost 10 orders of magnitude larger than the equilibrium constant for the formation of $[Ni(NH_3)_6]^{2+}$:

Equation 23.10

$$[Ni(H2O)6]2 + +6NH3[Ni(H2O)6]2 + +3en \square$$

$$[Ni(NH3)6]2 + +6H2O(l) \square \quad [Ni(NH3)6]2 + +6H2O(l)KfKf = 4´ 108 = 2´ 1018$$

Note the Pattern

Chelate complexes are more stable than the analogous complexes with monodentate ligands.

The stability of a chelate complex depends on the *size* of the chelate rings. For ligands with a flexible organic backbone like ethylenediamine, complexes that contain five-membered chelate rings, which have almost no strain, are significantly more stable than complexes with six-membered chelate rings, which are in turn much more stable than complexes with four- or seven-membered rings. For example, the complex of copper(II) with two ethylenediamine ligands is about 1000 times more stable than the corresponding complex with triethylenediamine ($H_2NCH_2CH_2CH_2NH_2$, abbreviated as trien):

EXAMPLE

Arrange $[Cr(en)_3]^{3+}$, $[CrCl_6]^{3-}$, $[CrF_6]^{3-}$, and $[Cr(NH_3)_6]^{3+}$ in order of increasing stability.

Given: four Cr(III) complexes

Asked for: relative stabilities

Strategy:

A Determine the relative basicity of the ligands to identify the most stable complexes.

B Decide whether any complexes are further stabilized by a chelate effect and arrange the complexes in order of increasing stability.

Solution:

A The metal ion is the same in each case: Cr^{3+}. Consequently, we must focus on the properties of the ligands to determine the stabilities of the complexes. Because the stability of a metal complex increases as the basicity of the ligands increases, we need to determine the relative basicity of the four ligands. Our earlier discussion of acid–base properties suggests that ammonia and ethylenediamine, with nitrogen donor atoms, are the most basic ligands. The fluoride ion is a stronger base (it has a higher charge-to-radius ratio) than chloride, so the order of stability expected due to ligand basicity is $[CrCl_6]^{3-} < [CrF_6]^{3-} < [Cr(NH_3)_6]^{3+} \approx [Cr(en)_3]^{3+}$.

B Because of the chelate effect, we expect ethylenediamine to form a stronger complex with Cr^{3+} than ammonia. Consequently, the likely order of increasing stability is $[CrCl_6]^{3-} < [CrF_6]^{3-} < [Cr(NH_3)_6]^{3+} < [Cr(en)_3]^{3+}$.

Exercise

Arrange $[Co(NH_3)_6]^{3+}$, $[CoF_6]^{3-}$, and $[Co(en)_3]^{3+}$ in order of decreasing stability.

Answer: $[Co(en)_3]^{3+} > [Co(NH_3)_6]^{3+} > [CoF_6]^{3-}$

Isomers of Metal Complexes

As we discussed earlier in this section, the existence of coordination compounds with the same formula but different arrangements of the ligands was crucial in the development of coordination chemistry. Two or more compounds with the same formula but different arrangements of the atoms are called isomers. Because isomers usually have different physical and chemical properties, it is important to know which isomer we are dealing with if more than one isomer is possible. Recall from Chapter 2 "Molecules, Ions, and Chemical Formulas" that in many cases more than one structure is possible for organic compounds with the same molecular formula; examples discussed previously include *n*-butane versus isobutane and *cis*-2-butene versus*trans*-2-butene. As we will see, coordination compounds exhibit the same types of isomers as organic compounds, as well as several kinds of isomers that are unique. (For more information on isomers in organic compounds, see Chapter 24 "Organic Compounds", Section 24.2 "Isomers of Organic Compounds".)

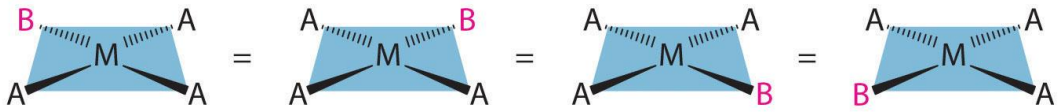
Structural Isomers

Isomers that contain the same number of atoms of each kind but differ in which atoms are bonded to one another are called structural isomers. Isobutane and *n*-butane are examples of structural isomers. One kind of isomerism consists of two compounds that have the same empirical formula but differ in the number of formula units present in the molecular formula. An example in coordination compounds is two compounds with the empirical formula $Pt(NH_3)_2Cl_2$. One is a simple square planar platinum(II) complex, $Pt(NH_3)_2Cl_2$, and the other is an ionic compound that contains the $[Pt(NH_3)_4]^{2+}$ cation and the $[PtCl_4]^{2-}$ anion, $[Pt(NH_3)_4][PtCl_4]$. As you might expect, these compounds have very different physical and chemical properties. One arrangement of the Cl^- and NH_3 ligands around the platinum ion in the former gives the anticancer drug cisplatin, whereas the other arrangement has no known biomedical applications.

Geometrical Isomers

Metal complexes that differ only in which ligands are adjacent to one another (cis) or directly across from one another (trans) in the coordination sphere of the metal are called geometrical isomers. They are most important for square planar and octahedral complexes.

Because all vertices of a square are equivalent, it does not matter which vertex is occupied by the ligand B in a square planar MA_3B complex; hence only a single geometrical isomer is possible in this case (and in the analogous MAB_3 case). All four structures shown here are chemically identical because they can be superimposed simply by rotating the complex in space:



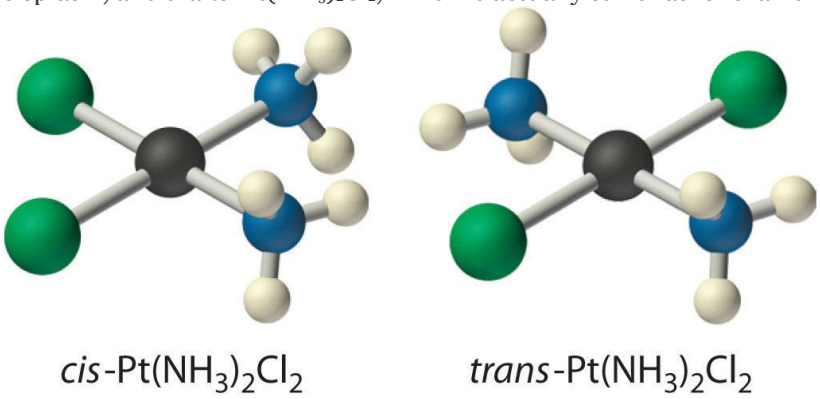
MA_3B square planar complex

For an MA_2B_2 complex, there are two possible isomers: either the A ligands can be adjacent to one another (*cis*), in which case the B ligands must also be *cis*, or the A ligands can be across from one another (*trans*), in which case the B ligands must also be *trans*. Even though it is possible to draw the *cis* isomer in four different ways and the*trans* isomer in two different ways, all members of each set are chemically equivalent:

MA_2B_2 square planar complex, *cis* isomer

MA_2B_2 square planar complex, *trans* isomer

Because there is no way to convert the *cis* structure to the *trans* by rotating or flipping the molecule in space, they are fundamentally different arrangements of atoms in space. Probably the best-known examples of *cis* and *trans* isomers of an MA_2B_2 square planar complex are *cis*-$Pt(NH_3)_2Cl_2$, also known as cisplatin, and *trans*-$Pt(NH_3)_2Cl_2$, which is actually toxic rather than therapeutic.



The anticancer drug cisplatin and its inactive *trans* isomer. *Cisplatin is especially effective against tumors of the reproductive organs (the testes in males and the ovaries in females), which primarily affect individuals in their 20s and were notoriously difficult to cure. For example, after being diagnosed with metastasized testicular cancer in 1991 and given only a 50% chance of survival, Lance Armstrong was cured by treatment with cisplatin and went on to win an unprecedented seven Tour de France bicycle races.*

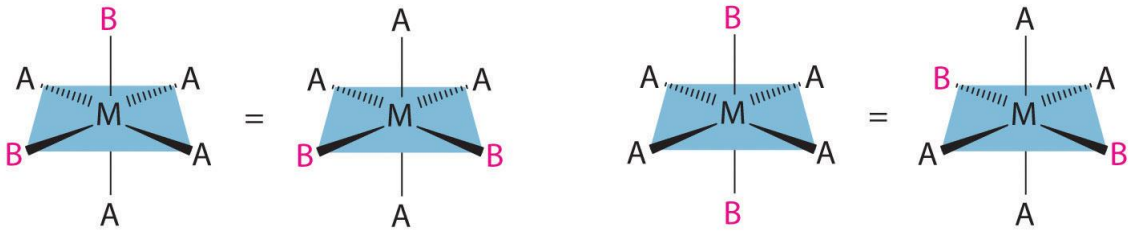
Square planar complexes that contain symmetrical bidentate ligands, such as $[Pt(en)_2]^{2+}$, have only one possible structure, in which curved lines linking the two N atoms indicate the ethylenediamine ligands:

$[Pt(en)_2]^{2+}$

Octahedral complexes also exhibit *cis* and *trans* isomers. Like square planar complexes, only one structure is possible for octahedral complexes in which only one ligand is different from the other five (MA_5B). Even though we usually draw an octahedron in a way that suggests that the four "in-plane" ligands are different from the two "axial" ligands, in fact all six vertices of an octahedron are equivalent. Consequently, no matter how we draw an MA_5B structure, it can be superimposed on any other representation simply by rotating the molecule in space. Two of the many possible orientations of an MA_5B structure are as follows:

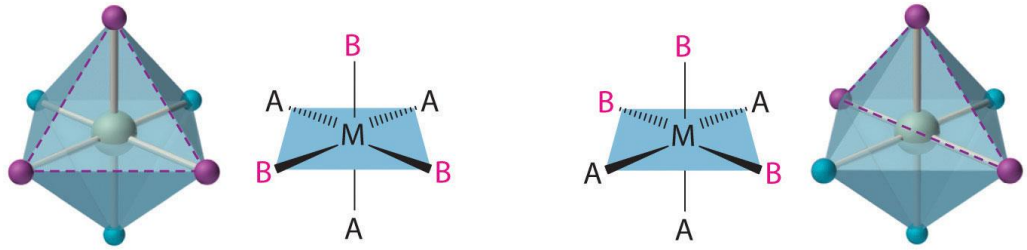
MA_5B octahedral complex

If two ligands in an octahedral complex are different from the other four, giving an MA_4B_2 complex, two isomers are possible. The two B ligands can be *cis* or *trans*. *Cis*- and *trans*-$[Co(NH_3)_4Cl_2]Cl$ are examples of this type of system:



MA_4B_2 octahedral complex, *cis* isomer **MA_4B_2 octahedral complex, *trans* isomer**

Replacing another A ligand by B gives an MA_3B_3 complex for which there are also two possible isomers. In one, the three ligands of each kind occupy opposite triangular faces of the octahedron; this is called the fac isomer (for facial). In the other, the three ligands of each kind lie on what would be the meridian if the complex were viewed as a sphere; this is called the mer isomer (for meridional):



MA_3B_3 octahedral complex, *fac* isomer **MA_3B_3 octahedral complex, *mer* isomer**

EXAMPLE 6

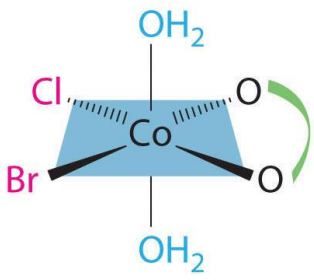
Draw all the possible geometrical isomers for the complex $[Co(H_2O)_2(ox)BrCl]^-$, where ox is $^-O_2CCO_2^-$, which stands for oxalate.

Given: formula of complex

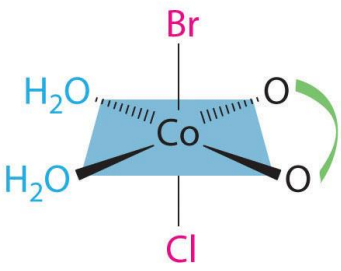
Asked for: structures of geometrical isomers

Solution:

This complex contains one bidentate ligand (oxalate), which can occupy only adjacent (cis) positions, and four monodentate ligands, two of which are identical (H_2O). The easiest way to attack the problem is to go through the various combinations of ligands systematically to determine which ligands can be *trans*. Thus either the water ligands can be *trans* to one another or the two halide ligands can be *trans* to one another, giving the two geometrical isomers shown here:

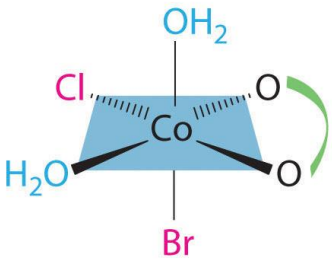


H_2O's *trans*

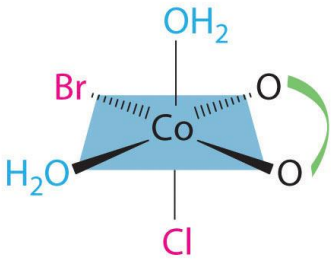


Br, Cl *trans*

In addition, two structures are possible in which one of the halides is *trans* to a water ligand. In the first, the chloride ligand is in the same plane as the oxalate ligand and*trans* to one of the oxalate oxygens. Exchanging the chloride and bromide ligands gives the other, in which the bromide ligand is in the same plane as the oxalate ligand and *trans* to one of the oxalate oxygens:



H_2O's *cis*; Br, Cl *cis*; Cl *trans* to O



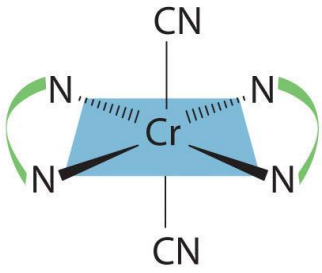
H_2O's *cis*; Br, Cl *cis*; Br *trans* to O

This complex can therefore exist as four different geometrical isomers.

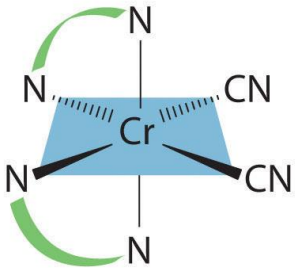
Exercise

Draw all the possible geometrical isomers for the complex $[Cr(en)_2(CN)_2]^+$.

Answer:



trans



cis

Two geometrical isomers are possible: *trans* and *cis*.

Summary

Transition metals form **metal complexes**, polyatomic species in which a metal ion is bound to one or more **ligands**, which are groups bound to a metal ion.**Complex ions** are electrically charged metal complexes, and a **coordination compound** contains one or more metal complexes. Metal complexes with low coordination numbers generally have only one or two possible structures, whereas those with coordination numbers greater than six can have several different structures. Coordination numbers of two and three are common for d^{10} metal ions. Tetrahedral and square planar complexes have a coordination number of four; trigonal bipyramidal and square pyramidal complexes have a coordination number of five; and octahedral complexes have a coordination number of six. At least three structures are known for a coordination number of seven, which is generally found for only large metal ions. Coordination numbers of eight and nine are also found for larger metal ions. The stability of metal complexes with first-row transition metals in a +2 oxidation state varies inversely with their ionic radius. Lewis bases can be **hard bases**, which have small, relatively nonpolarizable donor atoms, or**soft bases**, with larger, relatively polarizable donor atoms. **Hard acids** have the highest affinity for hard bases, and **soft acids** have the highest affinity for soft bases. Soft metals and soft bases form complexes that are more stable than would be predicted based on electrostatic arguments, which suggests that metal-to-ligand π bonding is important. Ligands that are strong bases form the most stable complexes with metal ions that are hard acids. Exceptionally stable complexes are formed by chelates, which are polyatomic ligands with two or more donor atoms; this enhanced stability is known as the chelate effect. Many metal complexes form**isomers**, which are two or more compounds with the same formula but different arrangements of atoms. **Structural isomers** differ in which atoms are bonded to one another, while **geometrical isomers** differ only in the arrangement of ligands around the metal ion. Ligands adjacent to one another are **cis**, while ligands across from one another are **trans**.

KEY TAKEAWAYS

- Coordination compounds are a major feature of the chemistry of over half the elements.
- Coordination compounds have important roles as industrial catalysts in controlling reactivity, and they are essential in biochemical processes.

CONCEPTUAL PROBLEMS

1. Give two reasons a metal can bind to only a finite number of ligands. Based on this reasoning, what do you predict is the maximum coordination number of Ti? of Ac?

2. Can a tetrahedral MA_2B_2 complex form *cis* and *trans* isomers? Explain your answer.
3. The group 12 elements are never found in their native (free) form but always in combination with one other element. What element is this? Why? Which of the group 12 elements has the highest affinity for the element you selected?

ANSWER

1.
2.
3. The group 12 metals are rather soft and prefer to bind to a soft anion such as sulfide rather than to a hard anion like oxide; hence they are usually found in nature as sulfide ores. Because it is the softest of these metals, mercury has the highest affinity for sulfide.

STRUCTURE AND REACTIVITY

1. Complexes of metals in the +6 oxidation state usually contain bonds to which two Lewis bases? Why are these bonds best described as covalent rather than ionic? Do Ca, Sr, and Ba also form covalent bonds with these two Lewis bases, or is their bonding best described as ionic?
2. Cr, Mn, Fe, Co, and Ni form stable CO complexes. In contrast, the earlier transition metals do not form similar stable complexes. Why?
3. The transition metals Cr through Ni form very stable cyanide complexes. Why are these complexes so much more stable than similar compounds formed from the early transition metals?
4. Of $Co(en)_3^{3+}$, CoF_6^{3-}, $Co(NH_3)_6^{3+}$, and $Co(dien)_2^{3+}$, which species do you expect to be the most stable? Why?
5. Of Ca^{2+}, Ti^{2+}, V^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}, which divalent metal ions forms the most stable complexes with ligands such as NH_3? Why?
6. Match each Lewis base with the metal ions with which it is most likely to form a stable complex:

Lewis bases: NH_3, F^-, RS^-, OH^-, and Cl^-

Metals: Sc^{3+}, Cu^+, W^{6+}, Mg^{2+}, V^{3+}, Fe^{3+}, Zr^{4+}, Co^{2+}, Ti^{4+}, Au^+, Al^{3+}, and Mn^{7+}

7. Of ReF_2, $ReCl_5$, MnF_6, Mn_2O_7, and ReO, which are not likely to exist?
8. Of WF_2, CrF_6, $MoBr_6$, WI_6, CrO_3, MoS_2, W_2S_3, and MoH, which are not likely to exist?

ANSWERS

1. Metals in the +6 oxidation state are stabilized by oxide (O^{2-}) and fluoride (F^-). The M–F and M–O bonds are polar covalent due to extreme polarization of the anions by the highly charged metal. Ca, Sr, and Ba can be oxidized only to the dications (M^{2+}), which form ionic oxides and fluorides.
2.
3. Cyanide is a relatively soft base, and the early transition-metal cations are harder acids than the later transition metals.
4.
5. The formation of complexes between NH_3 and a divalent cation is largely due to electrostatic interactions between the negative end of the ammonia dipole moment and the positively charged cation. Thus the smallest divalent cations (Ni^2+, Zn^{2+}, and Cu^{2+}) will form the most stable complexes with ammonia.
6.
7. Re^{2+} is a very soft cation, and F^- and O^{2-} are very hard bases, so ReO and ReF_2 are unlikely to exist. MnF_6 is also unlikely to exist: although fluoride should stabilize high oxidation states, in this case Mn^{6+} is probably too small to accommodate six F^- ions.
8.

[1] The inversion in the order at copper is due to the anomalous structure of copper(II) complexes, which will be discussed shortly.

23.5 Crystal Field Theory

LEARNING OBJECTIVE

1. To understand how crystal field theory explains the electronic structures and colors of metal complexes.

One of the most striking characteristics of transition-metal complexes is the wide range of colors they exhibit (Figure 23.4 "Aqueous Solutions of Vanadium Ions in Oxidation States of +2 to +5" and Figure 23.5 "Compounds of Manganese in Oxidation States +2 to +7"). In this section, we describe crystal field theory (CFT), a bonding model that explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. The central assumption of CFT is that metal–ligand interactions are purely electrostatic in nature. Even though this assumption is clearly not valid for many complexes, such as those that contain neutral

ligands like CO, CFT enables chemists to explain many of the properties of transition-metal complexes with a reasonable degree of accuracy.

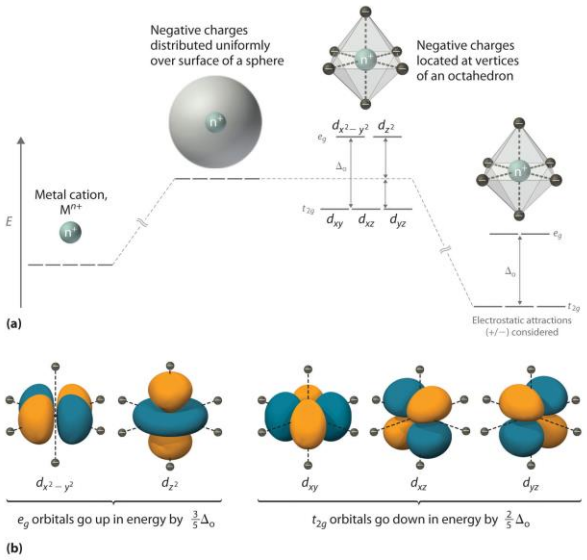
d-Orbital Splittings

CFT focuses on the interaction of the five $(n - 1)d$ orbitals with ligands arranged in a regular array around a transition-metal ion. We will focus on the application of CFT to octahedral complexes, which are by far the most common and the easiest to visualize. Other common structures, such as square planar complexes, can be treated as a distortion of the octahedral model. According to CFT, an octahedral metal complex forms because of the electrostatic interaction of a positively charged metal ion with six negatively charged ligands or with the negative ends of dipoles associated with the six ligands. In addition, the ligands interact with one other electrostatically. As you learned in our discussion of the valence-shell electron-pair repulsion (VSEPR) model inChapter 9 "Molecular Geometry and Covalent Bonding Models", the lowest-energy arrangement of six identical negative charges is an octahedron, which minimizes repulsive interactions between the ligands.

We begin by considering how the energies of the *d* orbitals of a transition-metal ion are affected by an octahedral arrangement of six negative charges. Recall from Chapter 6 "The Structure of Atoms" that the five *d* orbitals are initially degenerate (have the same energy). If we distribute six negative charges *uniformly* over the surface of a sphere, the*d* orbitals remain degenerate, but their energy will be higher due to repulsive electrostatic interactions between the spherical shell of negative charge and electrons in the *d* orbitals (part (a) in Figure 23.10 "An Octahedral Arrangement of Six Negative Charges around a Metal Ion Causes the Five "). Placing the six negative charges at the vertices of an octahedron does not change the average energy of the *d* orbitals, but it does remove their degeneracy: the five *d* orbitals split into two groups whose energies depend on their orientations. As shown in part (b) in Figure 23.10 "An Octahedral Arrangement of Six Negative Charges around a Metal Ion Causes the Five ", the $dz2\ and\ dx2 - y2\ orbitals$ point *directly* at the six negative charges located on the *x*, *y*, and *z* axes. Consequently, the energy of an electron in these two orbitals (collectively labeled the *eg*orbitals) will be greater than it will be for a spherical distribution of negative charge because of increased electrostatic repulsions. In contrast, the other three *d* orbitals (*dxy*, *dxz*, and *dyz*, collectively called the t_{2g} orbitals) are all oriented at a 45° angle to the coordinate axes, so they point *between* the six

negative charges. The energy of an electron in any of these three orbitals is lower than the energy for a spherical distribution of negative charge.

Figure 23.10 *An Octahedral Arrangement of Six Negative Charges around a Metal Ion Causes the Five d Orbitals to Split into Two Sets with Different Energies*



(a) Distributing a charge of –6 uniformly over a spherical surface surrounding a metal ion causes the energy of all five d orbitals to increase due to electrostatic repulsions, but the five d orbitals remain degenerate. Placing a charge of –1 at each vertex of an octahedron causes the d orbitals to split into two groups with different energies: the $dx2 - y2$ *and* $dz2$ *orbitals increase in energy, while the,* dxy*,* dxz*, and* dyz*orbitals decrease in energy. The average energy of the five d orbitals is the same as for a spherical distribution of a –6 charge, however. Attractive electrostatic interactions between the negatively charged ligands and the positively charged metal ion (far right) cause all five d orbitals to decrease in energy but does not affect the splittings of the orbitals. (b) The two* e_g *orbitals (left) point directly at the six negatively charged ligands, which increases their energy compared with a spherical distribution of negative charge. In contrast, the three* t_{2g} *orbitals (right) point between the negatively charged ligands, which decreases their energy compared with a spherical distribution of charge.*

The difference in energy between the two sets of *d* orbitals is called thecrystal field splitting energy (Δ_o), where the subscript *o* stands for octahedral. As we shall see, the magnitude of the splitting depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands.

(Crystal field splitting energy also applies to tetrahedral complexes: Δ_t.) It is important to note that the splitting of the *d* orbitals in a crystal field does *not* change the total energy of the five *d* orbitals: the two *eg* orbitals *increase* in energy by $0.6\Delta_o$, whereas the three t_{2g}orbitals decrease in energy by $0.4\Delta_o$. Thus the total change in energy is $2(0.6\Delta_o) + 3(-0.4\Delta_o) = 0$.

Note the Pattern

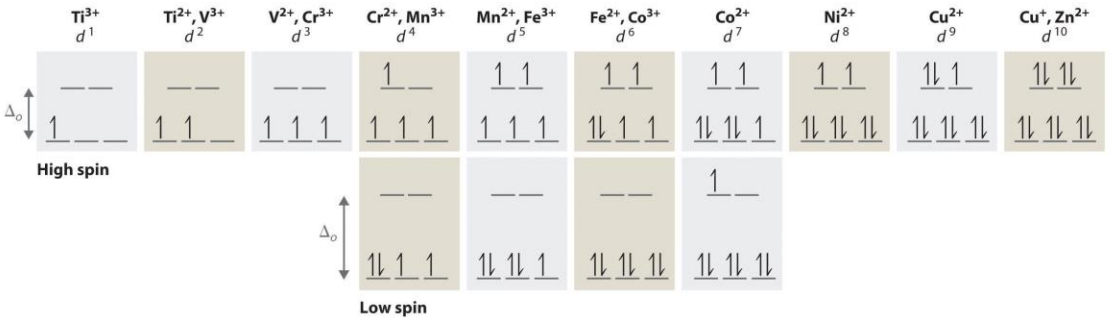
Crystal field splitting does not change the total energy of the *d* orbitals.

Thus far, we have considered only the effect of repulsive electrostatic interactions between electrons in the *d* orbitals and the six negatively charged ligands, which increases the total energy of the system and splits the *d* orbitals. Interactions between the positively charged metal ion and the ligands results in a net stabilization of the system, which decreases the energy of all five *d* orbitals without affecting their splitting (as shown at the far right in part (a) in Figure 23.10 "An Octahedral Arrangement of Six Negative Charges around a Metal Ion Causes the Five ").

Electronic Structures of Metal Complexes

We can use the *d*-orbital energy-level diagram in Figure 23.10 "An Octahedral Arrangement of Six Negative Charges around a Metal Ion Causes the Five " to predict electronic structures and some of the properties of transition-metal complexes. We start with the Ti^{3+} ion, which contains a single *d* electron, and proceed across the first row of the transition metals by adding a single electron at a time. We place additional electrons in the lowest-energy orbital available, while keeping their spins parallel as required by Hund's rule. As shown in Figure 23.11 "The Possible Electron Configurations for Octahedral ", for d^1–d^3 systems—such as $[Ti(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{3+}$, and $[Cr(H_2O)_6]^{3+}$, respectively—the electrons successively occupy the three degenerate t_{2g} orbitals with their spins parallel, giving one, two, and three unpaired electrons, respectively. We can summarize this for the complex $[Cr(H_2O)_6]^{3+}$, for example, by saying that the chromium ion has a d^3 electron configuration or, more succinctly, Cr^{3+} is a d^3 ion.

Figure 23.11 The Possible Electron Configurations for Octahedral d^n Transition-Metal Complexes ($n = 1–10$)



Two different configurations are possible for octahedral complexes of metals with d^4,d^5, d^6, and d^7 configurations; the magnitude of Δ_o determines which configuration is observed.

When we reach the d^4 configuration, there are two possible choices for the fourth electron: it can occupy either one of the empty e_g orbitals or one of the singly occupiedt_{2g} orbitals. Recall from Chapter 6 "The Structure of Atoms" that placing an electron in an already occupied orbital results in electrostatic repulsions that increase the energy of the system; this increase in energy is called the spin-pairing energy (P). If Δ_o is less than P, then the lowest-energy arrangement has the fourth electron in one of the emptye_g orbitals. Because this arrangement results in four unpaired electrons, it is called a*high-spin configuration*, and a complex with this electron configuration, such as the $[Cr(H_2O)_6]^{2+}$ ion, is called a *high-spin complex*. Conversely, if Δ_o is greater than P, then the lowest-energy arrangement has the fourth electron in one of the occupied t_{2g}orbitals. Because this arrangement results in only two unpaired electrons, it is called a*low-spin configuration*, and a complex with this electron configuration, such as the $[Mn(CN)_6]^{3-}$ ion, is called a *low-spin complex*. Similarly, metal ions with the d^5, d^6, or d^7 electron configurations can be either high spin or low spin, depending on the magnitude of Δ_o.

In contrast, only one arrangement of *d* electrons is possible for metal ions with d^8–d^{10}electron configurations. For example, the $[Ni(H_2O)_6]^{2+}$ ion is d^8 with two unpaired electrons, the $[Cu(H_2O)_6]^{2+}$ ion is d^9 with one unpaired electron, and the $[Zn(H_2O)_6]^{2+}$ ion is d^{10} with no unpaired electrons.

Note the Pattern

If Δ_o is less than the spin-pairing energy, a high-spin configuration results. Conversely, if Δ_o is greater, a low-spin configuration forms.

Factors That Affect the Magnitude of Δ_o

The magnitude of Δ_o dictates whether a complex with four, five, six, or seven *d*electrons is high spin or low spin, which affects its magnetic properties, structure, and reactivity. Large values of Δ_o (i.e., $\Delta_o > P$) yield a low-spin complex, whereas small values of Δ_o (i.e., $\Delta_o < P$) produce a high-spin complex. As we noted, the

magnitude of Δ_o depends on three factors: the charge on the metal ion, the principal quantum number of the metal (and thus its location in the periodic table), and the nature of the ligand. Values of Δ_o for some representative transition-metal complexes are given inTable 23.10 "Crystal Field Splitting Energies for Some Octahedral (Δ".

Table 23.10 Crystal Field Splitting Energies for Some Octahedral (Δ_o)* and Tetrahedral (Δ_t) Transition-Metal Complexes

Octahedral Complexes	Δ_o(cm^{-1})	Octahedral Complexes	Δ_o(cm^{-1})	Tetrahedral Complexes	Δ_t(cm^{-1})
$[Ti(H_2O)_6]^{3+}$	20,300	$[Fe(CN)_6]^{4-}$	32,800	VCl_4	9010
$[V(H_2O)_6]^{2+}$	12,600	$[Fe(CN)_6]^{3-}$	35,000	$[CoCl_4]^{2-}$	3300
$[V(H_2O)_6]^{3+}$	18,900	$[CoF_6]^{3-}$	13,000	$[CoBr_4]^{2-}$	2900
$[CrCl_6]^{3-}$	13,000	$[Co(H_2O)_6]^{2+}$	9300	$[CoI_4]^{2-}$	2700
$[Cr(H_2O)_6]^{2+}$	13,900	$[Co(H_2O)_6]^{3+}$	27,000		
$[Cr(H_2O)_6]^{3+}$	17,400	$[Co(NH_3)_6]^{3+}$	22,900		
$[Cr(NH_3)_6]^{3+}$	21,500	$[Co(CN)_6]^{3-}$	34,800		
$[Cr(CN)_6]^{3-}$	26,600	$[Ni(H_2O)_6]^{2+}$	8500		
$Cr(CO)_6$	34,150	$[Ni(NH_3)_6]^{2+}$	10,800		
$[MnCl_6]^{4-}$	7500	$[RhCl_6]^{3-}$	20,400		
$[Mn(H_2O)_6]^{2+}$	8500	$[Rh(H_2O)_6]^{3+}$	27,000		
$[MnCl_6]^{3-}$	20,000	$[Rh(NH_3)_6]^{3+}$	34,000		
$[Mn(H_2O)_6]^{3+}$	21,000	$[Rh(CN)_6]^{3-}$	45,500		
$[Fe(H_2O)_6]^{2+}$	10,400	$[IrCl_6]^{3-}$	25,000		
$[Fe(H_2O)_6]^{3+}$	14,300	$[Ir(NH_3)_6]^{3+}$	41,000		

***Energies obtained by spectroscopic measurements are often given in units of*wave numbers* (cm^{-1}); the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters: 1 cm^{-1} = 11.96 J/mol.**

Source of data: Duward F. Shriver, Peter W. Atkins, and Cooper H. Langford,*Inorganic Chemistry*, 2nd ed. (New York: W. H. Freeman and Company, 1994).

Charge on the Metal Ion

Increasing the charge on a metal ion has two effects: the radius of the metal ion decreases, and negatively charged ligands are more strongly attracted to it. Both factors decrease the metal–ligand distance, which

in turn causes the negatively charged ligands to interact more strongly with the *d* orbitals. Consequently, the magnitude of $\Delta_o$increases as the charge on the metal ion increases. Typically, Δ_o for a tripositive ion is about 50% greater than for the dipositive ion of the same metal; for example, for $[V(H_2O)_6]^{2+}$, Δ_o = 11,800 cm^{-1}; for $[V(H_2O)_6]^{3+}$, Δ_o = 17,850 cm^{-1}.

Principal Quantum Number of the Metal

For a series of complexes of metals from the same group in the periodic table with the same charge and the same ligands, the magnitude of Δ_o increases with increasing principal quantum number: Δ_o (3*d*) < Δ_o (4*d*) < Δ_o (5*d*). The data for hexaammine complexes of the trivalent group 9 metals illustrate this point:

$$[Co(NH3)6]3+[Rh(NH3)6]3+[Ir(NH3)6]3+DoDoDo=22,900\ cm-1$$
$$=34,100\ cm-1=40,000\ cm-1$$

The increase in Δ_o with increasing principal quantum number is due to the larger radius of valence orbitals down a column. In addition, repulsive ligand–ligand interactions are most important for smaller metal ions. Relatively speaking, this results in shorter M–L distances and stronger *d* orbital–ligand interactions.

The Nature of the Ligands

Experimentally, it is found that the Δ_o observed for a series of complexes of the same metal ion depends strongly on the nature of the ligands. For a series of chemically similar ligands, the magnitude of Δ_o decreases as the size of the donor atom increases. For example, Δ_o values for halide complexes generally decrease in the order $F^- > Cl^- > Br^- > I^-$ because smaller, more localized charges, such as we see for F^-, interact more strongly with the *d* orbitals of the metal ion. In addition, a small neutral ligand with a highly localized lone pair, such as NH_3, results in significantly larger Δ_o values than might be expected. Because the lone pair points directly at the metal ion, the electron density along the M–L axis is greater than for a spherical anion such as F^-. The experimentally observed order of the crystal field splitting energies produced by different ligands is called the spectrochemical series, shown here in order of decreasing Δ_o:

$$field\ ligands > OH- > F > acetate- >$$
$$Cl- > Br- > I- > weak- field\ ligands$$
$$field\ ligands > OH- > F > acetate- > Cl- > Br- > I- > weak- field\ ligands$$

The values of Δ_o listed in Table 23.10 "Crystal Field Splitting Energies for Some Octahedral (Δ" illustrate the effects of the charge on the metal ion, the principal quantum number of the metal, and the nature of the ligand.

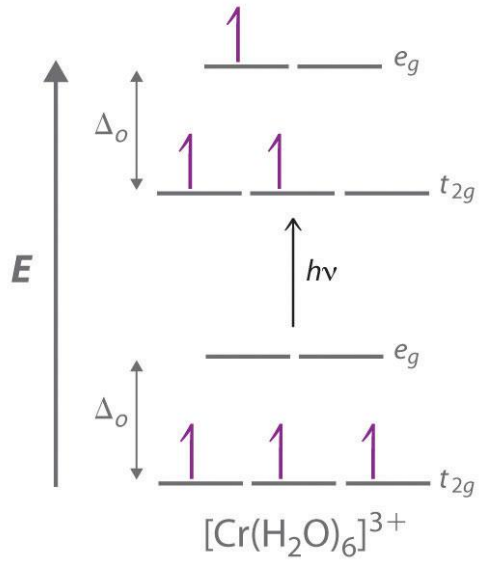
Note the Pattern

The largest Δ_os are found in complexes of metal ions from the third row of the transition metals with charges of at least +3 and ligands with localized lone pairs of electrons.

Colors of Transition-Metal Complexes

The striking colors exhibited by transition-metal complexes are caused by excitation of an electron from a lower-energy *d* orbital to a higher-energy *d* orbital, which is called a*d–d transition* (Figure 23.12 "A "). For a photon to effect such a transition, its energy must be equal to the difference in energy between the two *d* orbitals, which depends on the magnitude of Δ_o.

Figure 23.12 A d–dTransition



In a d–d transition, an electron in one of the t_{2g}orbitals of an octahedral complex such as the $[Cr(H_2O)_6]^{3+}$ ion absorbs a photon of light with energy equal to Δ_o, which causes the electron to move to an empty or singly occupied e_g orbital.

Recall from Chapter 6 "The Structure of Atoms" that the color we observe when we look at an object or a compound is due to light that is transmitted or reflected, not light that is absorbed, and that reflected or transmitted light is complementary in color to the light that is absorbed. Thus a green compound absorbs light in the red portion of the visible spectrum and vice versa, as indicated by the color wheel in End-of-Chapter Application Problem 6 in Chapter 6 "The Structure of Atoms". Because the energy of a photon of light is inversely proportional to its wavelength, the color of a complex depends on the magnitude of Δ_o, which depends on the structure of the complex. For example, the complex $[Cr(NH_3)_6]^{3+}$ has strong-field

ligands and a relatively large Δ_o. Consequently, it absorbs relatively high-energy photons, corresponding to blue-violet light, which gives it a yellow color. A related complex with weak-field ligands, the $[Cr(H_2O)_6]^{3+}$ ion, absorbs lower-energy photons corresponding to the yellow-green portion of the visible spectrum, giving it a deep violet color.

We can now understand why emeralds and rubies have such different colors, even though both contain Cr^{3+} in an octahedral environment provided by six oxide ions. Although the chemical identity of the six ligands is the same in both cases, the Cr–O distances are different because the compositions of the host lattices are different (Al_2O_3 in rubies and $Be_3Al_2Si_6O_{18}$ in emeralds). In ruby, the Cr–O distances are relatively short because of the constraints of the host lattice, which increases the *d* orbital–ligand interactions and makes Δ_o relatively large. Consequently, rubies absorb green light and the transmitted or reflected light is red, which gives the gem its characteristic color. In emerald, the Cr–O distances are longer due to relatively large $[Si_6O_{18}]^{12-}$ silicate rings; this results in decreased *d* orbital–ligand interactions and a smaller Δ_o. Consequently, emeralds absorb light of a longer wavelength (red), which gives the gem its characteristic green color. It is clear that the environment of the transition-metal ion, which is determined by the host lattice, dramatically affects the spectroscopic properties of a metal ion.

Crystal Field Stabilization Energies

Recall from Chapter 9 "Molecular Geometry and Covalent Bonding Models" that stable molecules contain more electrons in the lower-energy (bonding) molecular orbitals in a molecular orbital diagram than in the higher-energy (antibonding) molecular orbitals. If the lower-energy set of *d* orbitals (the t_2g orbitals) is selectively populated by electrons, then the stability of the complex increases. For example, the single *d* electron in a d^1 complex such as $[Ti(H_2O)_6]^{3+}$ is located in one of the t_2g orbitals. *Consequently, this complex will be more stable than expected on purely electrostatic grounds by* $0.4\Delta_o$. The additional stabilization of a metal complex by selective population of the lower-energy *d* orbitals is called itscrystal field stabilization energy (CFSE). The CFSE of a complex can be calculated by multiplying the number of electrons in t_2g orbitals by the energy of those orbitals ($-0.4\Delta_o$), multiplying the number of electrons in eg orbitals by the energy of those orbitals ($+0.6\Delta_o$), and summing the two. Table 23.11 "CFSEs for Octahedral Complexes with Different Electron Configurations (in Units of Δ" gives CFSE values for octahedral complexes with different *d* electron configurations. The CFSE is highest for low-

spin d^6 complexes, which accounts in part for the extraordinarily large number of Co(III) complexes known. The other low-spin configurations also have high CFSEs, as does the d^3 configuration.

Table 23.11 CFSEs for Octahedral Complexes with Different Electron Configurations (in Units of Δ_o)

	High Spin		CFSE (Δ_o)	Low Spin		CFSE (Δ_o)
d^0			0			
d^1	↑		0.4			
d^2	↑ ↑		0.8			
d^3	↑ ↑ ↑		1.2			
d^4	↑ ↑ ↑	↑	0.6	↑↓ ↑ ↑		1.6
d^5	↑ ↑ ↑	↑ ↑	0.0	↑↓ ↑↓ ↑		2.0
d^6	↑↓ ↑ ↑	↑ ↑	0.4	↑↓ ↑↓ ↑↓		2.4
d^7	↑↓ ↑↓ ↑	↑ ↑	0.8	↑↓ ↑↓ ↑↓	↑	1.8
d^8	↑↓ ↑↓ ↑↓	↑ ↑	1.2			
d^9	↑↓ ↑↓ ↑↓	↑↓ ↑	0.6			
d^{10}	↑↓ ↑↓ ↑↓	↑↓ ↑↓	0.0			

CFSEs are important for two reasons. First, the existence of CFSE nicely accounts for the difference between experimentally measured values for bond energies in metal complexes and values calculated based solely on electrostatic interactions. Second, CFSEs represent relatively large amounts of energy (up to several hundred kilojoules per mole), which has important chemical consequences.

Note the Pattern

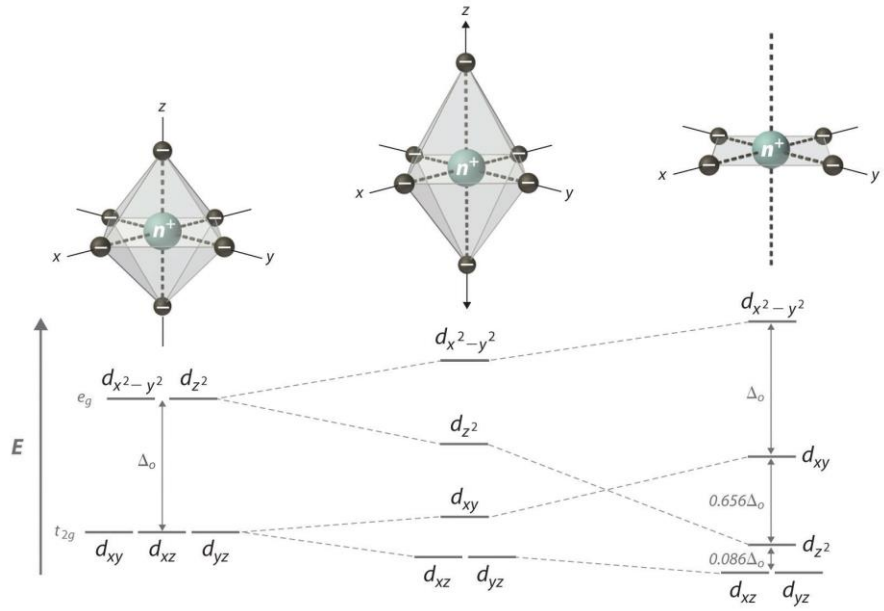
Octahedral d^3 and d^8 complexes and low-spin d^6, d^5, d^7, and d^4 complexes exhibit large CFSEs.

Tetragonal and Square Planar Complexes

If two *trans* ligands in an octahedral complex are either chemically different from the other four, as in the *trans*-$[Co(NH_3)_4Cl_2]^+$ ion, or at a different distance from the metal than the other four, the result is a tetragonally distorted octahedral complex. The electronic structures of such complexes are best viewed as the result of distorting an octahedral complex. Consider, for example, an octahedral complex such as $[Co(NH_3)_6]^{3+}$ and then slowly remove two *trans* NH_3 molecules by moving them away from the metal along the $\pm z$ axes, as shown in the top half of Figure 23.13. As the two axial Co–N distances increase simultaneously, the *d* orbitals that interact most strongly with the two axial ligands will *decrease* in energy due to a decrease in electrostatic repulsions between electrons in these orbitals and the negative

ends of the ligand dipoles. The affected *d* orbitals are those with a component along the ±*z* axes—namely, $dz2$, *dxz*, and *dyz*. They will not be affected equally, however. Because the $dz2$ orbital points directly at the two ligands being removed, its energy will decrease much more rapidly than the energy of the other two, as shown in the bottom half of Figure 23.13. In addition, the positive charge on the metal will increase somewhat as the axial ligands are removed, causing the four remaining in-plane ligands to be more strongly attracted to the metal. This will increase their interactions with the other two *d* orbitals and increase their energy. Again, the two *d* orbitals will not be affected equally. Because the $dx2 - y2\ orbital$ points directly at the four in-plane ligands, its energy will increase more rapidly than the energy of the *dxy* orbital, which points between the in-plane ligands. If we remove the two axial ligands to an infinite distance, we obtain a square planar complex. The energies of the $dz2$ and *dxy* orbitals actually cross as the axial ligands are removed, and the largest orbital spliting in a square planar complex is identical in magnitude to Δ_o.

Figure 23.13 d-Orbital Splittings for Tetragonal and Square Planar Complexes



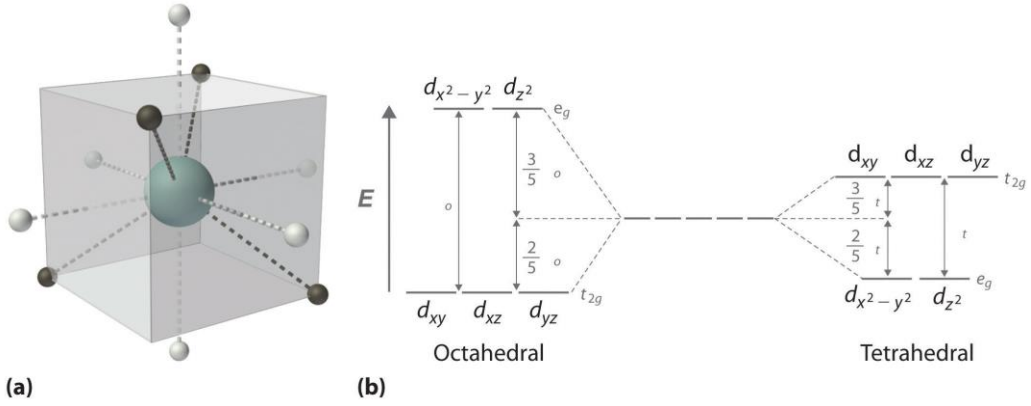
Moving the two axial ligands away from the metal ion along the z axis initially gives an elongated octahedral complex (center) and eventually produces a square planar complex (right). As shown below the structures, an axial elongation causes $the\ dz2\ dxzand$ *dyz orbitals to decrease in energy and* $the\ dx2 - y2\ and$ *dxy orbitals to increase in energy. As explained in the text, the change in*

energy is not the same for all five dorbitals. Removing the two axial ligands completely causes the energy of the dz2orbital to decrease so much that the order of the dz2 and dxy orbitals is reversed.

Tetrahedral Complexes

In a tetrahedral arrangement of four ligands around a metal ion, none of the ligands lies on any of the three coordinate axes (part (a) in Figure 23.14); consequently, none of the five *d* orbitals points directly at the ligands. Nonetheless, the *dxy*, *dxz*, and *dyz*orbitals interact more strongly with the ligands than do *dx2 - y2 and dz2 again* resulting in a splitting of the five *d* orbitals into two sets. The splitting of the energies of the orbitals in a tetrahedral complex (Δ_t) is much smaller than that for Δ_o, however, for two reasons. First, the *d* orbitals interact less strongly with the ligands in a tetrahedral arrangement. Second, there are only four negative charges rather than six, which decreases the electrostatic interactions by one-third if all other factors are equal. It can be shown that, for complexes of the same metal ion with the same charge, the same ligands, and the same M–L distance, $\Delta t = 49\Delta o$. *The* relationship between the splitting of the five *d* orbitals in octahedral and tetrahedral crystal fields imposed by the same ligands is shown schematically in part (b) in Figure 23.14.

Figure 23.14 d-Orbital Splittings for a Tetrahedral Complex



(a) In a tetrahedral complex, none of the five d orbitals points directly at or between the ligands. (b) Because the dxy, dxz, and dyz orbitals (the t_{2g} orbitals) interact more strongly with the ligands than do the dx2 - y2 and dz2 orbitals (the e_g orbitals), the order of orbital energies in a tetrahedral complex is the opposite of the order in an octahedral complex.

Note the Pattern

$\Delta_t < \Delta_o$ because of weaker *d*-orbital–ligand interactions and decreased electrostatic interactions.

Because Δ_o is so large for the second- and third-row transition metals, *all* four-coordinate complexes of these metals are square planar due to the much higher CFSE for square planar versus tetrahedral structures. The only exception is for d^{10} metal ions such as Cd^{2+}, which have zero CFSE and are therefore tetrahedral as predicted by the VSEPR model. Four-coordinate complexes of the first-row transition metals can be either square planar or tetrahedral. The former is favored by strong-field ligands, whereas the latter is favored by weak-field ligands. For example, the $[Ni(CN)_4]^{2-}$ ion is square planar, while the $[NiCl_4]^{2-}$ ion is tetrahedral.

EXAMPLE 7

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

a. $[CoF_6]^{3-}$

b. $[Rh(CO)_2Cl_2]^-$

Given: complexes

Asked for: structure, high spin versus low spin, and the number of unpaired electrons

Strategy:

A From the number of ligands, determine the coordination number of the compound.

B Classify the ligands as either strong field or weak field and determine the electron configuration of the metal ion.

C Predict the relative magnitude of Δ_o and decide whether the compound is high spin or low spin.

D Place the appropriate number of electrons in the *d* orbitals and determine the number of unpaired electrons.

Solution:

a. **A** With six ligands, we expect this complex to be octahedral.

B The fluoride ion is a small anion with a concentrated negative charge, but compared with ligands with localized lone pairs of electrons, it is weak field. The charge on the metal ion is +3, giving a d^6 electron configuration.

C Because of the weak-field ligands, we expect a relatively small Δ_o, making the compound high spin.

D In a high-spin octahedral d^6 complex, the first five electrons are placed individually in each of the *d* orbitals with their spins parallel, and the sixth electron is paired in one of the t_{2g} orbitals, giving four unpaired electrons.

b. **A** This complex has four ligands, so it is either square planar or tetrahedral.

B C Because rhodium is a second-row transition metal ion with a d^8electron configuration and CO is a strong-field ligand, the complex is likely to be square planar with a large Δ_o, making it low spin. Because the strongest *d*-orbital interactions are along the *x* and *y* axes, the orbital energies increase in the order $dz2dyz$, and *dxz* (these are degenerate); *dxy*; and $dx2 - y2.$

D The eight electrons occupy the first four of these orbitals, leaving $the\ dx2 - y2.\ orbital$ empty. Thus there are no unpaired electrons.

Exercise

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

a. $[Mn(H_2O)_6]^{2+}$

b. $[PtCl_4]^{2-}$

Answer:

a. octahedral; high spin; five

b. square planar; low spin; no unpaired electrons

Consequences of *d*-Orbital Splitting

The splitting of the *d* orbitals because of their interaction with the ligands in a complex has important consequences for the chemistry of transition-metal complexes; they can be divided into structural effects and thermodynamic effects. Although the two kinds of effects are interrelated, we will consider them separately.

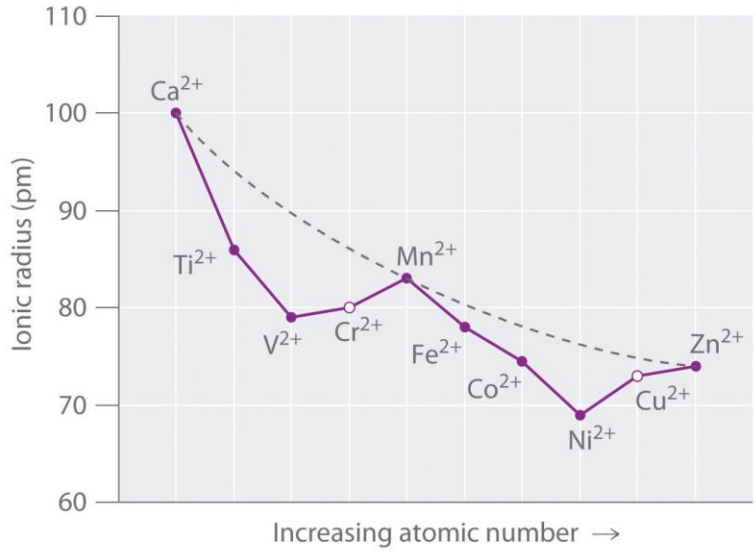
Structural Effects

There are two major kinds of structural effects: effects on the ionic radius of metal ions with regular octahedral or tetrahedral geometries, and structural distortions that are observed for specific electron configurations.

Ionic Radii

Figure 23.15 "The Effect of " is a plot of the ionic radii of the divalent fourth-period metal ions versus atomic number. Only Ca^{2+}(d^0), Mn^{2+} (high-spin d^5), and Zn^{2+} (d^{10}) fall on the smooth curve calculated based on the effective nuclear charge (Z_{eff}), which assumes that the distribution of *d* electrons is spherically symmetrical. *All the other divalent ions fall below this curve because they have asymmetrical distributions of d electrons*. (The points shown for Cr^{2+} and Cu^{2+} are only estimated values; as you will learn shortly, these two ions do not form any truly octahedral complexes.) To see why an asymmetrical distribution of *d* electrons makes a metal ion smaller than expected, consider the Ti^{2+} ion, which has a d^2 configuration with both electrons in the t_{2g}orbitals. Because the t_{2g} orbitals are directed *between the ligands*, the two *d* electrons are unable to shield the ligands from the nuclear charge. Consequently, the ligands experience a higher effective nuclear charge than expected, the metal–ligand distance is unusually short, and the ionic radius is smaller than expected. If instead the two electrons were distributed uniformly over all five *d* orbitals, they would be much more effective at screening the ligands from the nuclear charge, making the metal–ligand distances longer and giving a larger ionic radius.

Figure 23.15 *The Effect of d-Orbital Splittings on the Radii of the Divalent Ions of the Fourth-Period Metals*



Because these radii are based on the structures of octahedral complexes and Cr^{2+} and Cu^{2+} do not form truly octahedral complexes, the points for these ions are shown as open circles. The dashed

line represents the behavior predicted based on the effects of screening and variation in effective nuclear charge (Z_{eff}), assuming a spherical distribution of the 3d electrons.

A similar effect is observed for the V^{2+} ion, which has a d^3 configuration. Because the three electrons in the t_{2g} orbitals provide essentially no shielding of the ligands from the metal, the ligands experience the full increase of +1 in nuclear charge that occurs in going from Ti^{2+} to V^{2+}. Consequently, the observed ionic radius of the V^{2+} ion is significantly smaller than that of the Ti^{2+} ion.

Skipping the Cr^{2+} ion for the moment, we next consider the d^5 Mn^{2+} ion. Because the nuclear charge increases by +2 from V^{2+} to Mn^{2+}, we might expect Mn^{2+} to be smaller than V^{2+}. The two electrons that are also added from V^{2+} to Mn^{2+} occupy the $e_g$orbitals, however, which point directly at the six ligands. Because these electrons are localized directly between the metal ion and the ligands, they are effective at screening the ligands from the increased nuclear charge. As a result, the ionic radius actually*increases* significantly as we go from V^{2+} to Mn^{2+}, despite the higher nuclear charge of the latter.

Exactly the same effects are seen in the second half of the first-row transition metals. In the Fe^{2+}, Co^{2+}, and Ni^{2+} ions, the extra electrons are added successively to the t_{2g}orbitals, resulting in poor shielding of the ligands from the nuclear charge and abnormally small ionic radii. Skipping over Cu^{2+}, we again see that adding the last two electrons causes a significant increase in the ionic radius of Zn^{2+}, despite its higher nuclear charge.

The Jahn–Teller Effect

Because simple octahedral complexes are not known for the Cr^{2+} and Cu^{2+} ions, only estimated values for their radii are shown in Figure 23.15 "The Effect of ". We see inFigure 23.11 "The Possible Electron Configurations for Octahedral " that both the $Cr^{2+}$and Cu^{2+} ions have electron configurations with an odd number of electrons in the $e_g$orbitals. Because the single electron (in the case of Cr^{2+}) or the third electron (in the case of Cu^{2+}) can occupy either one of two degenerate e_g orbitals, they have what is called a *degenerate ground state*. The Jahn–Teller theorem states that such non-linear systems are not stable; they will undergo a distortion that makes the complex less symmetrical and splits the degenerate states, which decreases the energy of the system. The distortion and resulting decrease in energy are collectively referred to as the*Jahn–Teller effect*. Neither the nature of the distortion nor its magnitude is specified, and in fact, they are difficult to predict. In principle, Jahn–Teller distortions are possible for many

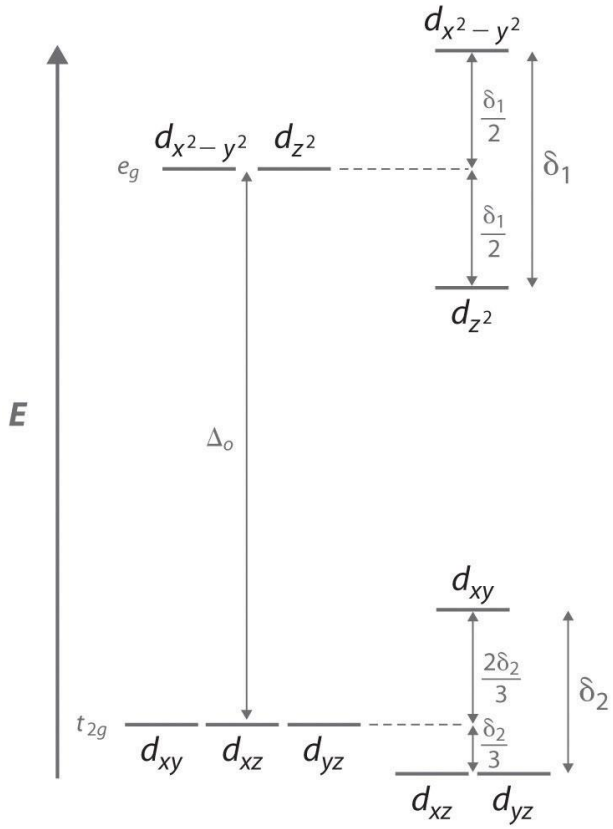
transition-metal ions; in practice, however, they are observed only for systems with an odd number of electrons in the *eg* orbitals, such as the Cr^{2+} and Cu^{2+} ions.

To see how a geometrical distortion can decrease the energy of such a system, consider an octahedral Cu^{2+} complex, the $[Cu(H_2O)_6]^{2+}$ ion, which has been elongated along the *z* axis. As indicated in Figure 23.16 "The Jahn–Teller Effect", this kind of distortion splits both *the eg and t_2g sets of orbitals. Because the axial ligands interact most strongly with the dz2 orbital*, the splitting of the *eg* set (δ_1) is significantly larger than the splitting of the t_2g set (δ_2), but both δ_1 and δ_2 are much, much smaller than the Δ_o. This splitting does not change the center of gravity of the energy within each set, so a Jahn–Teller distortion results in no net change in energy for a filled or half-filled set of orbitals. If, however, the *eg* set contains one (as in the d^4 ions, Cr^{2+} and Mn^{3+}) or three (as in the d^9 ion, Cu^{2+}) electrons, the distortion decreases the energy of the system. For Cu^{2+}, for example, the change in energy after distortion is $2(-\delta_1/2) + 1(\delta_1/2) = -\delta_1/2$. For Cu^{2+} complexes, the observed distortion is *always* an elongation along the *z* axis by as much as 50 pm; in fact, many Cu^{2+} complexes are so distorted that they are effectively square planar. In contrast, the distortion observed for most Cr^{2+} complexes is a *compression* along the *z* axis. In both cases, however, the net effect is the same: the distorted system is more stable than the undistorted system.

Note the Pattern

Jahn–Teller distortions are most important for d^9 and high-spin d^4 complexes; the distorted system is more stable than the undistorted one.

Figure 23.16 The Jahn–Teller Effect



Increasing the axial metal–ligand distances in an octahedral d^9 complex is an example of a Jahn–Teller distortion, which causes the degenerate pair of e_g orbitals to split in energy by an amount δ_1; δ_1 and δ_2 are much smaller than Δ_o. As a result, the distorted system is more stable (lower in energy) than the undistorted complex by $\delta_1/2$.

Thermodynamic Effects

As we previously noted, CFSEs can be as large as several hundred kilojoules per mole, which is the same magnitude as the strength of many chemical bonds or the energy change in most chemical reactions. Consequently, CFSEs are important factors in determining the magnitude of hydration energies, lattice energies, and other thermodynamic properties of the transition metals.

Hydration Energies

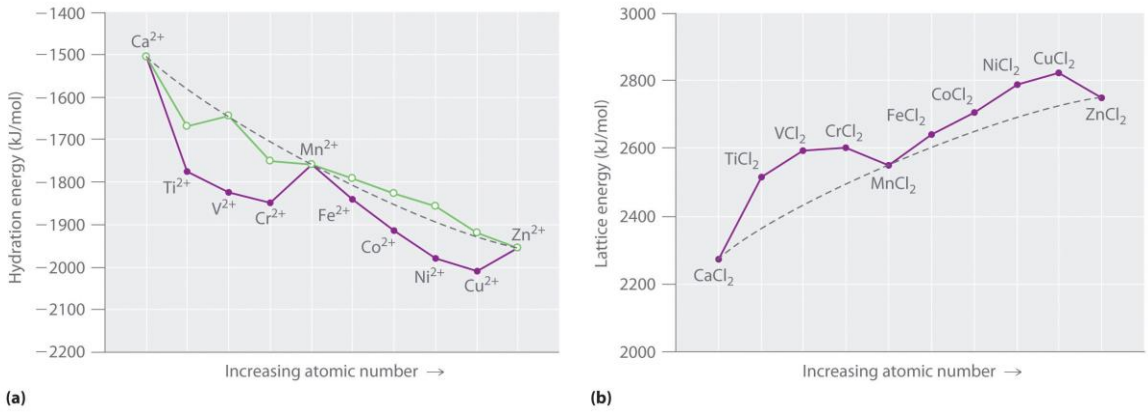
The hydration energy of a metal ion is defined as the change in enthalpy for the following reaction:

Equation 23.12

$$M^{2+}(g) + H_2O(l) \rightarrow M^{2+}(aq)$$

Although hydration energies cannot be measured directly, they can be calculated from experimentally measured quantities using thermochemical cycles. As shown in part (a) in Figure 23.17 "Thermochemical Effects of ", a plot of the hydration energies of the fourth-period metal dications versus atomic number gives a curve with two valleys. Note the relationship between the plot in part (a) in Figure 23.17 "Thermochemical Effects of " and the plot of ionic radii in Figure 23.15 "The Effect of ": the overall shapes are essentially identical, and only the three cations with spherically symmetrical distributions of *d* electrons (Ca^{2+}, Mn^{2+}, and Zn^{2+}) lie on the dashed lines. In part (a) in Figure 23.17 "Thermochemical Effects of ", the dashed line corresponds to hydration energies calculated based solely on electrostatic interactions. Subtracting the CFSE values for the $[M(H_2O)_6]^{2+}$ ions from the experimentally determined hydration energies gives the points shown as open circles, which lie very near the calculated curve. Thus CFSEs are primarily responsible for the differences between the measured and calculated values of hydration energies.

Figure 23.17 *Thermochemical Effects of d-Orbital Splittings*



(a) A plot of the hydration energies of the divalent fourth-period metal ions versus atomic number (solid circles) shows large deviations from the smooth curve calculated, assuming a spherical distribution of d electrons (dashed line). Correcting for CFSE gives the points shown as open circles, which, except for Ti^{2+} and Cr^{2+}, are close to the calculated values. The apparent deviations for these ions are caused by the fact that solutions of the Ti^{2+} ion in water are not stable, and Cr^{2+} does not form truly octahedral complexes. (b) A plot of the lattice energies for the fourth-period metal dichlorides versus atomic number shows similar deviations from the smooth curve calculated, assuming a spherical distribution of delectrons (dashed lines), again illustrating the importance of CFSEs.

Lattice Energies

Values of the lattice energies for the fourth-period metal dichlorides are plotted versus atomic number in part (b) in Figure 23.17 "Thermochemical Effects of ". Recall that the lattice energy is defined as the negative of the enthalpy change for the following reaction. Like hydration energies, lattice energies are determined indirectly by using a thermochemical cycle:

Equation 23.13

$$M^{2+}(g) + 2Cl^{-}(g) \rightarrow MCl_2(s)$$

The shape of the lattice-energy curve is essentially the mirror image of the hydration-energy curve in part (a) in Figure 23.19 "Ferritin, an Iron Storage Protein", with only Ca^{2+}, Mn^{2+}, and Zn^{2+} lying on the smooth curve. It is not surprising that the explanation for the deviations from the curve is exactly the same as for the hydration energy data: all the transition-metal dichlorides, except $MnCl_2$ and $ZnCl_2$, are more stable than expected due to CFSE.

Summary

Crystal field theory (CFT) is a bonding model that explains many properties of transition metals that cannot be explained using valence bond theory. In CFT, complex formation is assumed to be due to electrostatic interactions between a central metal ion and a set of negatively charged ligands or ligand dipoles arranged around the metal ion. Depending on the arrangement of the ligands, the*d* orbitals split into sets of orbitals with different energies. The difference between the energy levels in an octahedral complex is called the **crystal field splitting energy (Δ_o)**, whose magnitude depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. The **spin-pairing energy (P)** is the increase in energy that occurs when an electron is added to an already occupied orbital. A high-spin configuration occurs when the Δ_o is less than P, which produces complexes with the maximum number of unpaired electrons possible. Conversely, a low-spin configuration occurs when the Δ_o is greater than P, which produces complexes with the minimum number of unpaired electrons possible. Strong-field ligands interact strongly with the *d*orbitals of the metal ions and give a large Δ_o, whereas weak-field ligands interact more weakly and give a smaller Δ_o. The colors of transition-metal complexes depend on the environment of the metal ion and can be explained by CFT. Distorting an octahedral complex by moving opposite ligands away from the metal produces a tetragonal or square planar arrangement, in which interactions with equatorial ligands become stronger. Because none of the *d* orbitals points directly at the ligands in a tetrahedral complex, these complexes have smaller values of the crystal field splitting energy Δ_t. The **crystal field stabilization energy (CFSE)**is the additional

stabilization of a complex due to placing electrons in the lower-energy set of *d* orbitals. CFSE explains the unusual curves seen in plots of ionic radii, hydration energies, and lattice energies versus atomic number. The **Jahn–Teller theorem** states that a non-linear molecule with a spatially degenerate electronic ground state will undergo a geometrical distortion to remove the degeneracy and lower the overall energy of the system.

KEY TAKEAWAY

- Crystal field theory, which assumes that metal–ligand interactions are only electrostatic in nature, explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity.

CONCEPTUAL PROBLEMS

1. Describe crystal field theory in terms of its

a. assumptions regarding metal–ligand interactions.

b. weaknesses and strengths compared with valence bond theory.

2. In CFT, what causes degenerate sets of *d* orbitals to split into different energy levels? What is this splitting called? On what does the magnitude of the splitting depend?
3. Will the value of Δ_o increase or decrease if I^- ligands are replaced by NO_2^- ligands? Why?
4. For an octahedral complex of a metal ion with a d^6 configuration, what factors favor a high-spin configuration versus a low-spin configuration?
5. How can CFT explain the color of a transition-metal complex?

STRUCTURE AND REACTIVITY

1. Do strong-field ligands favor a tetrahedral or a square planar structure? Why?
2. For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

a. $[TiCl_6]^{3-}$

b. $[CoCl_4]^{2-}$

3. For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

a. $[Cu(NH_3)_4]^{2+}$

b. $[Ni(CN)_4]^{2-}$

4. The ionic radii of V^{2+}, Fe^{2+}, and Zn^{2+} are all roughly the same (approximately 76 pm). Given their positions in the periodic table, explain why their ionic radii are so similar.

ANSWER

1.
2.
3.

a. d^9, square planar, neither high nor low spin, single unpaired electron
b. d^8, square planar, low spin, no unpaired electrons

23.6 Transition Metals in Biology

LEARNING OBJECTIVE

1. To become familiar with some of the roles of transition-metal complexes in biological systems.

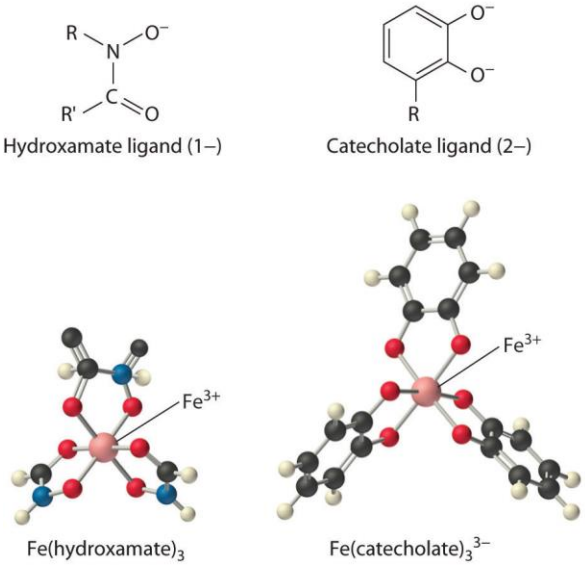
In Chapter 1 "Introduction to Chemistry", you learned that 19 of the elements in the periodic table are *essential elements* that are necessary for most organisms, including humans, and in Chapter 7 "The Periodic Table and Periodic Trends" we discussed some of the biological functions of these elements. In this section, we describe several systems that illustrate the roles transition metals play in biological systems. Our goal is for you to understand why the chemical properties of these elements make them essential for life. We begin with a discussion of the strategies organisms use to extract transition metals from their environment. The section continues with a brief discussion of the use of transition metals in reactions that involve the transfer of electrons, reactions of small molecules such as O_2, Lewis-acid catalysis, and the generation of reactive organic radicals.

Uptake and Storage of Transition Metals

In Chapter 1 "Introduction to Chemistry", we described the three possible dietary levels for any essential element: deficient, optimal, and toxic, in order of increasing concentration in the diet (Figure 1.27 "Possible Concentrations of an Essential Element in the Diet"). If the concentration of an essential element in the diet is too low, an organism must be able to extract the element from the environment and concentrate it. If the concentration of an essential element in the diet is too high, an organism must be able to limit its intake to avoid toxic effects. Moreover, organisms must be able to switch off the uptake

process rapidly if dietary levels rise suddenly, and they must be able to store essential elements for future use.

Three distinct steps are involved in transition metal uptake. First, the metal must be "mobilized" from the environment and brought into contact with a cell in a form that can be absorbed. Second, the metal must be transported across the cell membrane into the cell. Third, the element must be transported to its point of utilization within a cell or to other cells within the organism. In our discussion, we focus on the uptake, transport, and storage of iron, which illustrates the most important points. Because iron deficiency (anemia) is the most widespread nutritional deficiency known in humans, the uptake of iron is especially well understood.

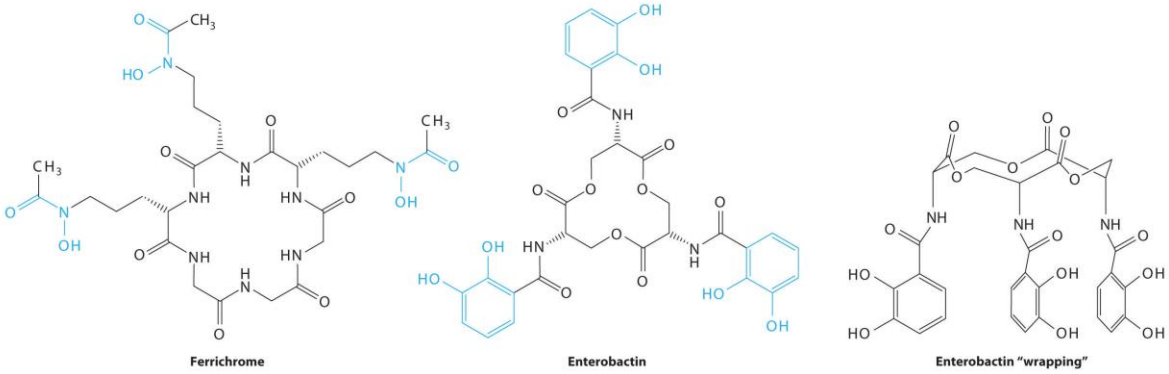


Iron complexes in biological systems. *Iron(III) forms very stable octahedral complexes with hydroxamate and catecholate ligands.*

In Chapter 17 "Solubility and Complexation Equilibriums", you learned that the solubility of metal ions such as Fe^{3+}, which form highly insoluble hydroxides, depends on the pH and the presence of complexing agents. In an oxygen-containing atmosphere, iron exists as Fe(III) because of the positive reduction potential of Fe^{3+}($Fe^{3+} + e^- \rightarrow Fe^{2+}$; $E^\circ = +0.77$ V). Because ferric hydroxide [$Fe(OH)_3$] is highly insoluble ($K_{sp} \approx 1 \times 10^{-39}$), the equilibrium concentration of Fe^{3+}(aq) at pH 7.0 is very low, about 10^{-18} M. You would have to drink 2×10^{13} L of iron-saturated water per day (roughly 5 mi^3) to consume the recommended daily intake of Fe for humans, which is about 1 mg/day. Animals such as humans can overcome this problem by consuming concentrated sources of iron, such as red meat, but microorganisms cannot.

Consequently, most microorganisms synthesize and secrete organic molecules calledsiderophores to increase the total concentration of available iron in the surrounding medium. Siderophores are generally cyclic compounds that use bidentate ligands, such as the *hydroxamate* and *catecholate* groups shown here, to bind Fe^{3+} in an octahedral arrangement. Typical siderophores are *ferrichrome*, a cyclic peptide produced by fungi, and *enterobactin*, a cyclic ester produced by bacteria (Figure 23.18 "Siderophores"). Attaching the three iron ligands to a cyclic framework greatly increases the stability of the resulting Fe^{3+} complex due to the chelate effect described in Section 23.4 "Coordination Compounds". The formation constants for the Fe^{3+} complexes of ferrichrome and enterobactin are about 10^{32} and 10^{40}, respectively, which are high enough to allow them to dissolve almost any Fe(III) compound.

Figure 23.18 Siderophores



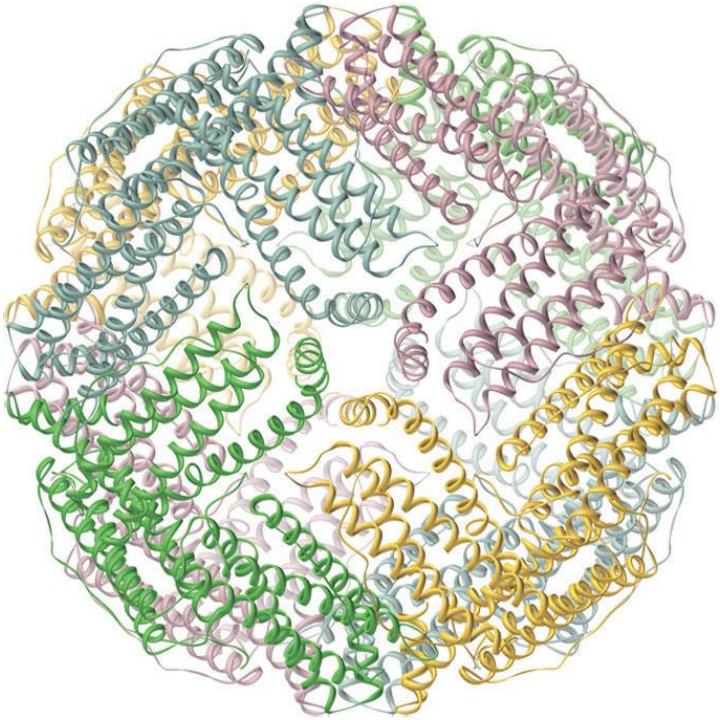
Ferrichrome (a) and enterobactin (b) are siderophores that use hydroxamate and catecholate ligands, respectively, to bind Fe^{3+}. The "wrapped" drawing of enterobactin (c) shows how the cyclic ester framework places the three catecholate ligands in the correct orientation to bind to a single Fe^{3+} ion, which is an application of the chelate effect. The actual structure of ferrichrome is similar to that of enterobactin, with the three hydroxamate ligands adjacent to one another for optimal binding of Fe^{3+}. Note: For clarity, most or all hydrogen atoms have been omitted in this and the following structures.

Siderophores increase the $[Fe^{3+}]$ in solution, providing the bacterium that synthesized them (as well as any competitors) with a supply of iron. In addition, siderophores neutralize the positive charge on the metal ion and provide a hydrophobic "wrapping" that enables the Fe^{3+}–siderophore complex to be recognized by a specific protein that transports it into the interior of a cell. Once it is inside a cell, the iron is reduced to Fe^{2+}, which has a much lower affinity for the siderophore and spontaneously dissociates.

In contrast, multicellular organisms can increase the concentration of iron in their diet by lowering the pH in the gastrointestinal tract. At pH 1.0 (the approximate pH of the stomach), most Fe(III) salts dissolve to form Fe^{3+}(aq), which is absorbed by specific proteins in the intestinal wall. A protein called *transferrin* forms a complex with iron(III), allowing it to be transported to other cells. Proteins that bind tightly to Fe(III) can also be used as antibacterial agents because iron is absolutely essential for bacterial growth. For example, milk, tears, and egg white all contain proteins similar to transferrin, and their high affinity for Fe^{3+} allows them to sequester iron, thereby preventing bacteria from growing in these nutrient-rich media.

Iron is released from transferrin by reduction to Fe^{2+}, and then it is either used immediately (e.g., for the synthesis of hemoglobin) or stored in a very large protein called *ferritin* for future use (Figure 23.19 "Ferritin, an Iron Storage Protein"). Ferritin uses oxygen to oxidize Fe^{2+} to Fe^{3+}, which at neutral pH precipitates in the central cavity of the protein as a polymeric mixture of $Fe(OH)_3$ and $FePO_4$. Because a fully loaded ferritin molecule can contain as many as 4500 Fe atoms, which corresponds to about 25% Fe by mass, ferritin is an effective way to store iron in a highly concentrated form. When iron is needed by a cell, the Fe^{3+} is reduced to the much more soluble $Fe^{2+}$by a reductant such as ascorbic acid (vitamin C). The structure of ferritin contains channels at the junctions of the subunits, which provide pathways for iron to enter and leave the interior of a molecule.

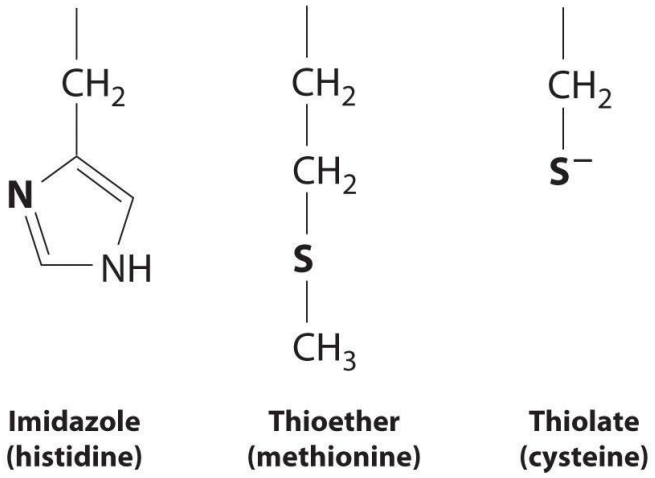
Figure 23.19 *Ferritin, an Iron Storage Protein*



A schematic drawing of the structure of iron-loaded ferritin, showing the almost spherical protein shell inside which the iron hydroxide/phosphate core is formed.

Metalloproteins and Metalloenzymes

A protein that contains one or more metal ions tightly bound to amino acid side chains is called a metalloprotein; some of the most common ligands provided by amino acids are shown here. A metalloprotein that catalyzes a chemical reaction is ametalloenzyme. Thus all metalloenzymes are metalloproteins, but the converse is not true. Recent estimates suggest that more than 40% of all known enzymes require at least one metal ion for activity, including almost all the enzymes responsible for the synthesis, duplication, and repair of DNA (deoxyribonucleic acid) and RNA (ribonucleic acid).



Ligands used in biological systems.*These metal ligands are commonly found in metalloproteins.*

Electron-Transfer Proteins

Proteins whose function is to transfer electrons from one place to another are called *electron-transfer proteins*. Because they do *not* catalyze a chemical reaction, electron-transfer proteins are *not* enzymes; they are biochemical reductants or oxidants consumed in an enzymatic reaction. The general reaction for an electron-transfer protein is as follows:

Equation 23.14

$$Mn++\ e- \square\ M(n-1)+$$

Because many transition metals can exist in more than one oxidation state, electron-transfer proteins usually contain one or more metal ions that can undergo a redox reaction. Incorporating a metal ion into a protein has three important biological consequences:

1. The protein environment can adjust the redox potential ($E^{\circ\prime}$), of the metal ion over a rather large potential range, whereas the redox potential of the simple hydrated metal ion [M^{n+}(aq)], is essentially fixed.
2. The protein can adjust the structure of the metal complex to ensure that electron transfer is rapid.
3. The protein environment provides specificity, ensuring that the electron is transferred to only the desired site.

Three important classes of metalloproteins transfer electrons: blue copper proteins, cytochromes, and iron–sulfur proteins, which generally transfer electrons at high (> 0.20 V), intermediate (±0 V), and low

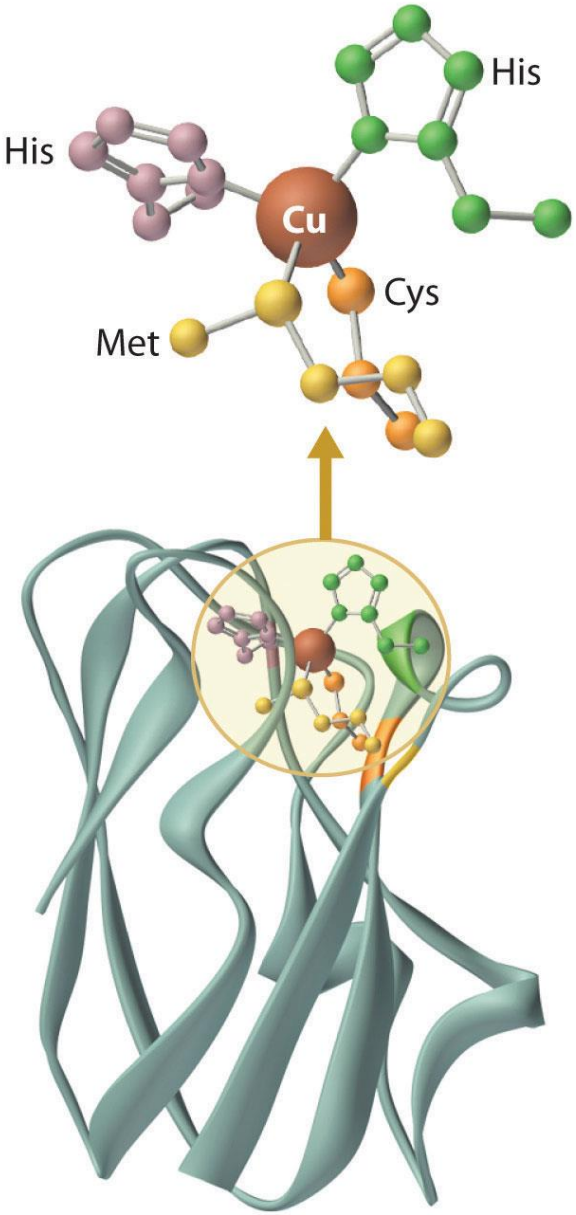
(−0.20 to −0.50 V) potentials, respectively (Table 23.12 "Some Properties of the Most Common Electron-Transfer Proteins"). Although these electron-transfer proteins contain different metals with different structures, they are all designed to ensure rapid electron transfer to and from the metal. Thus when the protein collides with its physiological oxidant or reductant, electron transfer can occur before the two proteins diffuse apart. For electron transfer to be rapid, the metal sites in the oxidized and reduced forms of the protein must have similar structures.

Table 23.12 Some Properties of the Most Common Electron-Transfer Proteins

Protein	Metal Center	M/e⁻Transferred	Reduction Potential (V)
iron–sulfur proteins*	$[Fe(SR)_4]^{2-}$	1 Fe	−0.1 to +0.1
	$[(RS)_2FeS_2Fe(SR)_2]^{2-}$	2 Fe	−0.2 to −0.4
	$[Fe_3S_4(SR)_3]^{3-}$	3 Fe	−0.1 to −0.2
	$[Fe_4S_4(SR)_4]^{2-}$	4 Fe	−0.3 to −0.5
cytochromes	Fe-heme (low spin)	1 Fe	~0
blue copper proteins†	$[Cu(Im)_2(SR)(SR_2)]^-$	1 Cu	≥ +0.20
*** A sulfur bound to an organic group is represented as SR.**			
† See Figure 23.20 "A Blue Copper Protein" for the structure of imidazole (Im).			

Blue Copper Proteins

Figure 23.20 *A Blue Copper Protein*



In both the oxidized and reduced forms of a blue copper protein, the copper is coordinated by four ligands (two histidine imidazole nitrogen atoms, a cysteine thiolate sulfur, and a thioether sulfur of a methionine) in a roughly tetrahedral arrangement.

Blue copper proteins were first isolated from bacteria in the 1950s and from plant tissues in the early 1960s. The intense blue color of these proteins is due to a strong absorption band at a wavelength of about 600 nm. Although simple Cu^{2+} complexes, such as $[Cu(H_2O)_6]^{2+}$and $[Cu(NH_3)_4]^{2+}$, are also blue due to an absorption band at 600 nm, the intensity of the absorption band is about 100 times less than that of a

blue copper protein. Moreover, the reduction potential for the Cu^{2+}/Cu^{+} couple in a blue copper protein is usually +0.3 to +0.5 V, considerably more positive than that of the aqueous Cu^{2+}/Cu^{+} couple (+0.15 V). The copper center in blue copper proteins has a distorted tetrahedral structure, in which the copper is bound to four amino acid side chains (Figure 23.20 "A Blue Copper Protein"). Although the most common structures for four-coordinate Cu^{2+} and Cu^{+} complexes are square planar and tetrahedral, respectively, the structures of the oxidized (Cu^{2+}) and reduced (Cu^{+}) forms of the protein are essentially identical. Thus the protein forces the Cu^{2+}ion to adopt a higher-energy structure that is more suitable for Cu^{+}, which makes the Cu^{2+} form easier to reduce and raises its reduction potential.

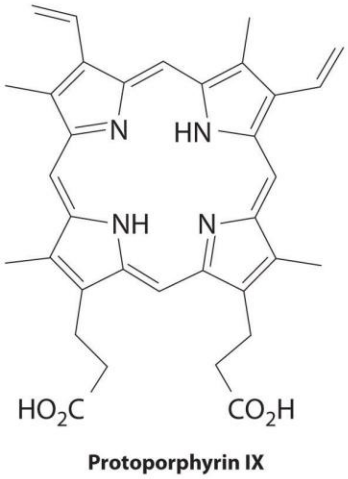
Moreover, by forcing the oxidized and reduced forms of the metal complex to have essentially the same structure, the protein ensures that electron transfer to and from the copper site is rapid because only minimal structural reorganization of the metal center is required. Kinetics studies on simple metal complexes have shown that electron-transfer reactions tend to be slow when the structures of the oxidized and reduced forms of a metal complex are very different, and fast when they are similar. You will see that other metal centers used for biological electron-transfer reactions are also set up for minimal structural reorganization after electron transfer, which ensures the rapid transfer of electrons.

Cytochromes

The cytochromes (from the Greek *cytos*, meaning “cell”, and *chroma*, meaning “color”) were first identified in the 1920s by spectroscopic studies of cell extracts. Based on the wavelength of the maximum absorption in the visible spectrum, they were classified as cytochromes *a* (with the longest wavelength), cytochromes *b* (intermediate wavelength), and cytochromes *c* (shortest wavelength). It quickly became apparent that there was a correlation between their spectroscopic properties and other physical properties. For examples, cytochromes *c* are generally small, soluble proteins with a reduction potential of about +0.25 V, whereas cytochromes *b* are larger, less-soluble proteins with reduction potentials of about 0 V.

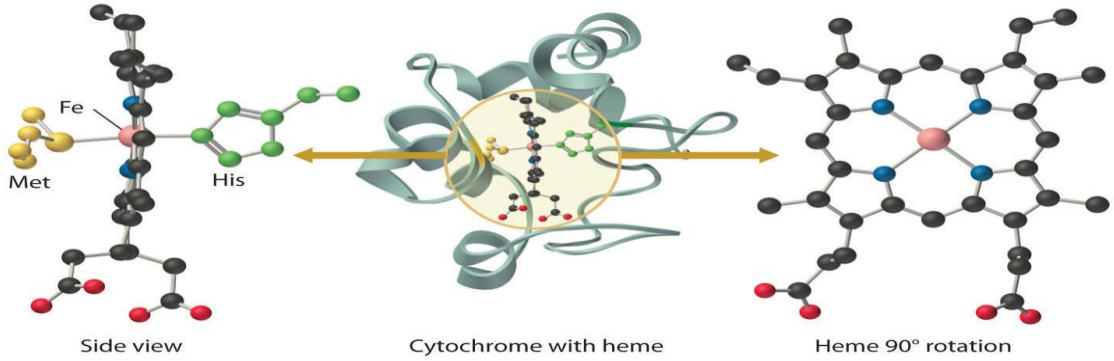
All cytochromes contain iron, and the iron atom in all cytochromes is coordinated by a planar array of four nitrogen atoms provided by a cyclic tetradentate ligand called a*porphyrin*. The iron–porphyrin unit is called a *heme* group. The structures of a typical porphyrin (protoporphyrin IX) and its iron complex (protoheme) are shown here. In addition to the four nitrogen atoms of the porphyrin, the iron in a

cytochrome is usually bonded to two additional ligands provided by the protein, as shown in Figure 23.21 "A Cytochrome ".



A cytochrome. *Shown here is protoporphyrin IX and its iron complex, protoheme.*

Figure 23.21 A Cytochrome c



In a cytochrome c, the heme iron is coordinated to the nitrogen atom of a histidine imidazole and the sulfur atom of a methionine thioether, in addition to the four nitrogen atoms provided by the porphyrin.

In contrast to the blue copper proteins, two electron configurations are possible for both the oxidized and reduced forms of a cytochrome, and this has significant structural consequences. Thus Fe^{2+} is d^6 and can be either high spin (with four unpaired electrons) or low spin (with no unpaired electrons; Figure 23.11 "The Possible Electron Configurations for Octahedral "). Similarly, Fe^{3+} is d^5 and can also be high spin (with five unpaired electrons) or low spin (with one unpaired electron). In low-spin heme complexes, both the Fe^{2+} and the Fe^{3+} ions are small enough to fit into the "hole" in the center of the porphyrin; hence the iron atom lies almost exactly in the plane of the four porphyrin nitrogen atoms in both cases. Because cytochromes *b* and *c* are low spin in both their oxidized and reduced forms, the structures of the oxidized and reduced cytochromes are essentially identical. Hence minimal structural changes occur after oxidation or reduction, which makes electron transfer to or from the heme very rapid.

Note the Pattern

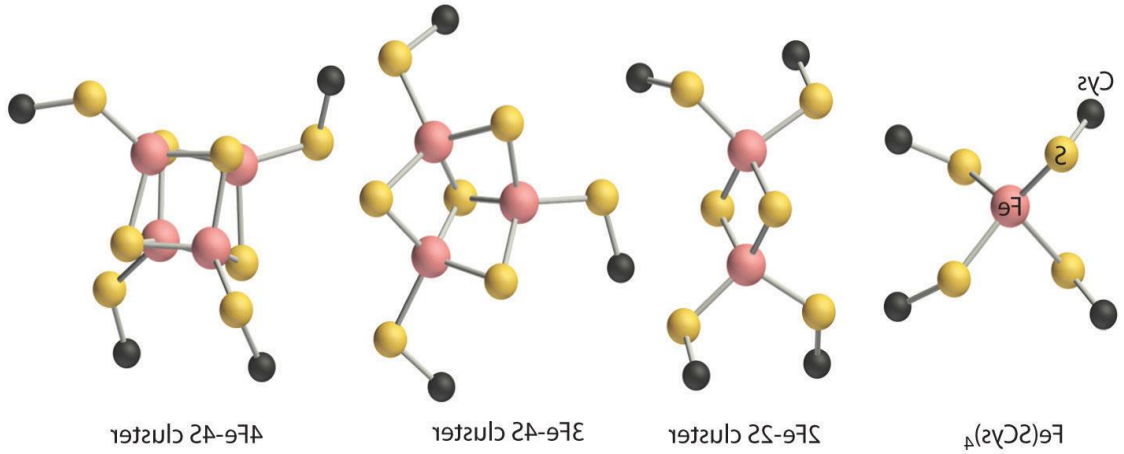
Electron transfer reactions occur most rapidly when minimal structural changes occur during oxidation or reduction.

Iron–Sulfur Proteins

Although all known bacteria, plants, and animals use iron–sulfur proteins to transfer electrons, the existence of these proteins was not recognized until the late 1950s. Iron–sulfur proteins transfer electrons over a wide range of reduction potentials, and their iron content can range from 1 to more than 12 Fe atoms per protein molecule. In addition, most iron–sulfur proteins contain stoichiometric amounts of sulfide (S^{2-}).

These properties are due to the presence of four different kinds of iron–sulfur units, which contain one, two, three, or four iron atoms per Fe–S complex (Figure 23.22 "Fe–S Centers in Proteins"). In all cases, the Fe^{2+} and Fe^{3+} ions are coordinated to four sulfur ligands in a tetrahedral environment. Due to tetrahedral coordination by weak-field sulfur ligands, the iron is high spin in both the Fe^{3+} and Fe^{2+} oxidation states, which results in similar structures for the oxidized and reduced forms of the Fe–S complexes. Consequently, only small structural changes occur after oxidation or reduction of the Fe–S center, which results in rapid electron transfer.

Figure 23.22 *Fe–S Centers in Proteins*



Four kinds of iron–sulfur centers, containing one, two, three, and four iron atoms, respectively, are known in electron-transfer proteins. Although they differ in the number of sulfur atoms provided by cysteine thiolates versus sulfide, in all cases the iron is coordinated to four sulfur ligands in a roughly tetrahedral environment.

Reactions of Small Molecules

Although small molecules, such as O_2, N_2, and H_2, do not react with organic compounds under ambient conditions, they do react with many transition-metal complexes. Consequently, virtually all organisms use metalloproteins to bind, transport, and catalyze the reactions of these molecules. Probably the best-known example is hemoglobin, which is used to transport O_2 in many multicellular organisms.

Note the Pattern

Under ambient conditions, small molecules, such as O_2, N_2, and H_2, react with transition-metal complexes but not with organic compounds.

Oxygen Transport

Many microorganisms and most animals obtain energy by *respiration*, the oxidation of organic or inorganic molecules by O_2. At 25°C, however, the concentration of dissolved oxygen in water in contact with air is only about 0.25 mM. Because of their high surface area-to-volume ratio, aerobic microorganisms can obtain enough oxygen for respiration by passive diffusion of O_2 through the cell membrane. As the size of an organism increases, however, its volume increases much more rapidly than its surface area, and the need for oxygen depends on its volume. Consequently, as a multicellular organism grows larger, its need for O_2 rapidly outstrips the supply available through diffusion. Unless a

transport system is available to provide an adequate supply of oxygen for the interior cells, organisms that contain more than a few cells cannot exist. In addition, O_2 is such a powerful oxidant that the oxidation reactions used to obtain metabolic energy must be carefully controlled to avoid releasing so much heat that the water in the cell boils. Consequently, in higher-level organisms, the respiratory apparatus is located in internal compartments called *mitochondria*, which are the power plants of a cell. Oxygen must therefore be transported not only to a cell but also to the proper compartment within a cell.

Three different chemical solutions to the problem of oxygen transport have developed independently in the course of evolution, as indicated in Table 23.13 "Some Properties of the Three Classes of Oxygen-Transport Proteins". Mammals, birds, reptiles, fish, and some insects use a heme protein called *hemoglobin* to transport oxygen from the lungs to the cells, and they use a related protein called *myoglobin* to temporarily store oxygen in the tissues. Several classes of invertebrates, including marine worms, use an iron-containing protein called *hemerythrin* to transport oxygen, whereas other classes of invertebrates (arthropods and mollusks) use a copper-containing protein called*hemocyanin*. Despite the presence of the *hem-* prefix, hemerythrin and hemocyanin do not contain a metal–porphyrin complex.

Table 23.13 Some Properties of the Three Classes of Oxygen-Transport Proteins

Protein	Source	M per Subunit	M per O_2Bound	Color (deoxy form)	Color (oxy form)
hemoglobin	mammals, birds, fish, reptiles, some insects	1 Fe	1 Fe	red-purple	red
hemerythrin	marine worms	2 Fe	2 Fe	colorless	red
hemocyanin	mollusks, crustaceans, spiders	2 Cu	2 Cu	colorless	blue

Myoglobin and Hemoglobin

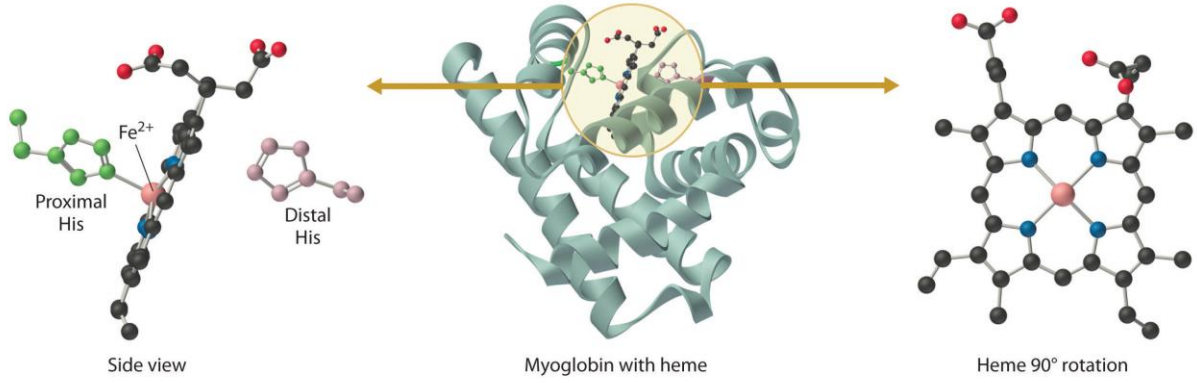
Myoglobin is a relatively small protein that contains 150 amino acids. The functional unit of myoglobin is an iron–porphyrin complex that is embedded in the protein (Figure 23.23 "The Structure of Deoxymyoglobin, Showing the Heme Group"). In myoglobin, the heme iron is five-coordinate, with only a single histidine imidazole ligand from the protein (called the *proximal histidine* because it is near the iron) in addition to the four nitrogen atoms of the porphyrin. A second histidine imidazole (the *distal histidine*because it is more distant from the iron) is located on the other side of the heme group, too far from the iron to be bonded to it. Consequently, the iron atom has a vacant coordination site, which is

where O_2 binds. In the ferrous form (*deoxymyoglobin*), the iron is five-coordinate and high spin. Because high-spin Fe^{2+} is too large to fit into the "hole" in the center of the porphyrin, it is about 60 pm above the plane of the porphyrin. When O_2 binds to deoxymyoglobin to form *oxymyoglobin*, the iron is converted from five-coordinate (high spin) to six-coordinate (low spin; Figure 23.24 "Oxygen Binding to Myoglobin and Hemoglobin"). Because low-spin Fe^{2+} and Fe^{3+} are smaller than high-spin Fe^{2+}, the iron atom moves into the plane of the porphyrin ring to form an octahedral complex. The O_2 pressure at which half of the molecules in a solution of myoglobin are bound to O_2 ($P_{1/2}$) is about 1 mm Hg (1.3×10^{-3} atm).

Note the Pattern

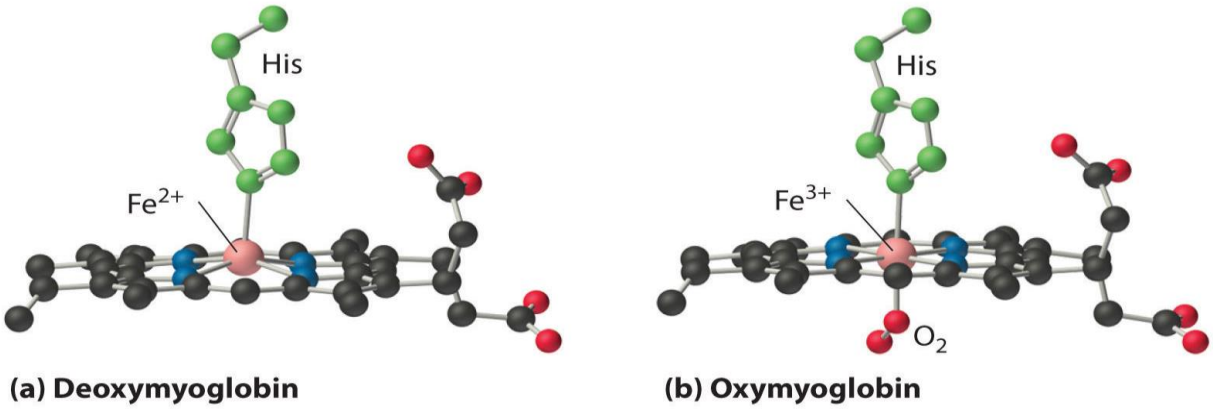
A vacant coordination site at a metal center in a protein usually indicates that a small molecule will bind to the metal ion, whereas a coordinatively saturated metal center is usually involved in electron transfer.

Figure 23.23 *The Structure of Deoxymyoglobin, Showing the Heme Group*



The iron in deoxymyoglobin is five-coordinate, with one histidine imidazole ligand from the protein. Oxygen binds at the vacant site on iron.

Figure 23.24 *Oxygen Binding to Myoglobin and Hemoglobin*



(a) The Fe^{2+} ion in deoxymyoglobin is high spin, which makes it too large to fit into the "hole" in the center of the porphyrin. (b) When O_2 binds to deoxymyoglobin, the iron is converted to low-spin Fe^{3+}, which is smaller, allowing the iron to move into the plane of the four nitrogen atoms of the porphyrin to form an octahedral complex.

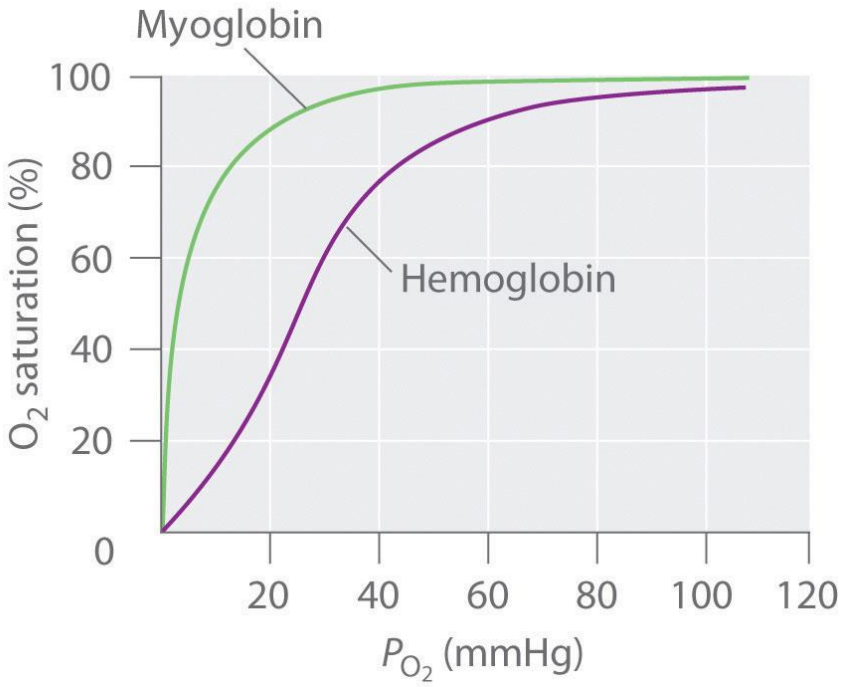
Hemoglobin consists of two subunits of 141 amino acids and two subunits of 146 amino acids, both similar to myoglobin; it is called a *tetramer* because of its four subunits. Because hemoglobin has very different O_2-binding properties, however, it is not simply a "super myoglobin" that can carry four O_2 molecules simultaneously (one per heme group). The shape of the O_2-binding curve of myoglobin (Mb; Figure 23.25 "The O") can be described mathematically by the following equilibrium:

Equation 23.15

$$MbO2 \square \quad Mb + O2Kdiss = [Mb][O2][MbO2]$$

In contrast, the O_2-binding curve of hemoglobin is S shaped (Figure 23.25 "The O"). As shown in the curves, at low oxygen pressures, the affinity of deoxyhemoglobin for O_2 is substantially lower than that of myoglobin, whereas at high O_2 pressures the two proteins have comparable O_2 affinities. The physiological consequences of the unusual S-shaped O_2-binding curve of hemoglobin are enormous. In the lungs, where O_2pressure is highest, the high oxygen affinity of deoxyhemoglobin allows it to be completely loaded with O_2, giving four O_2 molecules per hemoglobin. In the tissues, however, where the oxygen pressure is much lower, the decreased oxygen affinity of hemoglobin allows it to release O_2, resulting in a net transfer of oxygen to myoglobin.

Figure 23.25 *The O_2-Binding Curves of Myoglobin and Hemoglobin*



The curve for myoglobin can be described by a simple equilibrium between deoxy- and oxymyoglobin, but the S-shaped curve for hemoglobin can be described only in terms of a cooperative interaction between the four hemes.

The S-shaped O_2-binding curve of hemoglobin is due to a phenomenon called*cooperativity*, in which the affinity of one heme for O_2 depends on whether the other hemes are already bound to O_2. Cooperativity in hemoglobin requires an interaction between the four heme groups in the hemoglobin tetramer, even though they are more than 3000 pm apart, and depends on the change in structure of the heme group that occurs with oxygen binding. The structures of deoxyhemoglobin and oxyhemoglobin are slightly different, and as a result, deoxyhemoglobin has a much lower O_2 affinity than myoglobin, whereas the O_2 affinity of oxyhemoglobin is essentially identical to that of oxymyoglobin. Binding of the first two O_2 molecules to deoxyhemoglobin causes the overall structure of the protein to change to that of oxyhemoglobin; consequently, the last two heme groups have a much higher affinity for O_2 than the first two.

Oxygen is not unique in its ability to bind to a ferrous heme complex; small molecules such as CO and NO bind to deoxymyoglobin even more tightly than does O_2. The interaction of the heme iron with oxygen and other diatomic molecules involves the transfer of electron density from the filled t_{2g} orbitals of the low-spin d^6 Fe^{2+} ion to the empty π^* orbitals of the ligand. In the case of the Fe^{2+}–O_2 interaction, the transfer of

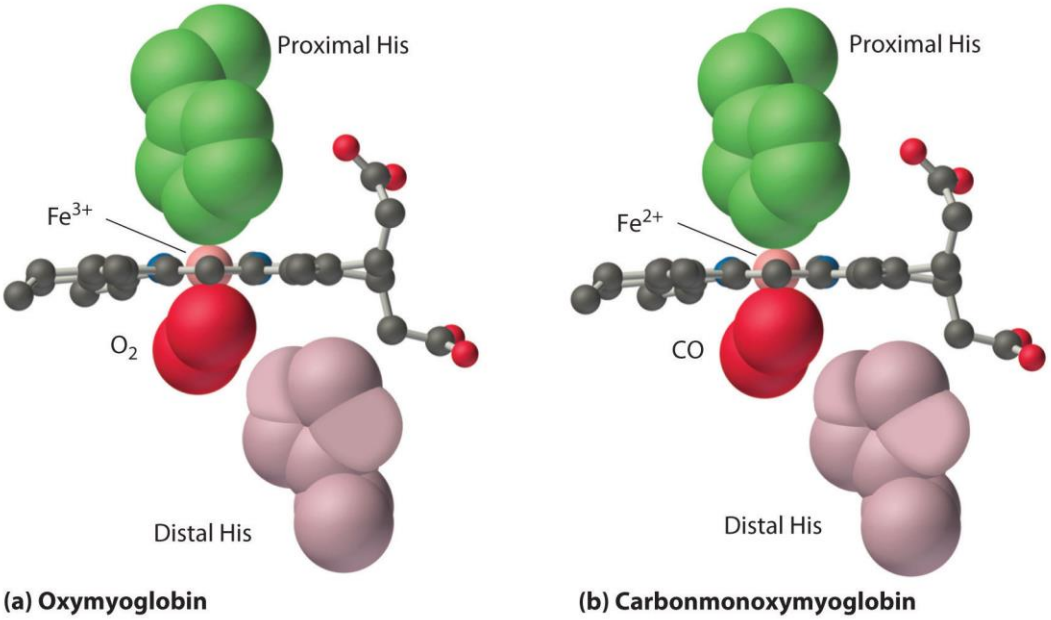
electron density is so great that the Fe–O_2 unit can be described as containing low-spin Fe^{3+} (d^5) and O_2^-. We can therefore represent the binding of O_2 to deoxyhemoglobin and its release as a reversible redox reaction:

Equation 23.16

$$Fe^{2+} + O_2 \rightleftharpoons Fe^{3+}–O_2^-$$

As shown in Figure 23.26 "Binding of O", the Fe–O_2 unit is bent, with an Fe–O–O angle of about 130°. Because the π* orbitals in CO are empty and those in NO are singly occupied, these ligands interact more strongly with Fe^{2+} than does O_2, in which the π* orbitals of the neutral ligand are doubly occupied.

Figure 23.26 *Binding of O_2 and CO to the Iron of Myoglobin*



Because the Fe–O–O unit is bent, while the Fe–C–O unit is linear, the imidazole group of the distal histidine in hemoglobin interferes with CO binding and decreases the affinity of hemoglobin for CO. Although CO has a much greater affinity for a ferrous heme than does O_2 (by a factor of about 25,000), the affinity of CO for deoxyhemoglobin is only about 200 times greater than that of O_2, which suggests that something in the protein is decreasing its affinity for CO by a factor of about 100. Both CO and NO bind to ferrous hemes in a linear fashion, with an Fe–C(N)–O angle of about 180°, and the difference in the preferred geometry of O_2 and CO provides a plausible explanation for the difference in affinities. As shown in Figure 23.26 "Binding of O", the imidazole group of the distal histidine is located precisely where the oxygen atom of bound CO would be if the Fe–C–O unit were linear. Consequently, CO cannot bind to the

heme in a linear fashion; instead, it is forced to bind in a bent mode that is similar to the preferred structure for the Fe–O_2unit. This results in a significant decrease in the affinity of the heme for CO, while leaving the O_2 affinity unchanged, which is important because carbon monoxide is produced continuously in the body by degradation of the porphyrin ligand (even in nonsmokers). Under normal conditions, CO occupies approximately 1% of the heme sites in hemoglobin and myoglobin. If the affinity of hemoglobin and myoglobin for CO were 100 times greater (due to the absence of the distal histidine), essentially 100% of the heme sites would be occupied by CO, and no oxygen could be transported to the tissues. Severe carbon-monoxide poisoning, which is frequently fatal, has exactly the same effect. Thus the primary function of the distal histidine appears to be to decrease the CO affinity of hemoglobin and myoglobin to avoid self-poisoning by CO.

Hemerythrin

Hemerythrin is used to transport O_2 in a variety of marine invertebrates. It is an*octamer* (eight subunits), with each subunit containing *two* iron atoms and binding one molecule of O_2. Deoxyhemerythrin contains two Fe^{2+} ions per subunit and is colorless, whereas oxyhemerythrin contains two Fe^{3+} ions and is bright reddish violet. These invertebrates also contain a monomeric form of hemerythrin that is located in the tissues, analogous to myoglobin. The binding of oxygen to hemerythrin and its release can be described by the following reaction, where the HO_2^- ligand is the hydroperoxide anion derived by the deprotonation of hydrogen peroxide (H_2O_2):

Equation 23.17

$$2Fe^{2+} + O_2 + H^+ \rightleftharpoons 2Fe^{3+}–O_2H$$

Thus O_2 binding is accompanied by the transfer of *two* electrons (one from each Fe^{2+}) and a proton to O_2.

Hemocyanin

Hemocyanin is used for oxygen transport in many arthropods (spiders, crabs, lobsters, and centipedes) and in mollusks (shellfish, octopi, and squid); it is responsible for the bluish-green color of their blood. The protein is a polymer of subunits that each contain two copper atoms (rather than iron), with an aggregate molecular mass of greater than 1,000,000 amu. Deoxyhemocyanin contains two Cu^+ ions per subunit and is colorless, whereas oxyhemocyanin contains two Cu^{2+} ions and is bright blue. As with hemerythrin, the binding and release of O_2 correspond to a two-electron reaction:

Equation 23.18

$$2Cu^+ + O_2 \rightleftharpoons Cu^{2+}–O_2^{2-}–Cu^{2+}$$

Although hemocyanin and hemerythrin perform the same basic function as hemoglobin, these proteins are not interchangeable. In fact, hemocyanin is so foreign to humans that it is one of the major factors responsible for the common allergies to shellfish.

Note the Pattern

Myoglobin, hemoglobin, hemerythrin, and hemocyanin all use a transition-metal complex to transport oxygen.

Enzymes Involved in Oxygen Activation

Many of the enzymes involved in the biological reactions of oxygen contain metal centers with structures that are similar to those used for O_2 transport. Many of these enzymes also contain metal centers that are used for electron transfer, which have structures similar to those of the electron-transfer proteins discussed previously. In this section, we briefly describe two of the most important examples: dioxygenases and methane monooxygenase.

Dioxygenases are enzymes that insert both atoms of O_2 into an organic molecule. In humans, dioxygenases are responsible for cross-linking collagen in connective tissue and for synthesizing complex organic molecules called *prostaglandins*, which trigger inflammation and immune reactions. Iron is by far the most common metal in dioxygenases; and the target of the most commonly used drug in the world, aspirin, is an iron enzyme that synthesizes a specific prostaglandin. Aspirin inhibits this enzyme by binding to the iron atom at the active site, which prevents oxygen from binding.

Methane monooxygenase catalyzes the conversion of methane to methanol. The enzyme is a monooxygenase because only one atom of O_2 is inserted into an organic molecule, while the other is reduced to water:

Equation 23.19

$$CH_4 + O_2 + 2e^- + 2H^+ \rightarrow CH_3OH + H_2O$$

Because methane is the major component of natural gas, there is enormous interest in using this reaction to convert methane to a liquid fuel (methanol) that is much more convenient to ship and store. Because the C–H bond in methane is one of the strongest C–H bonds known, however, an extraordinarily powerful oxidant is needed for this reaction. The active site of methane monooxygenase contains two Fe atoms that bind O_2, but the details of how the bound O_2 is converted to such a potent oxidant remain unclear.

Metal Ions as Lewis Acids

Reactions catalyzed by metal ions that do not change their oxidation states during the reaction are usually group transfer reactions, in which a group such as the phosphoryl group ($-PO_3^{2-}$) is transferred. These enzymes usually use metal ions such as Zn^{2+}, Mg^{2+}, and Mn^{2+}, and they range from true metalloenzymes, in which the metal ion is tightly bound, to metal-activated enzymes, which require the addition of metal ions for activity. Because tight binding is usually the result of specific metal–ligand interactions, metalloenzymes tend to be rather specific for a particular metal ion. In contrast, the binding of metal ions to metal-activated enzymes is largely electrostatic in nature; consequently, several different metal ions with similar charges and sizes can often be used to give an active enzyme.

Note the Pattern

Metalloenzymes generally contain a specific metal ion, whereas metal-activated enzymes can use any of several metal ions of similar size and charge.

A metal ion that acts as a Lewis acid can catalyze a group transfer reaction in many different ways, but we will focus on only one of these, using a zinc enzyme as an example. *Carbonic anhydrase* is found in red blood cells and catalyzes the reaction of CO_2 with water to give carbonic acid.

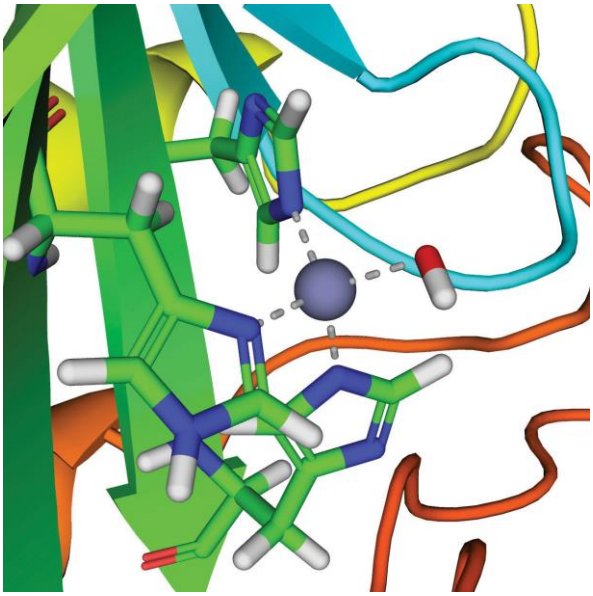
Equation 23.20

$$CO2(g) + H2O(l) \square H+(aq) + HCO3-(aq)$$

Although this reaction occurs spontaneously in the absence of a catalyst, it is too slow to absorb all the CO_2 generated during respiration. Without a catalyst, tissues would explode due to the buildup of excess CO_2 pressure. Carbonic anhydrase contains a single Zn^{2+} ion per molecule, which is coordinated by three histidine imidazole ligands and a molecule of water. Because Zn^{2+} is a Lewis acid, the pK_a of the Zn^{2+}–OH_2 unit is about 8 versus 14 for pure water. Thus at pH 7–8, a significant fraction of the enzyme molecules contain the Zn^{2+}–OH^- group, which is much more reactive than bulk water. When carbon dioxide binds in a nonpolar site next to the Zn^{2+}–OH^- unit, it reacts rapidly to give a coordinated bicarbonate ion that dissociates from the enzyme:

Equation 23.21

$$Zn^{2+}–OH^- + CO_2 \rightleftharpoons Zn^{2+}–OCO_2H^- \rightleftharpoons Zn^{2+} + HCO_3^-$$



The active site of carbonic anhydrase.

Thus the function of zinc in carbonic anhydrase is to generate the hydroxide ion at pH 7.0, far less than the pH required in the absence of the metal ion.

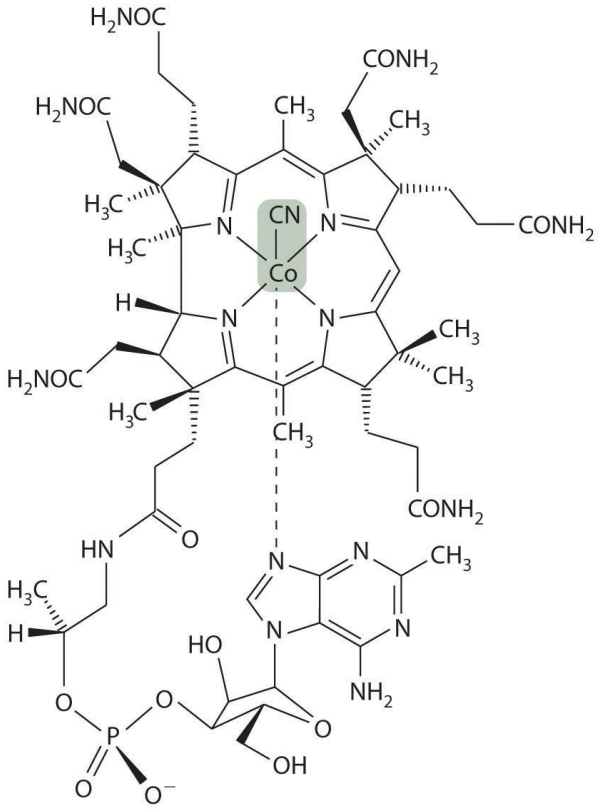
Enzymes That Use Metals to Generate Organic Radicals

An *organic radical* is an organic species that contains one or more unpaired electrons. Chemists often consider organic radicals to be highly reactive species that produce undesirable reactions. For example, they have been implicated in some of the irreversible chemical changes that accompany aging. It is surprising, however, that organic radicals are also essential components of many important enzymes, almost all of which use a metal ion to generate the organic radical within the enzyme. These enzymes are involved in the synthesis of hemoglobin and DNA, among other important biological molecules, and they are the targets of pharmaceuticals for the treatment of diseases such as anemia, sickle-cell anemia, and cancer. In this section, we discuss one class of radical enzymes that use vitamin B_{12}.

Vitamin B_{12} was discovered in the 1940s as the active agent in the cure of pernicious anemia, which does not respond to increased iron in the diet. Humans need only tiny amounts of vitamin B_{12}, and the average blood concentration in a healthy adult is only about 3.5×10^{-8} M. The structure of vitamin B_{12}, shown in Figure 23.27 "Vitamin B", is similar to that of a heme, but it contains cobalt instead of iron, and its structure is much more complex. In fact, vitamin B_{12} has been called the most complex nonpolymeric biological molecule known and was the first naturally occurring organometallic compound to be isolated.

When vitamin B_{12} (the form present in vitamin tablets) is ingested, the axial cyanide ligand is replaced by a complex organic group.

Figure 23.27 *Vitamin B_{12}*



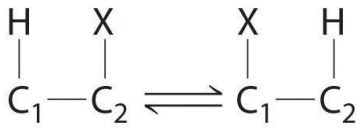
In the body, the axial cyanide ligand found in the vitamin is replaced by a complex organic unit. Heterolytic cleavage of the Co–C bond in the resulting organometallic complex generates an organic radical for the catalysis of rearrangement reactions.

The cobalt–carbon bond in the enzyme-bound form of vitamin B_{12} and related compounds is unusually weak, and it is particularly susceptible to *homolytic cleavage*:

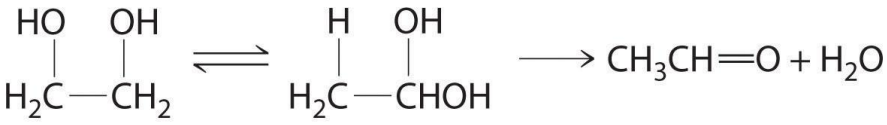
Equation 23.22

$$CoCH2R \square \quad Co2+\times+ \times CH2R$$

Homolytic cleavage of the Co^{3+}–CH_2R bond produces two species, each of which has an unpaired electron: a d^7 Co^{2+} derivative and an organic radical, $\cdot CH_2R$, which is used by vitamin B_{12}-dependent enzymes to catalyze a wide variety of reactions. Virtually all vitamin B_{12}-catalyzed reactions are rearrangements in which an H atom and an adjacent substituent exchange positions:



In the conversion of ethylene glycol to acetaldehyde, the initial product is the hydrated form of acetaldehyde, which rapidly loses water:



The enzyme uses the $\cdot CH_2R$ radical to temporarily remove a hydrogen atom from the organic substrate, which then rearranges to give a new radical. Transferring the hydrogen atom back to the rearranged radical gives the product and regenerates the $\cdot CH_2R$ radical.

The metal is not involved in the actual catalytic reaction; it provides the enzyme with a convenient mechanism for generating an organic radical, which does the actual work. Many examples of similar reactions are now known that use metals other than cobalt to generate an enzyme-bound organic radical.

Note the Pattern

Nearly all vitamin B_{12}-catalyzed reactions are rearrangements that occur via a radical reaction.

Summary

Three separate steps are required for organisms to obtain essential transition metals from their environment: mobilization of the metal, transport of the metal into the cell, and transfer of the metal to where it is needed within a cell or an organism. The process of iron uptake is best understood. To overcome the insolubility of $Fe(OH)_3$, many bacteria use organic ligands called **siderophores**, which have high affinity for Fe(III) and are secreted into the surrounding medium to increase the total concentration of dissolved iron. The iron–siderophore complex is absorbed by a cell, and the iron is released by reduction to Fe(II). Mammals use the low pH of the stomach to increase the concentration of dissolved iron. Iron is absorbed in the intestine, where it forms an Fe(III) complex with a protein called transferrin that is transferred to other cells for immediate use or storage in the form of ferritin.

Proteins that contain one or more tightly bound metal ions are called**metalloproteins**, and metalloproteins that catalyze biochemical reactions are called **metalloenzymes**. Proteins that transfer electrons from one place to another are called electron-transfer proteins. Most electron-transfer proteins are metalloproteins, such as iron–sulfur proteins, cytochromes, and blue copper proteins that accept and

donate electrons. The oxidized and reduced centers in all electron-transfer proteins have similar structures to ensure that electron transfer to and from the metal occurs rapidly. Metalloproteins also use the ability of transition metals to bind small molecules, such as O_2, N_2, and H_2, to transport or catalyze the reactions of these small molecules. For example, hemoglobin, hemerythrin, and hemocyanin, which contain heme iron, nonheme iron, and copper, respectively, are used by different kinds of organisms to bind and transfer O_2. Other metalloenzymes use transition-metal ions as Lewis acids to catalyze group transfer reactions. Finally, some metalloenzymes use homolytic cleavage of the cobalt–carbon bond in derivatives of vitamin B_{12} to generate an organic radical that can abstract a hydrogen atom and thus cause molecular rearrangements to occur.

KEY TAKEAWAY

- Organisms have developed strategies to extract transition metals from the environment and use the metals in electron-transfer reactions, reactions of small molecules, Lewis-acid catalysis, and the generation of reactive organic radicals.

CONCEPTUAL PROBLEMS

1. What are the advantages of having a metal ion at the active site of an enzyme?
2. Why does the structure of the metal center in a metalloprotein that transfers electrons show so little change after oxidation or reduction?

STRUCTURE AND REACTIVITY

1. In enzymes, explain how metal ions are particularly suitable for generating organic radicals.
2. A common method for treating carbon-monoxide poisoning is to have the patient inhale pure oxygen. Explain why this treatment is effective.

23.7 End-of-Chapter Material

APPLICATION PROBLEMS

1. Tungsten bronzes are semimetallic solids that are inert to strong acids and bases, lustrous, and good conductors of electricity; they are used in the production of bronze or metallic paints. These nonstoichiometric compounds have the general formula $MxWO_3$, where M = Na, K, a group 2 metal, or a lanthanide and $x < 1$. The properties of tungsten bronzes suggest that at least some of the tungsten atoms are in the +6 oxidation state. Given the high oxidation state, why do these solids conduct electricity?

2. Gout is a painful disorder caused by the overproduction of uric acid, which is deposited as sodium urate crystals in joints. The enzyme that catalyzes the production of uric acid contains Fe^{3+} and Mo^{6+}. Molecular oxygen is a substrate in this reaction. Based on the oxidation states of the metals, what do you expect one of the products of the reaction to be?
3. A laboratory technician added aqueous ammonia to an aqueous solution of Mn^{2+}, which produced a pale pink precipitate. She left the solution exposed to air and went home. The next day she returned to the lab and found that her pink precipitate had turned brown-black. Write balanced chemical equations to show what had happened.
4. Plants use Mn(IV) during photosynthesis to produce dioxygen from water. Write a balanced chemical equation showing this reaction and suggest why Mn is well suited for this purpose.
5. Rust stains (Fe_2O_3) can be removed from fabrics by oxalic acid (HO_2CCO_2H). Write a balanced chemical equation showing the reaction that occurs and predict the solubility of the product in water.
6. It has been suggested that complexes that can coordinate N_2 are used by bacteria to fix atmospheric nitrogen. One such complex is $[Ru(NH_3)_5 \cdot N_2]Cl_2$, which was first discovered in 1965. Sigma bonding with N_2 in this complex would be weak because the N_2 molecule is symmetrical and has zero dipole moment.

a. What is the oxidation state of Ru in this complex?

b. How does N_2 bond to the metal? Describe the type of bonding involved.

c. Speculate why this complex might be a suitable vehicle for nitrogen fixation.

7. Monel metal, which contains 68% Ni, 32% Cu, and traces of Fe and Mn, is highly corrosion resistant. It is used, for example, to make items that will be used in marine environments and to hold corrosive fluorine compounds. Based on its composition, why is Monel particularly suitable for these purposes?
8. From 1845 to 1850, a fungus known as “potato blight” caused a potato famine in Ireland. Approximately 25% of the Irish population either died or emigrated as a direct result. A spray called *Bordeaux mixture* is now used to kill the fungus; it is made by the reaction of $CuSO_4$ with $Ca(OH)_2$. What is the formula of the Bordeaux mixture? Write a balanced chemical equation for the reaction.
9. Many transition metals and their compounds are used as catalysts. Given MnO_2, $FeCl_3$, Pt, and Ni, which would you select for each purpose and why?

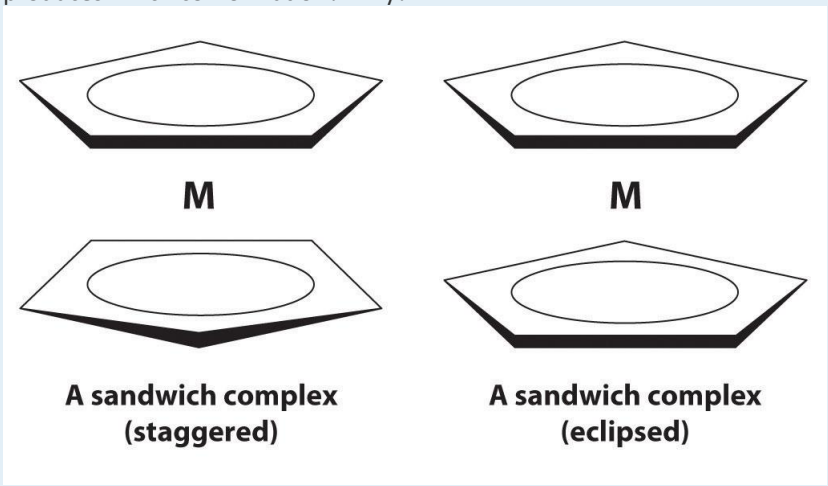
a. removing NO*x* from exhaust fumes

b. producing CCl_4 from CS_2 and Cl_2

c. producing H_2 from NH_3

d. decomposing $KClO_3$ to give O_2

10. The Fe^{2+} site in hemoglobin binds oxygen reversibly; consequently, it is suitable for transporting oxygen in blood. Various other small molecules can bind to the iron instead, thus preventing oxygen transport. Based on the type of bonding, why are CO and NO particularly toxic? Would they be as toxic if hemoglobin contained a V^{2+} center instead of Fe^{2+}? Why?
11. In 1951, G. Wilkinson reported a surprising iron–hydrocarbon compound that is now called *ferrocene*. Ferrocene is orange and has a structure in which the metal is sandwiched between two planar cyclopentadienyl ($C_5H_5^-$) rings. It can be viewed as a compound of Fe^{2+} with two $C_5H_5^-$ rings. Ferrocene does not contain Fe–C σ bonds but another type of bond formed by the lateral overlap of orbitals. Which metal orbitals are involved? A similar structure is obtained with Ru^{2+}. One of these metals forms a sandwich complex that has a staggered conformation, and the other forms a complex that is eclipsed. Which metal produces which conformation? Why?



12. The Ziegler–Natta catalyst is used for the polymerization of ethylene to form high-density polyethylene, a widely used lightweight plastic. The active form of the catalyst is believed to be $TiCl_3CH_2CH_3$, and the first step in the polymerization reaction is believed to be binding of the double bond in ethylene to Ti. If you were interested in developing a similar catalyst for this same purpose, would you choose chlorides of Zr, Hf, V, Nb, Ta, Cr, Mo, or W? Why?
13. Cobalt(II) chloride is used as a visual indicator of humidity because it exists as a blue complex when dry and a pink complex when exposed to moisture in the air. The bonding environment around the cobalt in one of

these complexes is octahedral; in the other, it is tetrahedral. What reaction occurs to produce the color change? Write a balanced chemical equation for this reaction, indicating the species present.

14. A platinum complex that is widely available commercially is chloroplatinic acid {$H_2[PtCl_6]$}, which is used to make platinized asbestos, a catalyst. What is the structure of chloroplatinic acid? Is it distorted from an idealized geometry? Do you expect it to be colored? Justify your answers.

ANSWERS

1. The tungsten bronzes can be viewed as the products of partial reduction of WO_3 by an active metal to give a mixture of W(VI) and W(V). In the solid, the *d* orbitals of the metal overlap to form a partially filled band, which is responsible for the luster and metallic conductivity.
2.
3.
4.
5.
6.
7.
8.
9.

a. Pt; it can oxidize ammonia to NO, so it should be able to reduce NO_x as well.

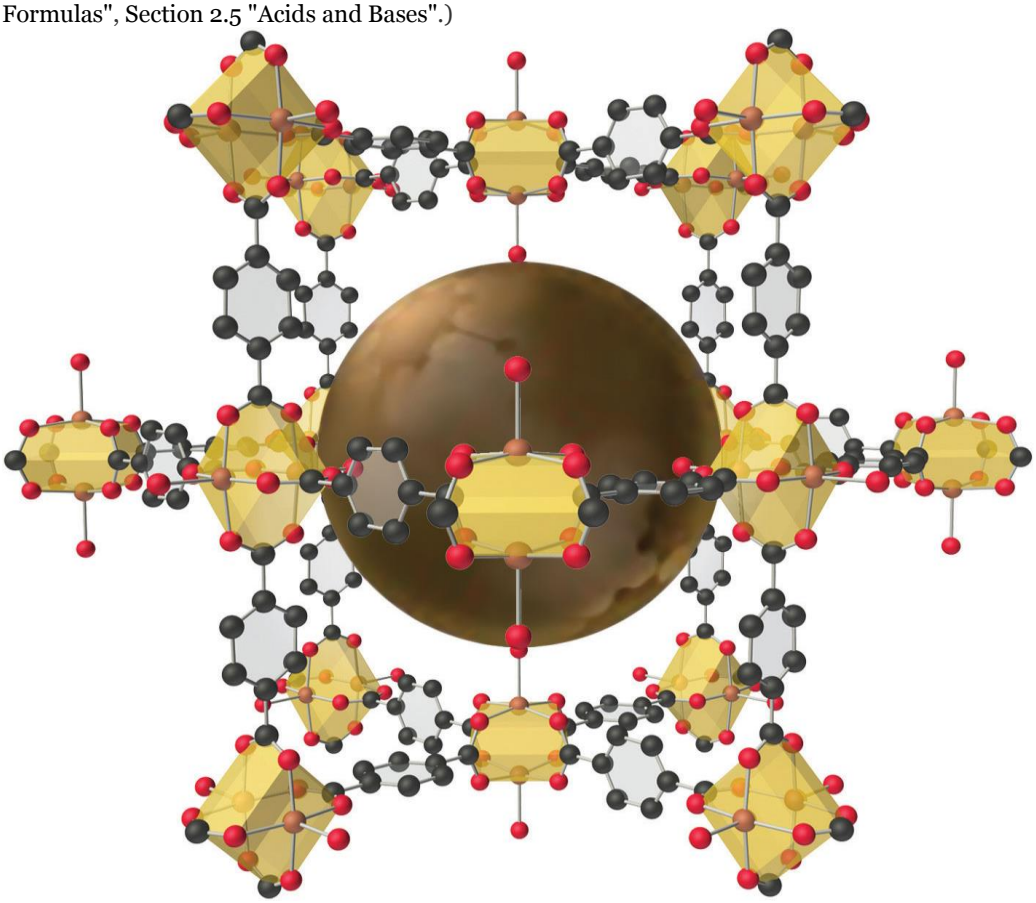
b. Ni; it has a low affinity for S and is hard to oxidize about the +2 state.

c. $FeCl_3$; it catalyzes the formation of NH_3 from the elements, so it must also catalyze its decomposition.

d. MnO_2; this is a well-known catalyst for decomposition of $KClO_3$ and has been mentioned several times in the text.

Chapter 24
Organic Compounds

In Chapter 2 "Molecules, Ions, and Chemical Formulas", you were introduced to the major classes of *organic compounds*, covalent compounds composed primarily of carbon and hydrogen. Organic substances have been used throughout this text to illustrate the differences between ionic and covalent bonding and to demonstrate the intimate connection between the structures of compounds and their chemical reactivity. You learned, for example, that even though NaOH and alcohols (ROH) both have OH in their formula, NaOH is an ionic compound that dissociates completely in water to produce a basic solution containing Na^+ and OH^- ions, whereas alcohols are covalent compounds that do not dissociate in water and instead form neutral aqueous solutions. You also learned that an amine (RNH_2), with its lone pairs of electrons, is a base, whereas a carboxylic acid (RCO_2H), with its dissociable proton, is an acid. (For more information on acids and bases, see Chapter 2 "Molecules, Ions, and Chemical Formulas", Section 2.5 "Acids and Bases".)



The structure of a solid with a hybrid metal-organic framework. *Organic and inorganic groups of the proper structure can be used to synthesize solids with very large pores (central sphere) that can accommodate a variety of small molecules. The rigid benzene rings are used as "props" to hold the metal units*

(carboxylate-bridged copper dimers) apart. Such solids have potential applications in hydrogen storage for use in fuel cells or automobiles.

Carbon is unique among the elements in its ability to *catenate*, to form a wide variety of compounds that contain long chains and/or rings of carbon atoms. (For more information on carbon, see Chapter 12 "Solids", Section 12.8 "Polymeric Solids", andChapter 22 "The ", Section 22.2 "The Elements of Group 14".) Some of the most complex chemical structures known are those of the organic molecules found in living organisms. (For more information on biopolymers, see Chapter 12 "Solids", Section 12.8 "Polymeric Solids".) In spite of their size and complexity, these biological molecules obey the same chemical principles as simpler organic molecules. Thus we can use Lewis electron structures to understand the preferred mode of reactivity of a variety of organic compounds, relative electronegativities and bond polarities to predict how certain groups of atoms will react, and molecular orbital theory to explain why certain organic species that contain multiple bonds are especially stable or undergo particular reactions when they interact with light. (For more information on Lewis electron structures, see Chapter 8 "Ionic versus Covalent Bonding", Section 8.5 "Lewis Structures and Covalent Bonding". For more information on bonding, see Chapter 8 "Ionic versus Covalent Bonding", Section 8.9 "Polar Covalent Bonds". For more information on light interactions, see Chapter 9 "Molecular Geometry and Covalent Bonding Models", Section 9.4 "Polyatomic Systems with Multiple Bonds".) In this chapter, we continue our description of organic compounds by focusing on their molecular structures and reactivity; we will also introduce some of the fundamental types of reactions and reaction mechanisms you will encounter in organic and biological chemistry. We discuss why butter is a solid and oils are liquids despite the apparent similarities in their structures, why the widely used anti-inflammatory drug ibuprofen takes longer than half an hour to relieve pain, and the identity of the major carcinogen in grilled meats and cigarette smoke. The chapter concludes with a brief introduction to the molecules of life, which will explain how the consumption of lactose can result in mental retardation and cirrhosis of the liver in some individuals, how hibernating animals survive during the winter, and how certain groups of antibiotics kill bacteria that are harmful to humans.

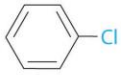
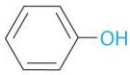
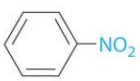
24.1 Functional Groups and Classes of Organic Compounds

LEARNING OBJECTIVE

1. To know the major classes of organic compounds and identify important functional groups.

In Chapter 2 "Molecules, Ions, and Chemical Formulas" and Chapter 5 "Energy Changes in Chemical Reactions", you were introduced to several structural units that chemists use to classify organic compounds and predict their reactivities. These**functional groups**, which determine the chemical reactivity of a molecule under a given set of conditions, can consist of a single atom (such as Cl) or a group of atoms (such as CO_2H). The major families of organic compounds are characterized by their functional groups. Figure 24.1 "Major Classes of Organic Compounds" summarizes five families introduced in earlier chapters, gives examples of compounds that contain each functional group, and lists the suffix or prefix used in the systematic nomenclature of compounds that contain each functional group.

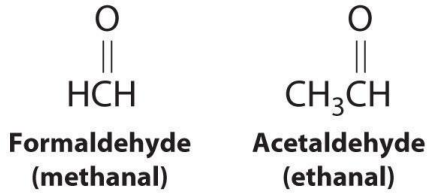
Figure 24.1 *Major Classes of Organic Compounds*

Class	General Formula	Example	Common Name (Systematic Name)	Common Suffix/Prefix (Systematic)
Hydrocarbons				
Alkanes	RH	CH_3CH_3	ethane	-ane
Alkenes	RR′C═CR″R‴	$H_2C{=}CH_2$	ethylene (ethene)	-ene
Alkynes	RC≡CR′	$HC{\equiv}CH$	acetylene (ethyne)	(-yne)
Arenes	ArH[a]		benzene	-ene
Halogen-Containing Compounds				
Alkyl halides	RX	CH_3CH_2Cl	ethyl chloride (chloroethane)	halide (halo-)
Aryl halides	ArX[a]		chlorobenzene	halo-
Oxygen-Containing Compounds				
Alcohols	ROH[a]	CH_3CH_2OH	ethyl alcohol (ethanol)	-ol
Phenols	ArOH[b]		phenol	-ol
Ethers	ROR′	$H_3CH_2COCH_2CH_3$	diethyl ether	ether
Aldehydes	RCHO		acetaldehyde (ethanal)	-aldehyde (-al)
Ketones	RR′C═O		acetone (2-propanone)	-one
Carboxylic acids	RCO_2H		acetic acid (ethanoic acid)	-ic acid (-oic acid)
Carboxylic Acid Derivatives				
Esters	RCO_2R'		methyl acetate (methyl ethanoate)	-ate (-oate)
Amides	RCONHR′		*N*-methylacetamide	-amide
Nitrogen-Containing Compounds				
Amines	RNH_2, RNHR′, RNR′R″	$CH_3CH_2NH_2$	ethylamine	-amine
Nitriles	RC≡N	$H_3CC{\equiv}N$	acetonitrile	-nitrile
Nitro compounds	$ArNO_2$[a]		nitrobenzene	nitro-

[a] R indicates an alkyl group [b] Ar indicates an *aryl* group.

The first family listed in Figure 24.1 "Major Classes of Organic Compounds" is the hydrocarbons. These include alkanes, with the general molecular formula C_nH_{2n+2} where n is an integer; alkenes, represented by C_nH_{2n}; alkynes, represented by C_nH_{2n-2}; and arenes. Halogen-substituted alkanes, alkenes, and arenes form a second major family of organic compounds, which include the alkyl halides and the aryl halides. Oxygen-containing organic compounds, a third family, may be divided into two main types: those that contain at least one C–O bond, which include alcohols, phenols (derivatives of benzene), and ethers, and those that contain a carbonyl group (C=O), which include aldehydes, ketones, and carboxylic acids. Carboxylic acid derivatives, the fourth family listed, are compounds in which the OH of the $-CO_2H$ functional group is replaced by either an alkoxy (–OR) group, producing an ester, or by an amido (–NRR′, where R and R′ can be H and/or alkyl groups), forming an amide. Nitrogen-containing organic compounds, the fifth family, include amines; nitriles, which have a C≡N bond; and nitro compounds, which contain the $-NO_2$ group.

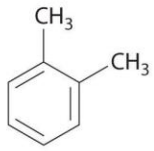
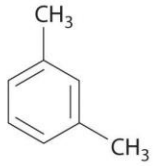
As you learned in Chapter 2 "Molecules, Ions, and Chemical Formulas", Section 2.4 "Naming Covalent Compounds", the systematic nomenclature of organic compounds indicates the positions of substituents using the lowest numbers possible to identify their locations in the carbon chain of the parent compound. If two compounds have the same systematic name, then they are the same compound. Although systematic names are preferred because they are unambiguous, many organic compounds are known by their common names rather than their systematic names. Common nomenclature uses the prefix *form*—for a compound that contains no carbons other than those in the functional group, and *acet*—for those that have one carbon atom in addition [two in the case of acetone, $(CH_3)_2C=O$]. Thus methanal and ethanal, respectively, are the systematic names for formaldehyde and acetaldehyde.



Recall that in the systematic nomenclature of aromatic compounds, the positions of groups attached to the aromatic ring are indicated by numbers, starting with 1 and proceeding around the ring in the direction that produces the lowest possible numbers. For example, the position of the first CH_3 group in dimethyl benzene is indicated with a 1, but the second CH_3 group, which can be placed in any one of three positions, produces 1,2-dimethylbenzene, 1,3-dimethylbenzene, or 1,4-dimethylbenzene (Figure 24.2 "Common Nomenclature for Aromatic Ring Substitutions"). In common nomenclature, in contrast, the prefixes *ortho*-, *meta*-, and *para*- are used to describe the relative

positions of groups attached to an aromatic ring. If the CH_3 groups in dimethylbenzene, whose common name is xylene, are adjacent to each other, the compound is commonly called *ortho*-xylene, abbreviated *o*-xylene. If they are across from each other on the ring, the compound is commonly called *para*-xylene or *p*-xylene. When the arrangement is intermediate between those of *ortho*- and *para*- compounds, the name is *meta*-xylene or *m*-xylene.

Figure 24.2 *Common Nomenclature for Aromatic Ring Substitutions*

Prefix	Positions of Methyl Groups	Example	Common Name (Systematic Name)
ortho-	1,2		*o*-xylene (1,2-dimethylbenzene)
meta-	1,3		*m*-xylene (1,3-dimethylbenzene)
para-	1,4		*p*-xylene (1,4-dimethylbenzene)

We begin our discussion of the structure and reactivity of organic compounds by exploring structural variations in the simple saturated hydrocarbons known as alkanes. These compounds serve as the scaffolding to which the various functional groups are most often attached.

Summary

Functional groups are structural units that determine the chemical reactivity of a molecule under a given set of conditions. Organic compounds are classified into several major categories based on the functional groups they contain. In the systematic names of organic compounds, numbers indicate the positions of functional groups in the basic hydrocarbon framework. Many organic compounds also have common names, which use the prefix *form*—for a compound that contains no carbons other than those in the functional group and *acet*—for those that have one additional carbon atom.

KEY TAKEAWAY

- Functional groups determine the chemical reactivity of an organic molecule.

CONCEPTUAL PROBLEMS

1. Can two substances have the same systematic name and be different compounds?
2. Is a carbon–carbon multiple bond considered a functional group?

24.2 Isomers of Organic Compounds

LEARNING OBJECTIVE

1. To learn how organic compounds with the same molecular formula can have different three-dimensional structures.

In earlier discussions of organic compounds, we focused on differences in how the functional groups were connected to the carbon framework. Differences in connectivity resulted in different chemical compounds with different names. You learned, for example, that although 1-propanol (*n*-propanol) and 2-propanol (isopropanol) have the same molecular formula (C_3H_8O), they have different physical and chemical properties. Just as with metal complexes, compounds that have the same molecular formula but different arrangements of atoms are called isomers. (For more information on metal complexes, see Chapter 23 "The ", Section 23.4 "Coordination Compounds".) In this section, we describe various types of isomers, beginning with those whose three-dimensional structures differ only as the result of rotation about a C–C bond.

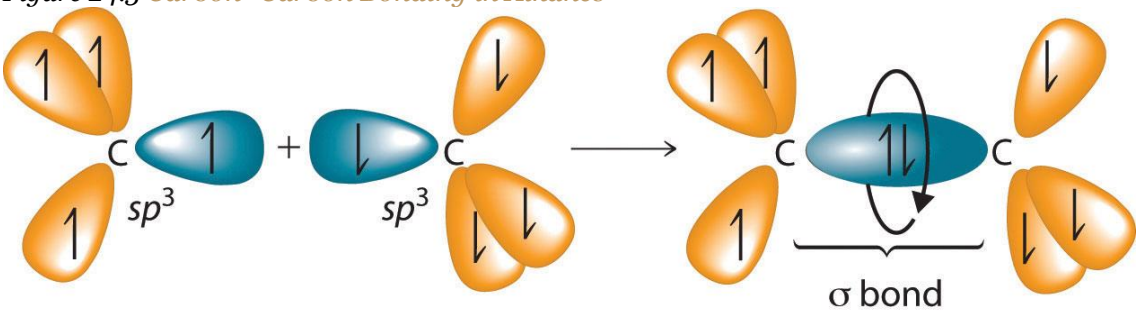
Conformational Isomers

The C–C single bonds in ethane, propane, and other alkanes are formed by the overlap of an sp^3 hybrid orbital on one carbon atom with an sp^3 hybrid orbital on another carbon atom, forming a σ bond (Figure 24.3 "Carbon–Carbon Bonding in Alkanes"). Each sp^3 hybrid orbital is cylindrically symmetrical (all cross-sections are circles), resulting in a carbon–carbon single bond that is also cylindrically symmetrical about the C–C axis. Because rotation about the carbon–carbon single bond can occur without changing the overlap of the sp^3 hybrid orbitals, there is no significant electronic energy barrier to rotation. Consequently, many different arrangements of the atoms are possible, each corresponding to different degrees of rotation. Differences in three-dimensional structure resulting from rotation about a σ bond are called differences in*conformation*, and each different arrangement is called aconformational isomer (or conformer).

Note the Pattern

Conformational isomers differ in their three-dimensional structure due to rotation about a σ bond.

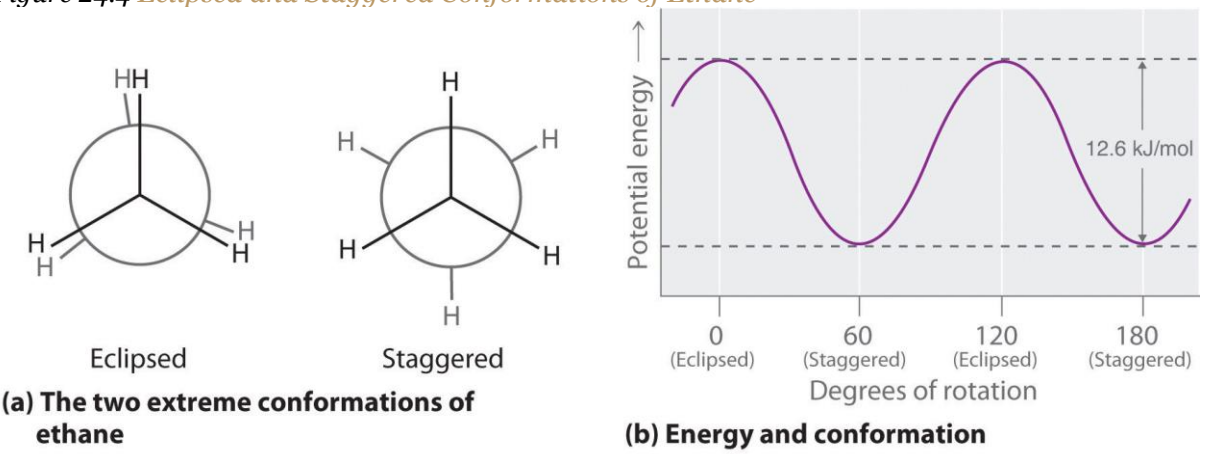
Figure 24.3 *Carbon–Carbon Bonding in Alkanes*



Overlapping sp^3 hybrid orbitals on adjacent carbon atoms form a cylindrically symmetrical σ bond. Because rotation about the bond does not affect the overlap of the bonding orbitals, there is no electronic energy barrier to rotation.

The simplest alkane to have a conformational isomer is ethane. Differences between the conformations of ethane are depicted especially clearly in drawings called *Newman projections*, such as those shown in part (a) in Figure 24.4 "Eclipsed and Staggered Conformations of Ethane". In a Newman projection, the ethane molecule is viewed along the C–C axis, with the carbon that is in front shown as a vertex and the carbon that is in back shown as a circle. The three hydrogen atoms nearest the viewer are shown bonded to the front carbon, and the three hydrogen atoms farthest from the viewer are shown bonded to the circle. In one extreme, called the *eclipsed conformation*, the C–H bonds on adjacent carbon atoms lie in the same plane. In the other extreme, called the *staggered conformation*, the hydrogen atoms are positioned as far from one another as possible. Rotation about the C–C bond produces an infinite number of conformations between these two extremes, but the staggered conformation is the most stable because it minimizes electrostatic repulsion between the hydrogen atoms on adjacent carbons.

Figure 24.4 *Eclipsed and Staggered Conformations of Ethane*

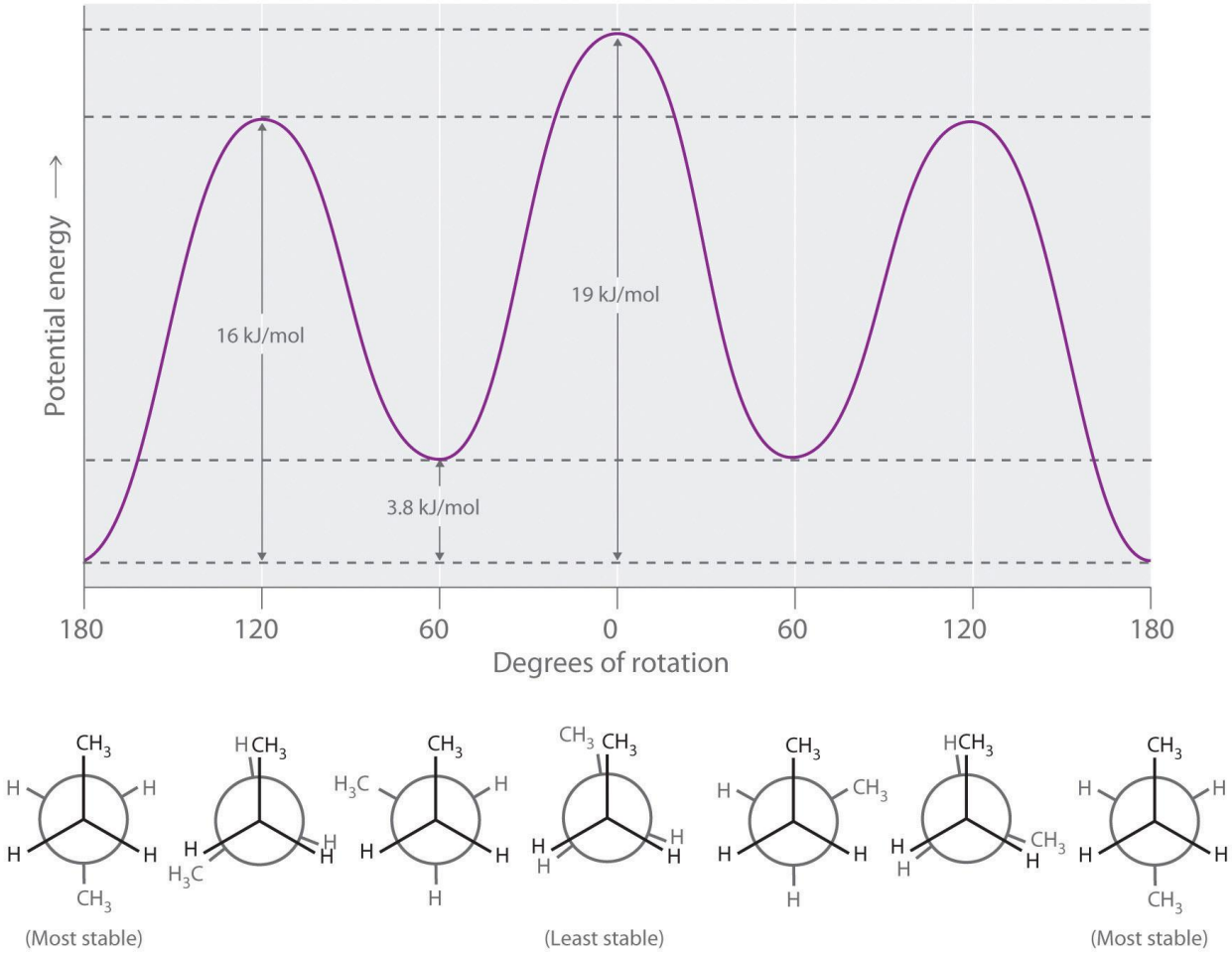


(a) In a Newman projection, the molecule is viewed along a C–C axis. The carbon in front is represented as a vertex, whereas the carbon that is bonded to it is represented as a circle. In ethane, the C–H bonds to each carbon are positioned at 120° from each other. In the fully eclipsed conformation, the C–H bonds on adjacent carbon atoms are parallel and lie in the same plane. In the staggered conformation, the hydrogen atoms are positioned as far apart as possible. (b) The eclipsed conformation is 12.6 kJ/mol higher in energy than the staggered conformation because of electrostatic repulsion between the hydrogen atoms. An infinite number of conformations of intermediate energy exist between the two extremes.

In a Newman projection, the angles between adjacent C–H bonds on the same carbon are drawn at 120°, although H–C–H angles in alkanes are actually tetrahedral angles of 109.5°, which for chains of more than three carbon atoms results in a *kinked*structure. (For more information on bond angles and molecular modeling, see Chapter 2 "Molecules, Ions, and Chemical Formulas", Section 2.1 "Chemical Compounds".) Despite this three-dimensional inaccuracy, Newman projections are useful for predicting the relative stability of conformational isomers. As shown in part (b) inFigure 24.4 "Eclipsed and Staggered Conformations of Ethane", the higher energy of the eclipsed conformation represents an energy barrier of 12.6 kJ/mol that must be overcome for rotation about the C–C bond to occur. This barrier is so low, however, that rotation about the C–C bond in ethane is very fast at room temperature and occurs several million times per second for each molecule.

Longer-chain alkanes can also be represented by Newman projections. In more complex alkanes and alkane derivatives, rotation can occur about *each* C–C bond in a molecule. Newman projections are therefore useful for revealing *steric barriers* to rotation at a particular C–C bond due to the presence of bulky substituents. Figure 24.5 "Potential Energy Plot and Newman Projections of Eclipsed and Staggered Conformations of " shows a plot of potential energy versus the angle of rotation about the central C–C bond (between carbon atoms 2 and 3) of *n*-butane (C_4H_{10}). The structure that minimizes electrostatic repulsion is the one in which the methyl groups, corresponding to carbon atoms 1 and 4, are as far apart as possible; that is, the staggered conformation. Notice that because the substituents on C2 and C3 in *n*-butane are not all the same, energetically nonequivalent eclipsed and staggered conformations are possible; most molecules interconvert rapidly between these conformations by a series of simple rotations.

Figure 24.5 *Potential Energy Plot and Newman Projections of Eclipsed and Staggered Conformations of n-Butane*



In these projections, the molecule is viewed along the C2–C3 axis. The least stable structure is the eclipsed conformation in which the two methyl groups (C1 and C4) are adjacent to each other. The most stable structure is the staggered conformation in which the methyl groups are as far apart as possible. Because the substituents on each central carbon atom are not all the same, a 120° rotation about the C2–C3 bond generates energetically nonequivalent eclipsed and staggered conformations.

EXAMPLE 1

Draw Newman projections showing the staggered and eclipsed conformations of 1,1,1-trichloroethane (CCl_3CH_3).

Given: organic molecule

Asked for: staggered and eclipsed conformations

Strategy:

A Identify the C–C bond of interest. Then draw the Newman projection by representing one carbon as a vertex and the other as a circle.

B Draw bonds to each carbon at 120° angles from one another, with one arrangement representing the staggered conformation and the other the eclipsed conformation.

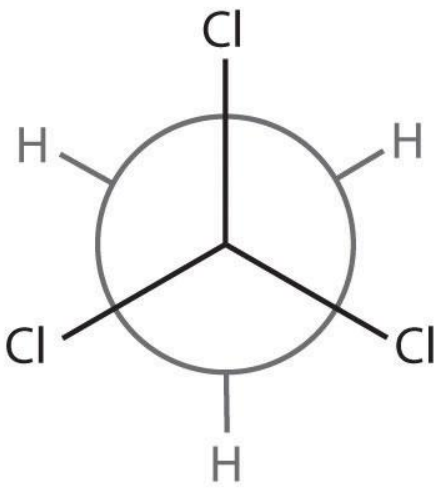
C Complete the Newman projections by attaching the appropriate atoms or substituent groups to the central C atoms in each conformation.

Solution:

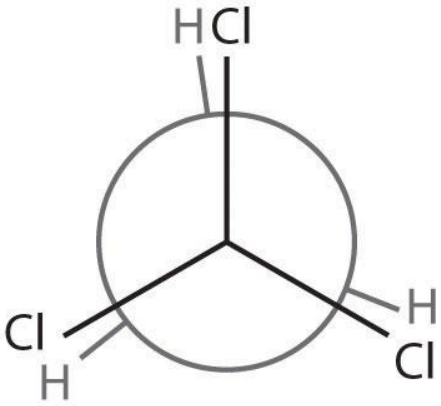
A There is only one C–C bond: C1 is connected to three Cl atoms and C2 to three H atoms. We draw C1 as a point and C2 as a circle.

B Now we draw bonds on each carbon at 120° angles from one another to represent the staggered conformation and the eclipsed conformation.

C We then attach the H and Cl atoms to the carbon atoms in each conformation as shown.



Staggered

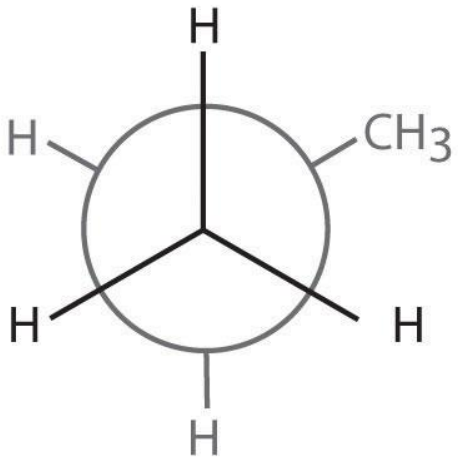


Eclipsed

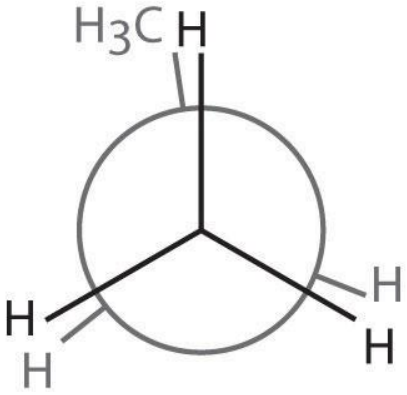
Exercise

Draw Newman projections to illustrate the staggered and eclipsed conformations of propane (C_3H_8) as viewed along the C1–C2 axis.

Answer:



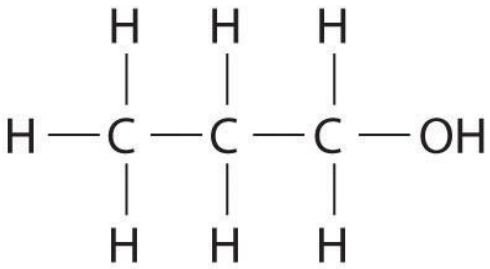
Staggered



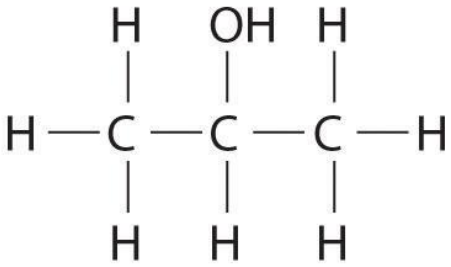
Eclipsed

Structural Isomers

Unlike conformational isomers, which do not differ in connectivity,structural isomers differ in connectivity, as illustrated here for 1-propanol and 2-propanol. (For more information on structural isomers, see Chapter 23 "The ", Section 23.4 "Coordination Compounds".) Although these two alcohols have the same molecular formula (C_3H_8O), the position of the –OH group differs, which leads to differences in their physical and chemical properties.

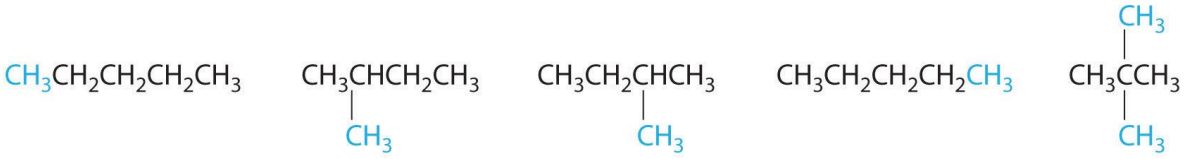


1-Propanol (*n*-propanol)



2-Propanol (isopropanol)

In the conversion of one structural isomer to another, *at least one bond must be broken and reformed at a different position in the molecule*. Consider, for example, the following five structures represented by the formula C_5H_{12}:



(a) **(b)** **(c)** **(d)** **(e)**

Of these structures, (a) and (d) represent the same compound, as do (b) and (c). No bonds have been broken and reformed; the molecules are simply rotated about a 180° vertical axis. Only three—*n*-pentane (a) and (d), 2-methylbutane (b) and (c), and 2,2-dimethylpropane (e)—are structural isomers. Because no bonds are broken in going from (a) to (d) or from (b) to (c), these alternative representations are not structural isomers. The three structural isomers—either (a) or (d), either (b) or (c), and (e)—have distinct physical and chemical properties.

Note the Pattern

Structural isomers differ in their connectivity.

EXAMPLE 2

Draw all the structural isomers of C_6H_{14}.

Given: organic molecule

Asked for: all structural isomers

Strategy:

A Draw the simplest structural isomer, which is often the straight-chain alkane.

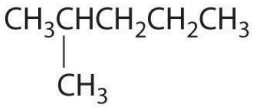
B Obtain branched isomers by substituting one hydrogen along the chain with an appropriate group from the chain.

C If possible, substitute more than one hydrogen with appropriate groups to obtain isomers that are more highly branched.

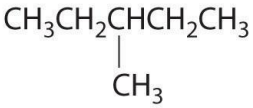
Solution:

A The simplest structural isomer is the straight-chain alkane *n*-hexane ($CH_3CH_2CH_2CH_2CH_2CH_3$).

B Removing a methyl group from one end and reattaching it to adjacent carbons while substituting hydrogen in its place give two other structures:

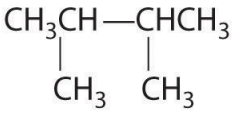


2-Methylpentane



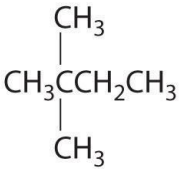
3-Methylpentane

C To obtain yet another structural isomer, move two methyl groups to create a molecule with two branches:



2,3-Dimethylbutane

We create one more structural isomer by attaching two methyl groups to the same carbon atom:



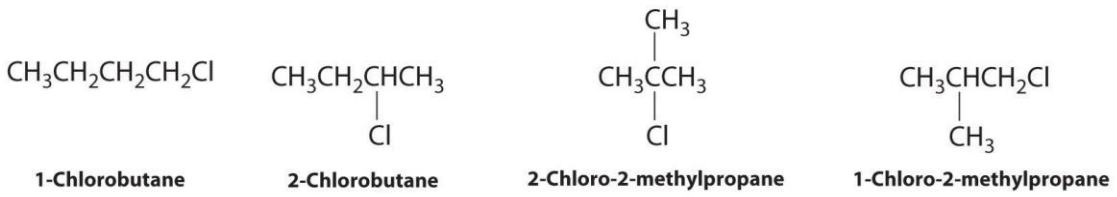
2,2-Dimethylbutane

Thus there are four structural isomers of C_6H_{14}.

Exercise

Draw all the structural isomers of C_4H_9Cl.

Answer:



1-Chlorobutane | 2-Chlorobutane | 2-Chloro-2-methylpropane | 1-Chloro-2-methylpropane

Stereoisomers

Molecules with the same connectivity but different arrangements of the atoms in space are called stereoisomers. There are two types of stereoisomers: geometric and optical. *Geometric isomers* differ in the relative position(s) of substituents in a rigid molecule. (For more information on stereoisomers, see Chapter 23 "The ", Section 23.4 "Coordination Compounds".) Simple rotation about a C–C σ bond in an alkene, for example, cannot occur because of the presence of the π bond. The substituents are therefore rigidly locked into a particular spatial arrangement (part (a) in Figure 2.16 "Some Simple (a) Alkenes, (b) Alkynes, and (c) Cyclic Hydrocarbons"). Thus a carbon–carbon multiple bond, or in some cases a ring, prevents one geometric isomer from being readily converted to the other. The members of an isomeric pair are identified as either *cis* or *trans*, and interconversion between the two forms requires breaking and reforming one or more bonds. Because their structural difference causes them to have different physical and chemical properties, *cis* and *trans* isomers are actually two distinct chemical compounds.

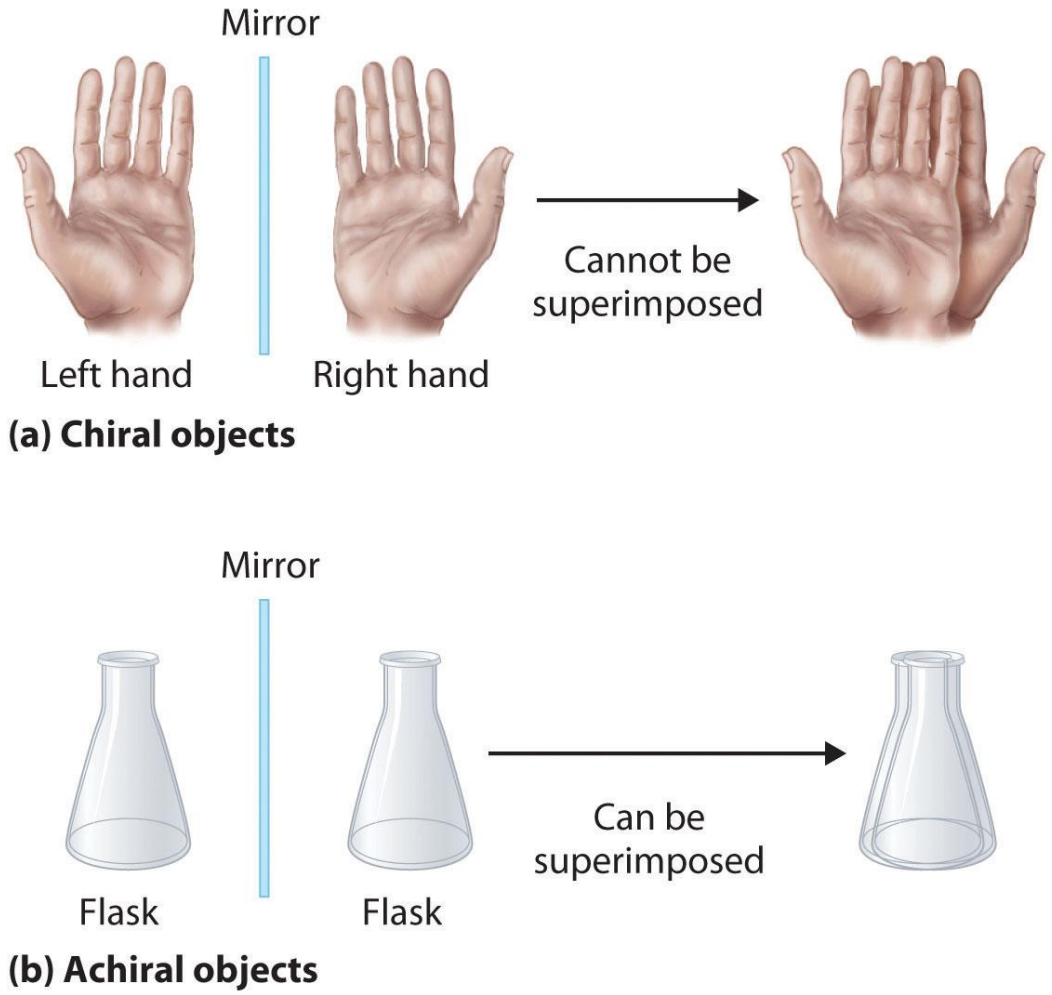
Note the Pattern

Stereoisomers have the same connectivity but different arrangements of atoms in space.

Optical isomers are molecules whose structures are mirror images but cannot be superimposed on one another in any orientation. Optical isomers have *identical physical properties*, although their chemical properties may differ in asymmetric environments. Molecules that are nonsuperimposable mirror images of each other are said to be *chiral* (pronounced “ky-ral,” from the Greek *cheir*, meaning “hand”). Examples of some familiar chiral objects are your hands, feet, and ears. As shown in part (a) in Figure 24.6 "Chiral and Achiral Objects", your left and right hands are nonsuperimposable mirror images. (Try putting your right shoe on your left foot—it just doesn’t work.) An *achiral* object is one that *can* be

superimposed on its mirror image, as shown by the superimposed flasks in part (b) in Figure 24.6 "Chiral and Achiral Objects".

Figure 24.6 *Chiral and Achiral Objects*

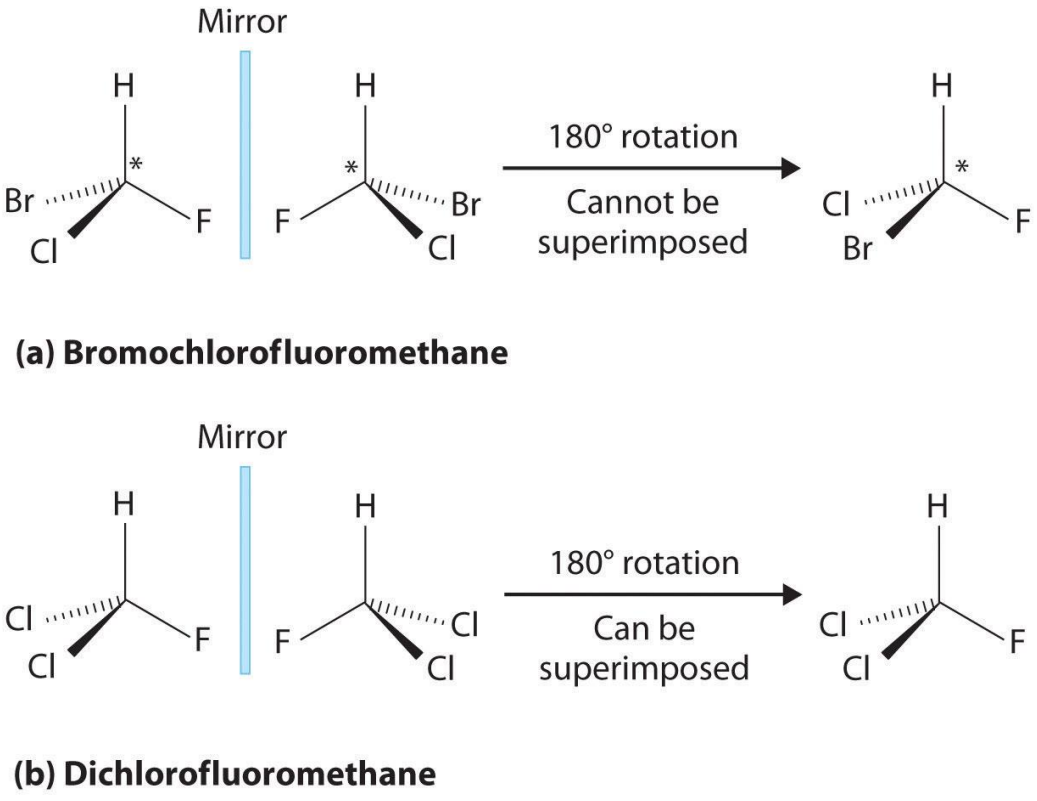


(a) Objects that are nonsuperimposable mirror images of each other are chiral, such as the left and the right hand. (b) The unmarked flask is achiral because it can be superimposed on its mirror image.

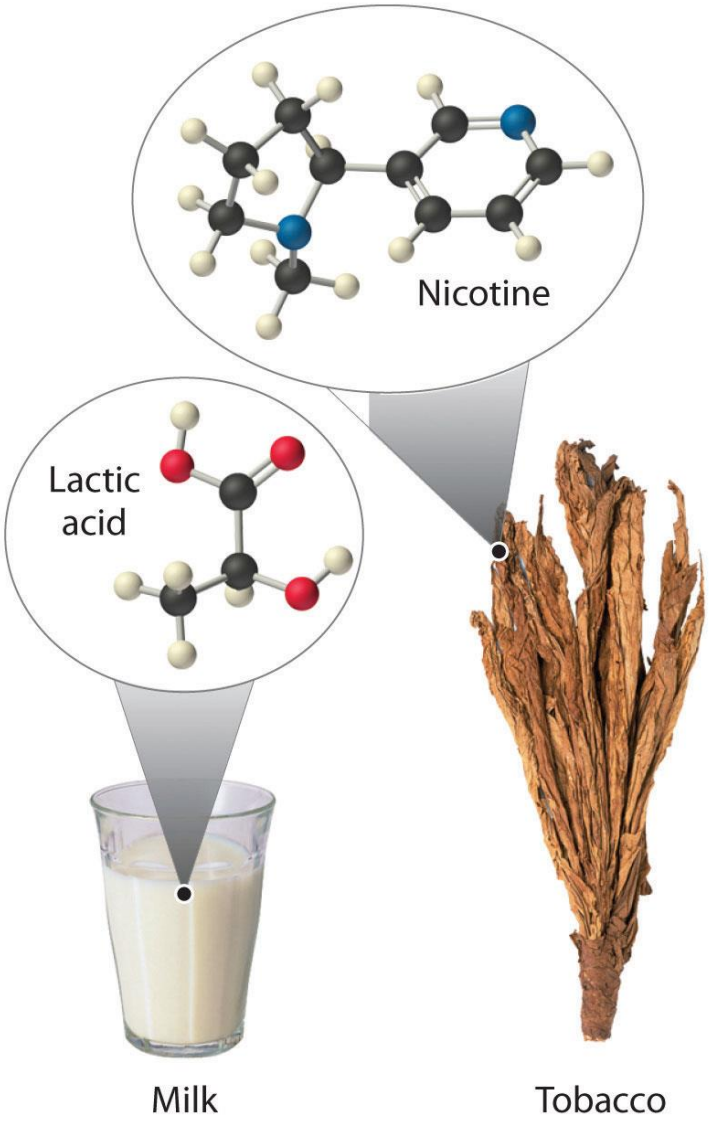
Most chiral organic molecules have at least one carbon atom that is bonded to four different groups, as occurs in the bromochlorofluoromethane molecule shown in part (a) in Figure 24.7 "Comparison of Chiral and Achiral Molecules". This carbon, often designated by an asterisk in structural drawings, is called a *chiral center* or*asymmetric carbon atom*. If the bromine atom is replaced by another chlorine (part (b) in Figure 24.7 "Comparison of Chiral and Achiral Molecules"), the molecule and its mirror image can now

be superimposed by simple rotation. Thus the carbon is no longer a chiral center. Asymmetric carbon atoms are found in many naturally occurring molecules, such as lactic acid, which is present in milk and muscles, and nicotine, a component of tobacco. A molecule and its nonsuperimposable mirror image are called*enantiomers* (from the Greek *enantiou*, meaning “opposite”).

Figure 24.7 *Comparison of Chiral and Achiral Molecules*



(a) Bromochlorofluoromethane is a chiral molecule whose stereocenter is designated with an asterisk. Rotation of its mirror image does not generate the original structure. To superimpose the mirror images, bonds must be broken and reformed. (b) In contrast, dichlorofluoromethane and its mirror image can be rotated so they are superimposable.



EXAMPLE 3

Draw the *cis* and *trans* isomers of each compound.

a. 1,3-dimethylcyclopentane

b. 3,4-dichloro-3-hexene

Given: organic compounds

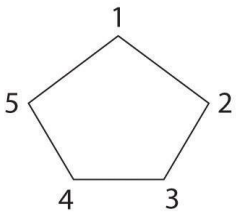
Asked for: *cis* and *trans* isomers

Strategy:

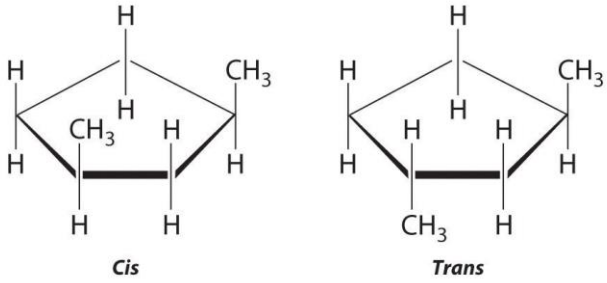
Draw the unsubstituted compound corresponding to the systematic name given. Then place substituents on the same side to obtain the *cis* isomer and on opposite sides to obtain the *trans* isomer.

Solution:

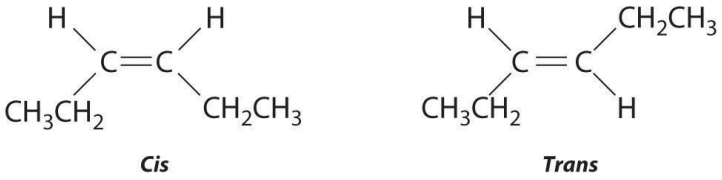
a. The name tells us that this compound contains a five-carbon ring with two methyl groups attached. The 1,3 notation means that the methyl groups are not adjacent in the five-membered ring:



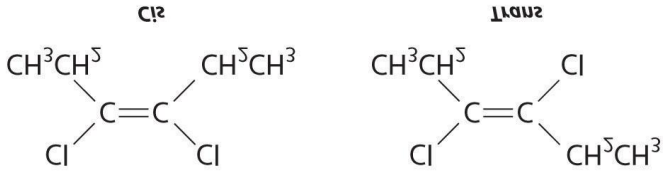
Placing the methyl substituents on the same side of the ring gives the *cis*isomer, whereas placing them on opposite sides of the ring gives the*trans* isomer:



The compound 3-hexene can exist as a *cis* or *trans* isomer:



Replacing the hydrogen atoms on the third and fourth carbons by chlorine does not change the overall structures of the isomers:



Exercise

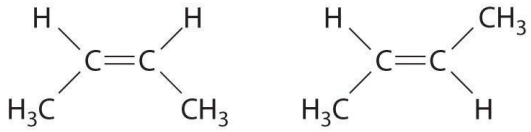
Draw the *cis* and *trans* isomers of each compound.

a. 2-butene

b. 1-methyl-3-chlorocyclopentane

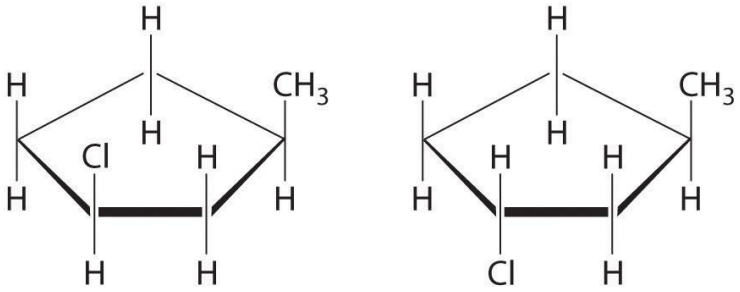
Answer:

a.



***Cis*-2-butene** ***Trans*-2-butene**

b.

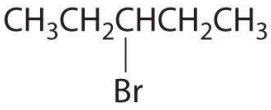


Cis ***Trans***

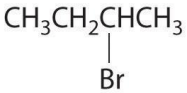
EXAMPLE 4

Which of these compounds exist as at least one pair of enantiomers?

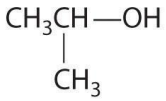
a.



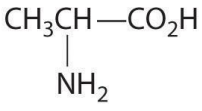
b.



c.



d.



Given: organic compounds

Asked for: existence of enantiomers

Strategy:

Determine whether the compound is chiral. In most cases, this means that at least one carbon is bonded to four different groups. If the compound is chiral, it exists as enantiomers.

Solution:

a. The carbons in $–CH_3$ and $–CH_2–$ are each bound to more than one hydrogen, so they are achiral. The central carbon is bound to two identical ethyl groups, so it is also achiral. Because there are no chiral centers in this compound, it has no enantiomers.

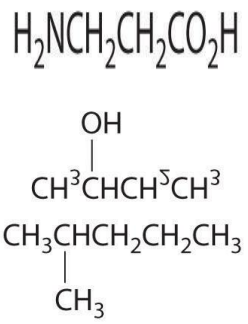
b. All carbons are bonded to at least two H atoms except for the one bonded to Br, which is bonded to four different groups: –Br, $–CH_3$, –H, and $–CH_2CH_3$. The compound therefore has one chiral center and, as a result, exists as enantiomers: the structure shown and its nonsuperimposable mirror image.

c. The carbons in each $–CH_3$ are bonded to more than one hydrogen, so they are achiral. One carbon is bonded to two $–CH_3$ groups, making it achiral also. This compound has no enantiomers.

d. One carbon is bonded to three hydrogens and one to two oxygens, so they are achiral. The central carbon is bonded to four different groups: $–CH_3$, –H, $–NH_2$, and $–CO_2H$, so it is chiral, and the compound has two enantiomers.

Exercise

Which of these compounds have at least one pair of enantiomers?



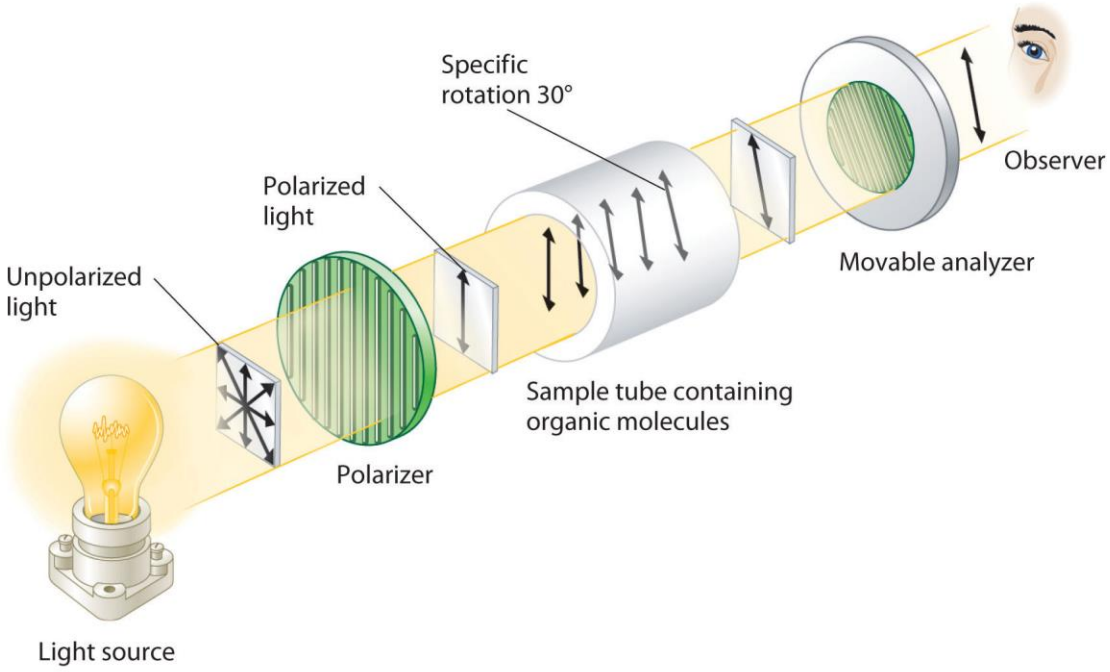
Answer:

(c)

Optical Activity of Enantiomers

Although enantiomers have identical densities, melting and boiling points, colors, and solubility in most solvents, they differ in their interaction with *plane-polarized light*, which consists of electromagnetic waves oscillating in a single plane. In contrast, normal (unpolarized) light consists of electromagnetic waves oscillating in all directions perpendicular to the axis of propagation. When normal light is passed through a substance called a polarizer, only light oscillating in one direction is transmitted. A polarizer selectively filters out light that oscillates in any but the desired plane (Figure 24.8 "Detecting the Optical Activity of Chiral Substances").

Figure 24.8 *Detecting the Optical Activity of Chiral Substances*



When polarized light is passed through a solution that contains an achiral compound, there is no net rotation of the plane of polarization of the light. In contrast, when polarized light is passed through a solution that contains one enantiomer of a chiral compound, as shown here, the light is rotated either clockwise [dextrorotatory, (+) enantiomer] or counterclockwise [levorotatory, (−) enantiomer] by an angle that depends on the molecular structure and concentration of the compound, the path length, and the wavelength of the light.

When plane-polarized light is passed through a solution, electromagnetic radiation interacts with the solute and solvent molecules. If the solution contains an achiral compound, the plane-polarized light enters and leaves the solution unchanged because achiral molecules cause it to rotate in random directions. The solute is therefore said to be *optically inactive*. If the solution contains a single enantiomer of a chiral compound, however, the plane-polarized light is rotated in only one direction, and

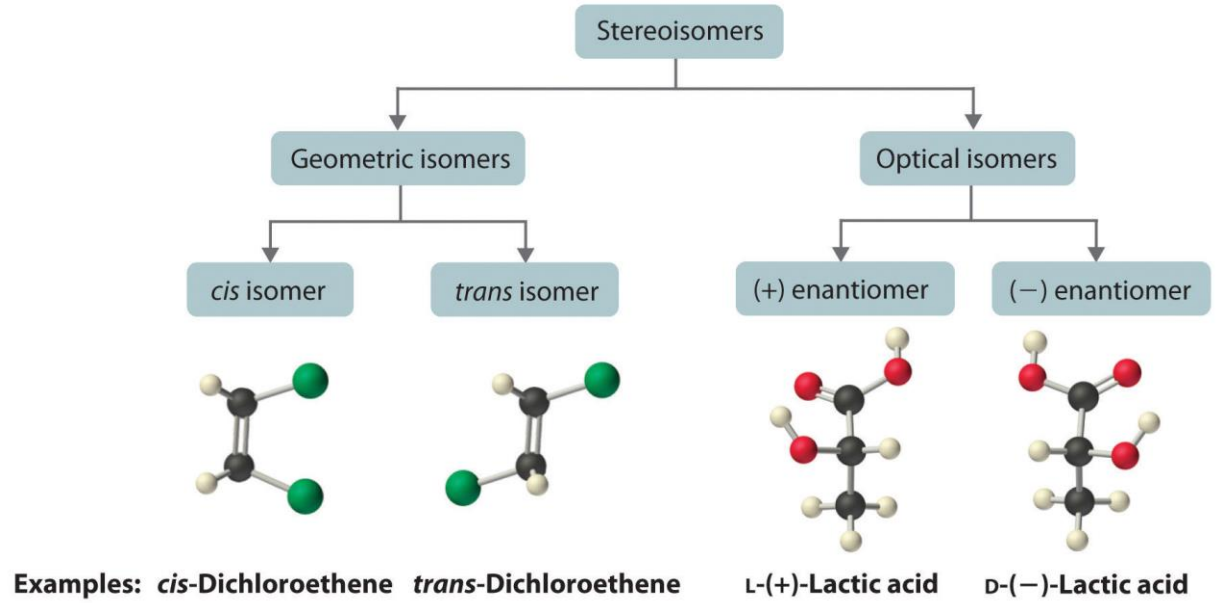
the solute is said to be *optically active*. A clockwise rotation is called *dextrorotatory* (from the Latin *dextro*, meaning “to the right”) and is indicated in the name of the compound by (+), whereas a counterclockwise rotation is called *levorotatory* (from the Latin *levo*, meaning “to the left”) and is designated (−). As you will soon discover, this designation is important in understanding how chiral molecules interact with one another.

Note the Pattern

Chiral molecules are optically active; achiral molecules are not.

The magnitude of the rotation of plane-polarized light is directly proportional to the number of chiral molecules in a solution; it also depends on their molecular structure, the temperature, and the wavelength of the light. Because of these variables, every chiral compound has a specific rotation, which is defined as the amount (in degrees) by which the plane of polarized light is rotated when the light is passed through a solution containing 1.0 g of solute per 1.0 mL of solvent in a tube 10.0 cm long. A chiral solution that contains equal concentrations of a pair of enantiomers is called a *racemic mixture*. In such a solution, the optical rotations exactly cancel one another, so there is no net rotation, and the solution is optically inactive. The categories of stereoisomers are summarized in Figure 24.9 "Classification of Stereoisomers".

Figure 24.9 *Classification of Stereoisomers*

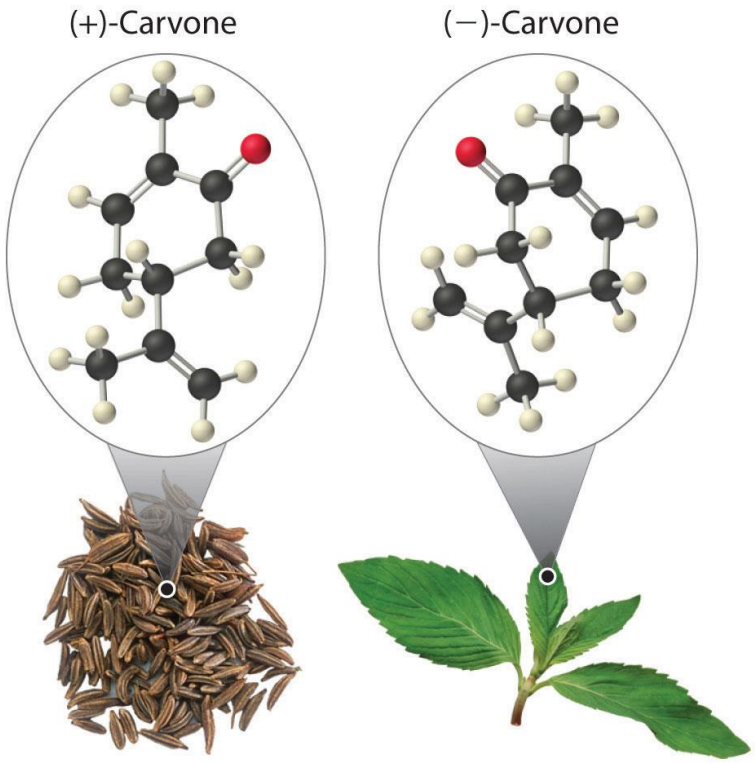


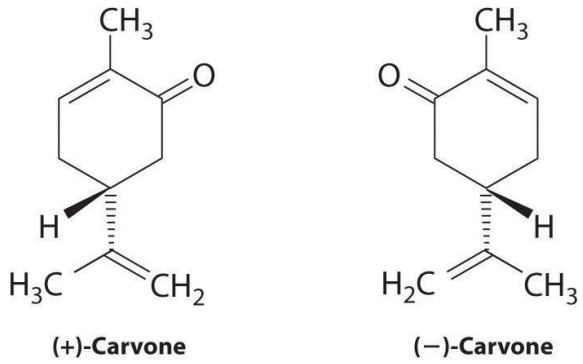
In both types of stereoisomer—geometric and optical—isomeric molecules have identical connectivity, but the arrangement of atoms in space differs. Cis and transisomers exhibit different

physical and chemical properties, whereas enantiomers differ only in their interaction with plane-polarized light and reactions in asymmetric environments. Depending on the direction in which they rotate polarized light, enantiomers are identified as (+) or (−). The designations L- and D- represent an alternative labeling system.

Interactions of Enantiomers with Other Chiral Molecules

In living organisms, virtually every molecule that contains a chiral center is found as a single enantiomer, not a racemic mixture. At the molecular level, our bodies are chiral and interact differently with the individual enantiomers of a particular compound. For example, the two enantiomers of carvone produce very different responses in humans: (−)-carvone is the substance responsible for the smell of spearment oil, and (+)-carvone—the major flavor component of caraway seeds—is responsible for the characteristic aroma of rye bread.





A pharmaceutical example of a chiral compound is ibuprofen, a common analgesic and anti-inflammatory agent that is the active ingredient in pain relievers such as Motrin and Advil (Figure 24.16 "Biologically Active Substituted Arenes"). The drug is sold as a racemic mixture that takes approximately 38 minutes to achieve its full effect in relieving pain and swelling in an adult human. Because only the (+) enantiomer is active in humans, however, the same mass of medication would relieve symptoms in only about 12 minutes if it consisted of only the (+) enantiomer. Unfortunately, isolating only the (+) enantiomer would substantially increase the cost of the drug. Conversion of the (−) to (+) enantiomer in the human body accounts for the delay in feeling the full effects of the drug. A racemic mixture of another drug, the sedative thalidomide, was sold in Europe from 1956 to the early 1960s. It was prescribed to treat nausea during

pregnancy, but unfortunately only the (+) enantiomer was safe for that purpose. The (−) enantiomer was discovered to be a relatively potent *teratogen*, a substance that causes birth defects, which caused the children of many women who had taken thalidomide to be born with missing or undeveloped limbs. As a result, thalidomide was quickly banned for this use. It is currently used to treat leprosy, however, and it has also shown promise as a treatment for AIDS (acquired immunodeficiency syndrome).

These examples dramatically illustrate the point that the biological activities of enantiomers may be very different. But how can two molecules that differ only by being nonsuperimposable mirror images cause such different responses? The biological effects of many substances—including molecules such as carvone that have a scent and drugs such as ibuprofen and thalidomide—depend on their interaction with chiral sites on specific receptor proteins. As schematically illustrated in Figure 24.10 "The Interaction of Chiral Molecules with Biological Receptors", only one enantiomer of a chiral substance interacts with a particular receptor, thereby initiating a response. The other enantiomer may not bind at all, or it may bind to *another* receptor, producing a different response.

Summary

Isomers are different compounds that have the same molecular formula. For an organic compound, rotation about a σ bond can produce different three-dimensional structures called **conformational isomers (or conformers)**. In a Newman projection, which represents the view along a C–C axis, the eclipsed conformation has the C–H bonds on adjacent carbon atoms parallel to each other and in the same plane, representing one conformational extreme. In the staggered conformation, the opposite extreme, the hydrogen atoms are as far from one another as possible. Electrostatic repulsions are minimized in the staggered conformation. **Structural isomers** differ in the connectivity of the atoms. Structures that have the same connectivity but whose components differ in their orientations in space are called **stereoisomers**. Stereoisomers can be geometric isomers, which differ in the placement of substituents in a rigid molecule, or optical isomers, nonsuperimposable mirror images. Molecules that are nonsuperimposable mirror images are chiral molecules. A molecule and its nonsuperimposable mirror image are called enantiomers. These differ in their interaction with plane-polarized light, light that oscillates in only one direction. A compound is optically active if its solution rotates plane-polarized light in only one direction and optically inactive if its rotations cancel to produce no net rotation. A clockwise rotation is called dextrorotatory and is indicated in the compound's name by (+), whereas a

counterclockwise rotation is called levorotatory, designated by (−). The **specific rotation** is the amount (in degrees) by which the plane of polarized light is rotated when light is passed through a solution containing 1.0 g of solute per 1.0 mL of solvent in a tube 10.0 cm long. A solution that contains equal concentrations of each enantiomer in a pair is a racemic mixture; such solutions are optically inactive.

KEY TAKEAWAYS

- Isomers can be conformational or structural.
- Stereoisomers have the same connectivity but can be optical or geometric isomers.

CONCEPTUAL PROBLEMS

1. What hybrid orbitals are used to form C–C bonds in saturated hydrocarbons? Describe the bond.
2. How are conformational isomers related? Sketch two conformational isomers of propane, looking along the C1–C2 axis.
3. Why do alkanes with more than two carbons have a kinked structure? Explain why a kinked structure is so stable.
4. Are *n*-pentane and 2-methylbutane conformational isomers or structural isomers? How would you separate these compounds from a mixture of the two?
5. How are structural isomers different from stereoisomers? Do stereoisomers have free rotation about all carbon–carbon bonds? Explain your answers.
6. Which of these objects is chiral?

a. a shoe
b. a laced football
c. an automobile
d. a fork

7. Which of these objects is chiral?

a. a rollerblade
b. an unmarked baseball bat
c. a bicycle
d. your arms
e. a spoon

8. Are all stereoisomers also enantiomers? Are all enantiomers stereoisomers? Explain your answers.

ANSWERS

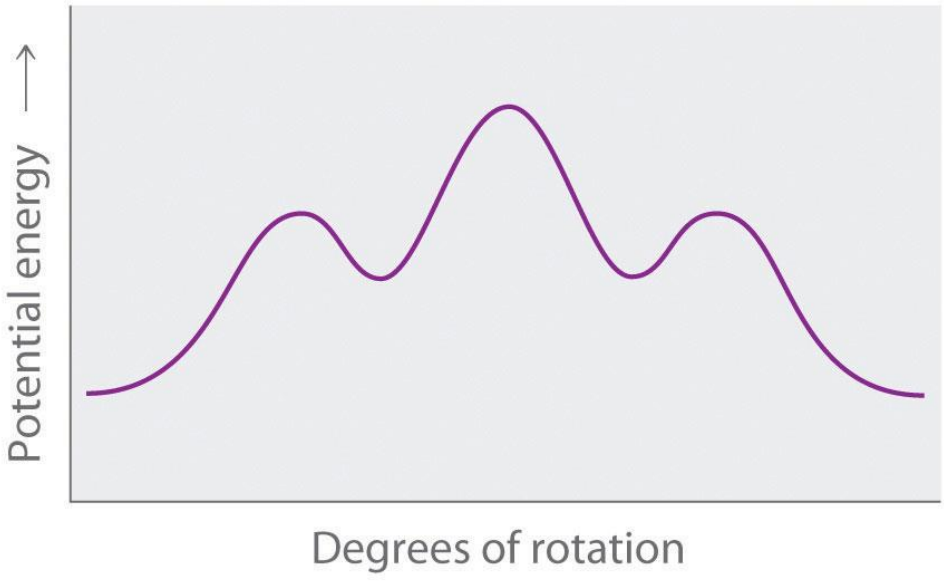
1. sp^3; it is a σ bond that is cylindrically symmetrical (all cross sections perpendicular to the internuclear axis are circles).
2.
3. The sp^3 hybridized orbitals form bonds at tetrahedral angles (109.5°), which forces the carbon atoms to form a zigzag chain.
4.
5.
6.
7. (a), (c), and (d)
8.

STRUCTURE AND REACTIVITY

1. Single bonds between carbon atoms are free to rotate 360°.

a. Explain what happens to the potential energy of an *n*-hexane molecule as rotation occurs around the C2–C3 bond.

b. Draw Newman projections of the *n*-hexane conformations corresponding to the energy minima and maxima in the diagram, which shows potential energy versus degrees of rotation about the C3–C4 axis.



Sketch all the structural isomers of each compound.

c. $C_6H_{13}Br$

d. $C_3H_6Cl_2$

2. Draw all the possible structural isomers of each compound.

a. $C_5H_{11}Br$

b. $C_4H_8Cl_2$

3. Sketch all the isomers of each compound. Identify the *cis*- and *trans*-isomers.

a. monochlorobutene

b. bromochloropropene

4. Which molecules are chiral? On the structural formulas of the chiral molecules, identify any chiral centers with an asterisk.

a. 2,2-dimethylpentane

b. 1,2-dimethylpentane

c. 2,4-dimethylpentane

d. 1-chloro-2-methylpentane

5. Which molecules are chiral? On the structural formulas of the chiral molecules, identify any chiral centers with an asterisk.

a. 1,1-dichloropropane

b. 1,2-dichloropropane

c. 1,3-dichloropropane

d. 1,1,2-trichloropropane

6. Draw the structures of the enantiomers of each compound.

a. $CH_2CHCHClBr$

b. 4-chloro-2-hexene

c. methylethylpropylamine

7. Draw the structures of the enantiomers of each compound.

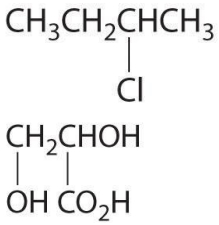
a. 4-methyl-2-hexene

b. methylethylhexylamine

c. $CH_3CH_2CH(CH_3)Cl$

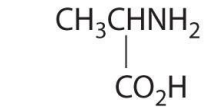
8. Draw the structures of the enantiomers of each compound.

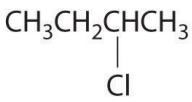
a.

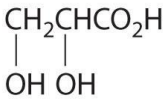


Draw the structures of the enantiomers of each compound.

b.







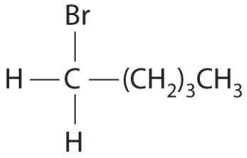
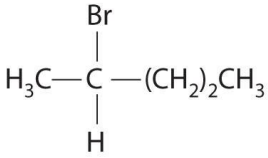
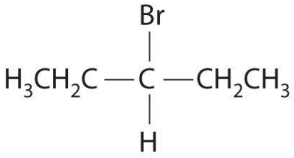
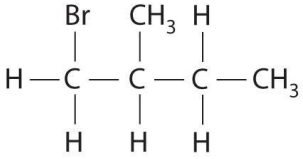
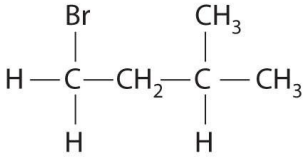
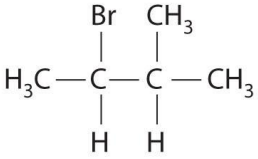
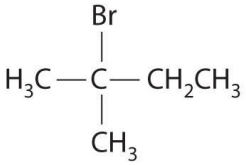
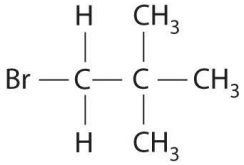
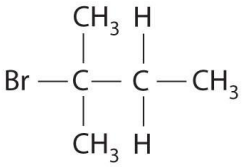
ANSWERS

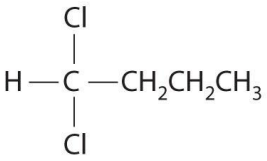
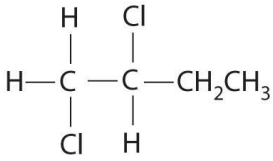
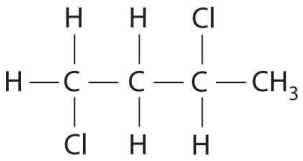
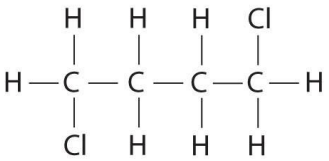
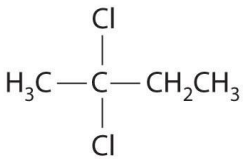
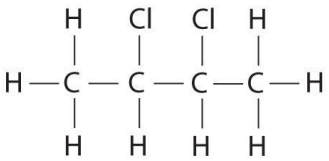
1.

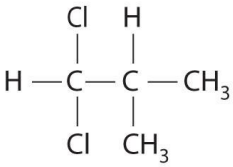
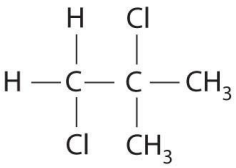
2.

3.

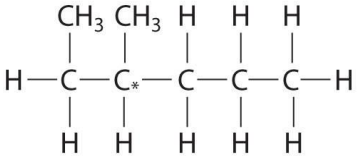
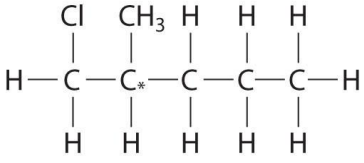
a.

4. (b) and (d);

24.3 Reactivity of Organic Molecules

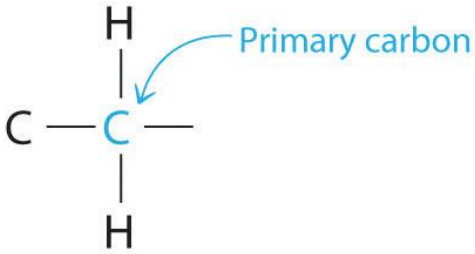
LEARNING OBJECTIVE

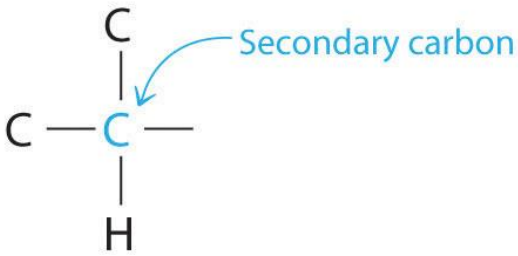
1. To understand the relationship between structure and reactivity for a series of related organic compounds.

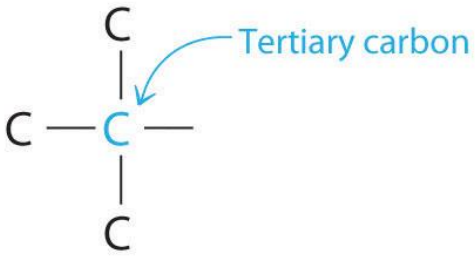
Understanding why organic molecules react as they do requires knowing something about the structure and properties of the transient species that are generated during chemical reactions. Identifying transient intermediates enables chemists to elucidate reaction mechanisms, which often allows them to control the products of a reaction. In designing the synthesis of a molecule, such as a new drug, for example, chemists must be able to understand the mechanisms of intermediate reactions to maximize the yield of the desired product and minimize the occurrence of unwanted reactions. Moreover, by recognizing the common reaction mechanisms of simple organic molecules, we can understand how more complex systems react, including the much larger molecules encountered in biochemistry.

Nearly all chemical reactions, whether organic or inorganic, proceed because atoms or groups of atoms having a positive charge or a partial positive charge interact with atoms or groups of atoms having a negative charge or a partial negative charge. Thus when a bond in a hydrocarbon is cleaved during a reaction, identifying the transient species formed, some of which are charged, allows chemists to determine the mechanism and predict the products of a reaction.

Chemists often find that the reactivity of a molecule is affected by the degree of substitution of a carbon that is bonded to a functional group. These carbons are designated as *primary*, *secondary*, or *tertiary*. A primary carbon is bonded to only one other carbon and a functional group, a secondary carbon is bonded to two other carbons and a functional group, and a tertiary carbon is bonded to three other carbons and a functional group.







Reactive Intermediates

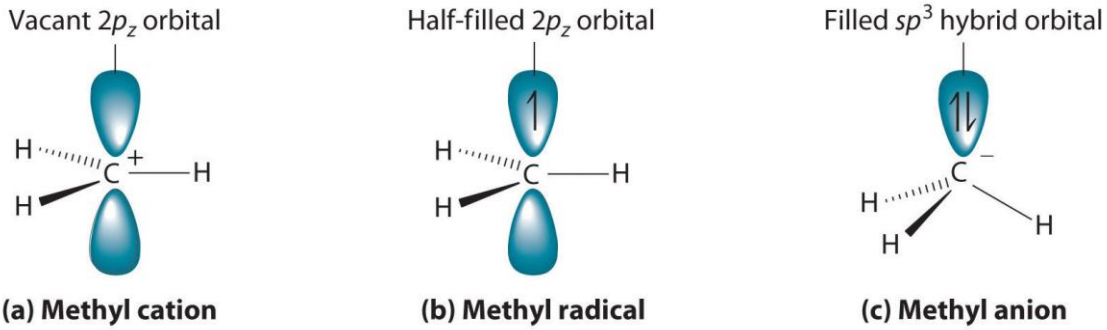
Cleaving a C–H bond can generate either $-C^+$ and H^-, $-C\cdot$ and $H\cdot$ or $-C^-$ and H^+, all of which are unstable and therefore highly reactive. The most common species formed is $-C^+$, which is called a carbocation (part (a) in Figure 24.11 "Transient Intermediates in Organic Reactions"). A carbocation has only six valence electrons and is therefore electron deficient. It is an electrophile (from “electron” and the Greek suffix *phile*, meaning “loving”), which is a species that needs electrons to complete its octet. (Recall that electron-deficient compounds, such as those of the group 13 elements, act as Lewis acids in inorganic reactions.) In general, when a highly electronegative atom, such as Cl, is bonded to a carbocation, it draws electrons away from the carbon and destabilizes the positive charge. In contrast, alkyl groups and other species stabilize the positive charge by increasing electron density at the carbocation. Thus a tertiary carbocation (R_3C^+) is more stable than a primary carbocation (RCH_2^+).

Note the Pattern

The reactivity of a molecule is often affected by the degree of substitution of the carbon bonded to a functional group.

Adding one electron to a carbocation produces a neutral species called a radical. (For more information on radicals, see Chapter 14 "Chemical Kinetics", Section 14.6 "Reaction Rates—A Microscopic View".) An example is the methyl radical ($\cdot CH_3$), shown in part (b) in Figure 24.11 "Transient Intermediates in Organic Reactions". Because the carbon still has less than an octet of electrons, it is electron deficient and also behaves as an electrophile. Like carbocations, radicals can be stabilized by carbon substituents that can donate some electron density to the electron-deficient carbon center. Like carbocations, a tertiary radical ($R_3C\cdot$) is more stable than a primary radical ($RCH_2\cdot$).

Figure 24.11 *Transient Intermediates in Organic Reactions*



(a) The simplest carbocation is the methyl cation (CH_3^+), which has six valence electrons and is an electrophile. Its structure is trigonal planar, with an sp^2-hybridized carbon and a vacant p orbital. (b) The methyl radical ($\cdot CH_3$) is a radical that, like the carbocation, is trigonal planar and an electrophile. It is also sp^2-hybridized, but there is a single electron in the unhybridized p orbital. (c) The simplest organic carbanion is CH_3^-, which has a trigonal pyramidal structure with an sp^3 hybridized carbon that has a lone pair of electrons. Because it has a strong tendency to share its lone pair with another atom or molecule, a carbanion is a nucleophile.

Adding an electron to a radical produces a carbanion, which contains a negatively charged carbon with eight valence electrons (part (c) in Figure 24.11 "Transient Intermediates in Organic Reactions"). The methyl anion (CH_3^-) has a structure that is similar to NH_3 with its lone pair of electrons, but it has a much stronger tendency to share its lone pair with another atom or molecule. A carbanion is a nucleophile (from "nucleus" and *phile*), an electron-rich species that has a pair of electrons available to share with another atom. Carbanions are destabilized by groups that donate electrons, so the relationship between their

structure and reactivity is exactly the opposite of carbocations and radicals. That is, a tertiary carbanion (R_3C^-) is less stable than a primary carbanion (RCH_2^-). Carbanions are most commonly encountered in organometallic compounds such as methyllithium (CH_3Li) or methylmagnesium chloride (CH_3MgCl), where the more electropositive metal ion stabilizes the negative charge on the more electronegative carbon atom.

Electrophiles such as carbocations seek to gain electrons and thus have a strong tendency to react with nucleophiles, which are negatively charged species or substances with lone pairs of electrons. Reacting electrophiles with nucleophiles is a central theme in organic reactions.

Note the Pattern

Electrophiles react with nucleophiles.

EXAMPLE 5

Classify each species as an electrophile, a nucleophile, or neither.

a. BF_3

b. CH_4

c. $(CH_3)_3C^+$

d. NH_2^-

Given: molecular formulas

Asked for: mode of reactivity

Strategy:

Determine whether the compound is electron deficient, in which case it is an electrophile; electron rich, in which case it is a nucleophile; or neither.

Solution:

a. The BF_3 molecule is a neutral compound that contains a group 13 element with three bonds to B. The boron atom has only six valence electrons, so it tends to accept an electron pair. The compound is therefore an electrophile.

b. The CH_4 molecule has four bonds to C, which is typical of a neutral group 14 compound. The carbon atom has no lone pairs to share and no tendency to gain electrons, and each hydrogen atom forms one bond that contains two valence electrons. Thus CH_4 is neither an electrophile nor a nucleophile.

c. The $(CH_3)_3C^+$ cation contains a group 14 atom (carbon) with only three bonds. It therefore has only six valence electrons and seeks electrons to complete an octet. Hence $(CH_3)_3C^+$, a carbocation, is an electrophile.

d. The NH_2^- anion contains a group 15 element with a lone pair of electrons, two bonds, and a negative charge, giving N a total of eight electrons. With its negative charge, the N atom has two lone pairs of electrons, making it a potent nucleophile.

Exercise

Classify each compound as an electrophile, a nucleophile, or neither.

a. C_6H_5OH

b. $AlBr_3$

c. $(CH_3)_4C$

Answer:

a. nucleophile

b. electrophile

c. neither

Summary

The reactivity of a molecule is often affected by the degree of substitution of the carbon bonded to a functional group; the carbon is designated as primary, secondary, or tertiary. Identifying the transient species formed in a chemical reaction, some of which are charged, enables chemists to predict the mechanism and products of the reaction. One common transient species is a **carbocation**, a carbon with six valence electrons that is an **electrophile**; that is, it needs electrons to complete its octet. A **radical** is a transient species that is neutral but electron deficient and thus acts as an electrophile. In contrast, a **carbanion** has eight valence electrons and is negatively charged. It is an electron-rich species that is a **nucleophile** because it can share a pair of electrons. In chemical reactions, electrophiles react with nucleophiles.

KEY TAKEAWAY

- Electrophiles have a strong tendency to react with nucleophiles.

CONCEPTUAL PROBLEMS

1. Arrange CH_2F^+, $CHCl_2^+$, CH_3^+, and CHF_2^+ in order of increasing stability. Explain your reasoning.
2. Arrange $CH_3CH_2^+$, $CHBr_2^+$, CH_3^+, and $CHBrCl^+$ in order of decreasing stability. Explain your reasoning.
3. Identify the electrophile and the nucleophile in each pair.

a. CH_3^- and Li^+

b. CH_3ONa and formaldehyde

c. H^+ and propene

d. benzene and Cl^-

4. Identify the electrophile and the nucleophile in each pair.

a. CH_3^+ and Br^-

b. HC≡CNa and pentanal

c. acetone and CN^-

d. $(CH_3)_2S$ and CH_3I

ANSWERS

1. $CHF_2^+ < CHCl_2^+ < CH_2F^+ < CH_3^+$; electronegative substituents destabilize the positive charge. The greater the number of electronegative substituents and the higher their electronegativity, the more unstable the carbocation.
2.
3.

a. CH_3^-, nucleophile; Li^+, electrophile

b. CH_3O^-, nucleophile; formaldehyde, electrophile

c. H^+, electrophile; propene, nucleophile

d. benzene, electrophile; Cl^-, nucleophile

4.

STRUCTURE AND REACTIVITY

1. Draw Lewis electron structures of the products of carbon–hydrogen cleavage reactions. What is the charge on each species?
2. Identify the electrophile and the nucleophile in each reaction; then complete each chemical equation.

a. $CH_3^+ + Cl^- \rightarrow$

b. $CH_3CH{=}CH_2 + HBr \rightarrow$

c. $(CH_3)_3N + BCl_3 \rightarrow$

24.4 Common Classes of Organic Reactions

LEARNING OBJECTIVE

1. To become familiar with the common classes of organic reactions.

Certain patterns are encountered repeatedly in organic reactions, many reflecting the interactions of nucleophiles and electrophiles. In this section, we discuss five common types of organic reactions: substitution reactions, elimination reactions, addition reactions, radical reactions, and oxidation–reduction reactions. You have encountered many of these types of reactions previously, such as the formation of peptides by the elimination of water, the oxidation–reduction reactions that generate voltage in batteries, and chain reactions that involve organic radicals. (For more information on peptide formation, see Chapter 12 "Solids", Section 12.8 "Polymeric Solids". For more information on batteries, see Chapter 19 "Electrochemistry". For more information on radicals, see Chapter 14 "Chemical Kinetics", Section 14.6 "Reaction Rates—A Microscopic View".) In this section, we expand our discussion to include some of the mechanisms behind these reactions.

Substitution

In a substitution reaction, one atom or a group of atoms in a substance is replaced by another atom or group of atoms from another substance. A typical substitution reaction is reacting the hydroxide ion with methyl chloride:

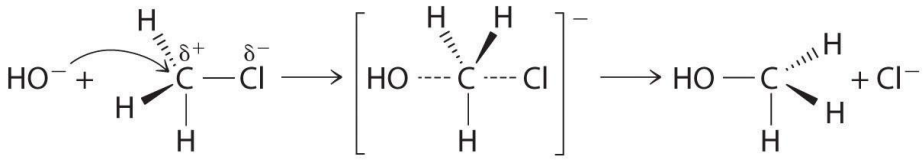
Equation 24.1

$$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$$

Methyl chloride has a polar C–Cl bond, with the carbon atom having a partial positive charge. In Equation 24.1, the electronegative Cl atom is replaced by another electronegative species that is a stronger nucleophile, in this case OH^-. Reactions of this sort are called *nucleophilic substitution reactions*. For this type of reaction to occur, the nucleophilic reactant must possess a pair of electrons and have a greater affinity for the electropositive carbon atom than the original substituent.

One type of nucleophilic substitution reaction is shown in Equation 24.1. It proceeds by a mechanism in which the lone pair of electrons on the entering nucleophile (OH^-) attacks the partially positively charged carbon atom of the polar C–Cl bond, causing the C–Cl bond to weaken and break:

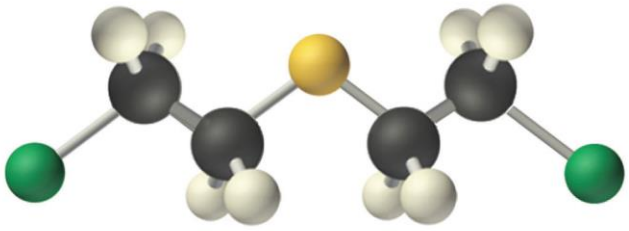
Figure 24.12



Note the Pattern

In nucleophilic substitution reactions, the nucleophile must possess a pair of electrons and have a greater affinity for the electropositive species than the original substituent.

The convention for writing such a mechanism is to draw arrows showing the direction of electron flow—that is, from the electron-rich center (the nucleophile) to the electron-poor center (the electrophile). The intermediate species, enclosed by square brackets, represents a transient arrangement of atoms that is only postulated to exist. If the atom under attack (in this case, the partially positively charged carbon atom) had $–CH_3$groups bonded to it rather than H atoms, the bulky methyl groups would interfere with the attack by OH^-, making the reaction *sterically hindered*. The reaction would then proceed in two discrete steps in a second type of substitution reaction: the C–Cl bond would break, forming the $(CH_3)_3C^+$ carbocation (the electrophile), which would then react with hydroxide (the nucleophile) in a separate step to give the product, $(CH_3)_3COH$.



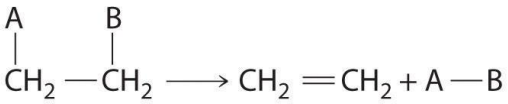
Mustard gas.

An example of a nucleophilic substitution reaction involves the chemical warfare agent known as *mustard gas* [$(ClCH_2CH_2)_2S$], which caused about 400,000 casualties during World War I. Mustard gas is toxic because it contains a chloride that can be displaced by nucleophilic amino groups in proteins, thereby allowing the molecule to irreversibly bond to a protein. Because the other product of the reaction is HCl, mustard gas causes severe burns to mucous membranes in the respiratory tract. If mustard gas reacts with DNA (deoxyribonucleic acid), cross-linking of the DNA strands through sulfur occurs, which results in coding errors, the inhibition of replication, and disruption of other DNA functions. If mustard gas reacts with RNA (ribonucleic acid), protein synthesis is altered (see Section 24.6 "The Molecules of Life").

Elimination

Some reactions involve the removal, or “elimination,” of adjacent atoms from a molecule. This results in the formation of a multiple bond and the release of a small molecule, so they are called elimination reactions. They have the general form

Figure 24.13



and are similar to cleavage reactions in inorganic compounds. (For more information on cleavage reactions, see Chapter 3 "Chemical Reactions", Section 3.5 "Classifying Chemical Reactions".) A typical example is the conversion of ethyl chloride to ethylene:

Equation 24.2

$CH_3CH_2Cl \rightarrow CH_2{=}CH_2 + HCl$

Note the Pattern

Elimination reactions are similar to cleavage reactions in inorganic compounds.

Much of the approximately 26 million tons of ethylene produced per year in the United States is used to synthesize plastics, such as polyethylene. In Equation 24.2, the A–B molecule eliminated is HCl, whose components are eliminated as H^+ from the carbon atom on the left and Cl^- from the carbon on the right. When an acid is produced, as occurs here, the reaction is generally carried out in the presence of a base (such as NaOH) to neutralize the acid.

Addition

A reaction in which the components of a species A–B are added to adjacent atoms across a carbon–carbon multiple bond is called an addition reaction. An example is the reverse of the reaction shown in Equation 24.2, reacting HCl with ethylene to give ethyl chloride:

Equation 24.3

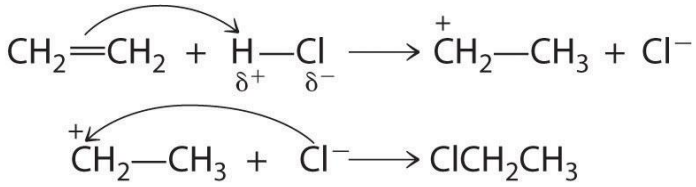
$HCl + CH_2{=}CH_2 \rightarrow CH_3CH_2Cl$

Note the Pattern

An addition reaction is the reverse of an elimination reaction.

Although a multiple bond is stronger than a single bond, the π bonds of the multiple bond are weaker than the σ bond. The high electron density located between multiply bonded carbon atoms, however, causes

alkenes and alkynes to behave like nucleophiles, where nucleophilic attack occurs from the more weakly bound π electrons. Hence alkenes and alkynes are regarded as functional groups. Nucleophilic attack occurs on the $H^{\delta+}$ atom of the polar HCl bond, initially producing a species with a carbon that has only three bonds, a carbocation. In a second nucleophilic attack, Cl^-, the electrophile in Equation 24.3, attacks the carbocation:



Alcohols, an important class of organic compounds, are often produced by addition reactions. Initial attack by the π bond of an alkene on a $H^{\delta+}$ of H_3O^+ produces a carbocation. The carbocation then undergoes nucleophilic attack by a lone pair of electrons from H_2O followed by elimination of H^+ to form the alcohol.

Radical Reactions

Many important organic reactions involve radicals, such as the combustion of fuels. Probably the best known is reacting a saturated hydrocarbon, such as ethane, with a halogen, such as Br_2. The overall reaction is as follows:

Equation 24.4

$$CH3CH3 + Br2 \xrightarrow{or\ h\nu\ 400°C} CH3CH2Br + HBr$$

Radical chain reactions occur in three stages: *initiation*, *propagation*, and*termination*. (For more information on radicals, see Chapter 14 "Chemical Kinetics",Section 14.6 "Reaction Rates—A Microscopic View".) At high temperature or in the presence of light, the relatively weak Br–Br bond is broken in an initiation step that produces an appreciable number of Br atoms (Br·). During propagation, a bromine atom attacks ethane, producing a radical, which then reacts with another bromine molecule to produce ethyl bromide:

Equation 24.5

$$Br\cdot + CH3CH3 \rightarrow CH3CH2\cdot + HBr \qquad CH3CH2\cdot + Br2 \rightarrow CH3CH2Br + Br\cdot$$

$$\text{Sum: } CH3CH3 + Br2 \rightarrow CH3CH2Br + HBr$$

The sum of the two propagation steps corresponds to the balanced chemical equation for the overall reaction. There are three possible termination steps: the combination of (1) two bromine atoms, (2) two ethyl radicals, or (3) an ethyl and a bromine radical:

Equation 24.6

$$Br\cdot + Br\cdot CH3CH2\cdot + \cdot CH2CH3CH3CH2\cdot$$
$$+ Br\cdot \rightarrow Br2 \rightarrow CH3CH2CH2CH3 \rightarrow CH3CH2Br$$

Because radicals are powerful nucleophiles and hence highly reactive, such reactions are not very selective. For example, the chlorination of *n*-butane gives a roughly 70:30 mixture of 2-chlorobutane, formed from the more stable radical by reacting a secondary carbon and 1-chlorobutane.

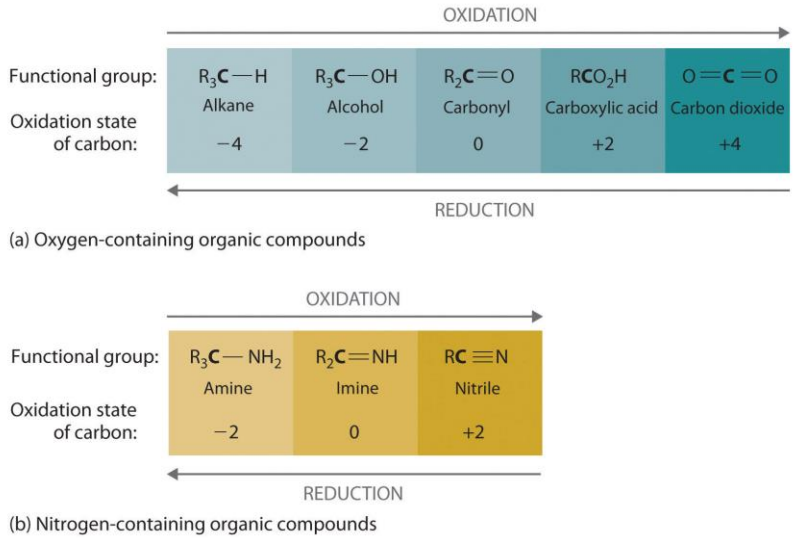
Note the Pattern

Because radicals are highly reactive, radical reactions are usually not very selective.

Oxidation–Reduction Reactions

Oxidation–reduction reactions, which are common in organic chemistry, can often be identified by changes in the number of oxygen atoms at a particular position in the hydrocarbon skeleton or in the number of bonds between carbon and oxygen at that position. An increase in either corresponds to an oxidation, whereas a decrease corresponds to a reduction. Conversely, an increase in the number of hydrogen atoms in a hydrocarbon is often an indication of a reduction. We can illustrate these points by considering how the oxidation state of the carbon atom changes in the series of compounds, which is shown in part (a) in Figure 24.14 "The Oxidation State of Carbon in Oxygen- and Nitrogen-Containing Functional Groups". (For a review of oxidation states and formal changes, see Chapter 3 "Chemical Reactions", Section 3.5 "Classifying Chemical Reactions", and Chapter 8 "Ionic versus Covalent Bonding",Section 8.5 "Lewis Structures and Covalent Bonding"). The number of oxygen atoms or the number of bonds to oxygen changes throughout the series. Hence the conversion of methane to formic acid is an oxidation, whereas the conversion of carbon dioxide to methanol is a reduction. Also, the number of hydrogen atoms increases in going from the most oxidized to least oxidized compound. As expected, as the oxidation state of carbon increases, the carbon becomes a more potent electrophile. Thus the carbon of CO_2 is a stronger electrophile (i.e., more susceptible to nucleophilic attack) than the carbon of an alkane such as methane.

Figure 24.14 The Oxidation State of Carbon in Oxygen- and Nitrogen-Containing Functional Groups



(a) In a hydrocarbon, oxidation is indicated by an increase in the number of oxygen atoms or carbon–oxygen bonds or a decrease in the number of hydrogen atoms. (b) In nitrogen-containing compounds, the number of carbon–nitrogen bonds changes with the oxidation state of carbon.

Similarly, in compounds with a carbon–nitrogen bond, the number of bonds between the C and N atoms increases as the oxidation state of the carbon increases (part (b) in Figure 24.14 "The Oxidation State of Carbon in Oxygen- and Nitrogen-Containing Functional Groups"). In a nitrile, which contains the –C≡N group, the carbon has the same oxidation state (+2) as in a carboxylic acid, characterized by the $–CO_2H$ group. We therefore expect the carbon of a nitrile to be a rather strong electrophile.

EXAMPLE 6

Write an equation to describe each reaction. Identify the electrophile and the nucleophile in each reaction.

a. the nucleophilic substitution reaction of potassium cyanide with 1-chloropropane to give $CH_3CH_2CH_2CN$ (butyronitrile)

b. the electrophilic addition reaction of HBr with *cis*-2-butene

Given: reactants, products, and reaction mechanism

Asked for: equation and identification of electrophile and nucleophile

Strategy:

Use the mechanisms described to show how the indicated products are formed from the reactants.

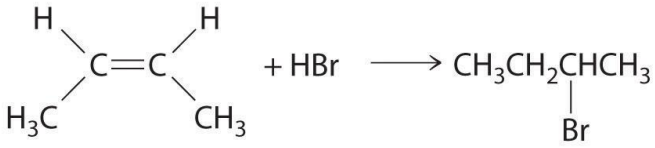
Solution:

a. The CN^- ion of KCN is a potent nucleophile that can displace the chlorine atom of 1-chloropropane, releasing a chloride ion. Substitution results in the formation of a new C–C bond:

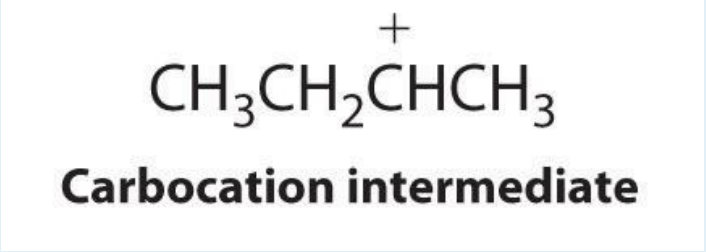
$$CN^- + CH_3CH_2CH_2Cl \; (1\text{-chloropropane}) \rightarrow CH_3CH_2CH_2CN \; (\text{butyronitrile}) + Cl^-$$

The carbon bonded to chlorine is an electrophile because of the highly polar C–Cl bond.

b. In the electrophilic addition of a hydrogen halide to an alkene, the reaction is as follows:



The first step is nucleophilic attack of the π electrons of the double bond on the electrophilic hydrogen of the polar H–Br bond to generate the transient carbocation, followed by nucleophilic attack by the halide to give the product. Thus the alkene is the nucleophile, and the proton of the acid is the electrophile.



Exercise

Write an equation to describe each reaction. In each reaction, identify the electrophile and nucleophile.

a. the nucleophilic substitution reaction of sodium methoxide ($NaOCH_3$) with benzyl bromide ($C_6H_5CH_2Br$)

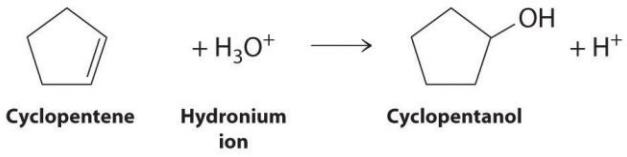
b. the acid-catalyzed electrophilic addition reaction of water with cyclopentene

Answer:

a. $OCH_3^- \; (\text{methoxide ion}) + C_6H_5CH_2Br \; (\text{benzyl bromide}) \rightarrow C_6H_5CH_2OCH_3 + Br^- \; (\text{benzylmethyl ether};\; OCH_3)$

b. $^-$ is the nucleophile, and $C_6H_5CH_2Br$ is the electrophile.

c.



Cyclopentene is the nucleophile, and H_3O^+ is the electrophile.

Summary

There are common patterns to how organic reactions occur. In a **substitution reaction**, one atom or a group of atoms in a substance is replaced by another atom or a group of atoms from another substance. Bulky groups that prevent attack cause the reaction to be sterically hindered. In an **elimination reaction**, adjacent atoms are removed with subsequent formation of a multiple bond and a small molecule. An **addition reaction** is the reverse of an elimination reaction. Radical reactions are not very selective and occur in three stages: initiation, propagation, and termination. **Oxidation–reduction reactions** in organic chemistry are identified by the change in the number of oxygens in the hydrocarbon skeleton or the number of bonds between carbon and oxygen or carbon and nitrogen.

KEY TAKEAWAY

- The common classes of organic reactions—substitution, elimination, addition, oxidation-reduction, and radical—all involve reacting electrophiles with nucleophiles.

CONCEPTUAL PROBLEMS

1. Identify the nucleophile and the electrophile in the nucleophilic substitution reaction of 2-bromobutane with KCN.
2. Identify the nucleophile and the electrophile in the nucleophilic substitution reaction of 1-chloropentane with sodium methoxide.
3. Do you expect an elimination reaction to be favored by a strong or a weak base? Why?
4. Why do molecules with π bonds behave as nucleophiles when mixed with strong electrophiles?

ANSWER

1. CN^- is the nucleophile, and $C_2H_5C^{\delta+}HBrCH_3$ is the electrophile.

STRUCTURE AND REACTIVITY

1. Sketch the mechanism for the nucleophilic substitution reaction of potassium cyanide with iodoethane.

2. Sketch the mechanism for the nucleophilic substitution reaction of NaSH with 1-bromopropane.
3. Sketch the mechanism for the elimination reaction of cyclohexylchloride with potassium ethoxide. Identify the electrophile and the nucleophile in this reaction.
4. What is the product of the elimination reaction of 1-bromo-2-methylpropane with sodium ethoxide?
5. Write the structure of the product expected from the electrophilic addition of HBr to*cis*-3-hexene.
6. Write the structure of the product expected from the electrophilic addition of 1-methylcyclopentene to HBr. Identify the electrophile and the nucleophile, and then write a mechanism for this reaction.
7. Write a synthetic scheme for making propene from propane. After synthesizing propene, how would you make 2-bromopropane?
8. Write a synthetic scheme for making ethylene from ethane. After synthesizing ethylene, how would you make iodoethane?
9. From the high-temperature reaction of Br_2 with 3-methylpentane, how many monobrominated isomers would you expect to be produced? Which isomer is produced from the most stable radical?
10. For the photochemical reaction of Cl_2 with 2,4-dimethylpentane, how many different monochlorinated isomers would you expect to be produced? Which isomer is produced from the most stable precursor radical?
11. How many different radicals can be formed from the photochemical reaction of Cl_2 with 3,3,4-trimethylhexane?
12. How many monobrominated isomers would you expect from the photochemical reaction of Br_2 with

a. isobutene?

b. 2,2,3-trimethylpentane?

13. Arrange acetone, ethane, carbon dioxide, acetaldehyde, and ethanol in order of increasing oxidation state of carbon.
14. What product(s) do you expect from the reduction of a ketone? the oxidation of an aldehyde?
15. What product(s) do you expect from the reduction of formaldehyde? the oxidation of ethanol?

ANSWERS

1.

2.

3.

4.
5.
6.
7.
8.
9. four; 3-bromo-3-methylpentane
10.
11. seven
12.
13.
14.
15. methanol; acetaldehyde, followed by acetic acid and finally CO_2

24.5 Common Classes of Organic Compounds

LEARNING OBJECTIVE

1. To understand the general properties of functional groups and the differences in their reactivity.

The general properties and reactivity of each class of organic compounds (Figure 24.1 "Major Classes of Organic Compounds") is largely determined by its functional groups. In this section, we describe the relationships between structure, physical properties, and reactivity for the major classes of organic compounds. We also show you how to apply these relationships to understand some common reactions that chemists use to synthesize organic compounds.

Alkanes, Alkenes, and Alkynes

The boiling points of alkanes increase smoothly with increasing molecular mass. They are similar to those of the corresponding alkenes and alkynes because of similarities in molecular mass between analogous structures (Table 24.1 "Boiling Points (in °C) of Alkanes, Alkenes, and Alkynes of Comparable Molecular Mass"). In contrast, the melting points of alkanes, alkenes, and alkynes with similar molecular masses show a much wider variation because the melting point strongly depends on how the molecules stack in

the solid state. It is therefore sensitive to relatively small differences in structure, such as the location of a double bond and whether the molecule is *cis* or*trans*.

Table 24.1 Boiling Points (in °C) of Alkanes, Alkenes, and Alkynes of Comparable Molecular Mass

	Length of Carbon Chain		
Class	**Two C Atoms**	**Three C Atoms**	**Four C Atoms**
alkane	−88.6	−42.1	−0.5
alkene	−103.8	−47.7	−6.3
alkyne	−84.7	−23.2	8.1

Because alkanes contain only C–C and C–H bonds, which are strong and not very polar (the electronegativities of C and H are similar; Figure 7.15 "Pauling Electronegativity Values of the "), they are not easily attacked by nucleophiles or electrophiles. Consequently, their reactivity is limited, and often their reactions occur only under extreme conditions. For example, *catalytic cracking* can be used to convert straight-chain alkanes to highly branched alkanes, which are better fuels for internal combustion engines. Catalytic cracking is one example of a pyrolysis reaction (from the Greek *pyros*, meaning "fire," and *lysis*, meaning "loosening"), in which alkanes are heated to a sufficiently high temperature to induce cleavage of the weakest bonds: the C–C single bonds. The result is a mixture of radicals derived from essentially random cleavage of the various C–C bonds in the chain. Pyrolysis of *n*-pentane, for example, is nonspecific and can produce these four radicals:

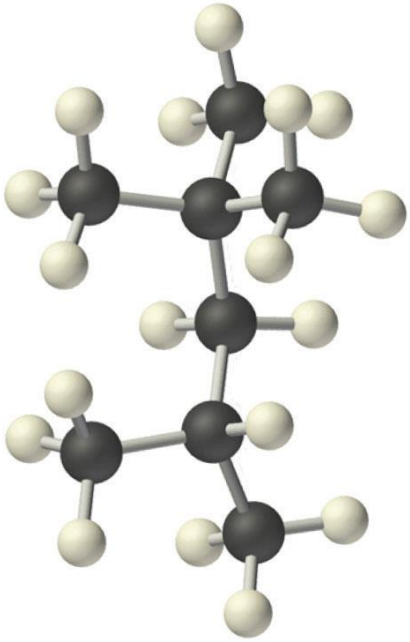
Equation 24.7

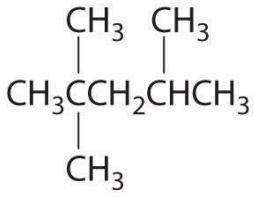
$$2CH3CH2CH2CH2CH3 \rightarrow DCH3\cdot + CH2CH2CH2\cdot + CH3CH2\cdot + CH3CH2CH2\cdot$$

Recombination of these radicals (a termination step) can produce ethane, propane, butane, *n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane. Radicals that are formed in the middle of a chain by cleaving a C–H bond tend to produce branched hydrocarbons. In catalytic cracking, lighter alkanes are removed from the mixture by distillation.

Radicals are also produced during the combustion of alkanes, with CO_2 and H_2O as the final products. As discussed in Section 24.3 "Reactivity of Organic Molecules", radicals are stabilized by the presence of multiple carbon substituents that can donate electron density to the electron-deficient carbon. The chemical explanation of octane ratings, as described in Chapter 2 "Molecules, Ions, and Chemical Formulas", Section 2.6 "Industrially Important Chemicals", rests partly on the stability of radicals

produced from the different hydrocarbon fuels. Recall that *n*-heptane, which does not burn smoothly, has an octane rating of 0, and 2,2,4-trimethylpentane (“isooctane”), which burns quite smoothly, has a rating of 100 (Figure 2.25 "The Octane Ratings of Some Hydrocarbons and Common Additives"). Isooctane has a branched structure and is capable of forming tertiary radicals that are comparatively stable.

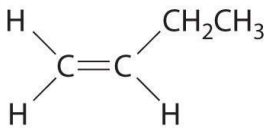




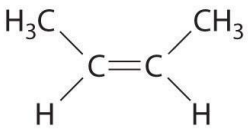
2,2,4-Trimethylpentane
(“isooctane”)

In contrast, the radicals formed during the combustion of*n*-heptane, whether primary or secondary, are less stable and hence more reactive, which partly explains why burning *n*-heptane causes premature ignition and engine knocking.

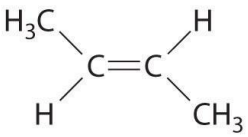
In Section 24.2 "Isomers of Organic Compounds", we explained that rotation about the carbon–carbon multiple bonds of alkenes and alkynes cannot occur without breaking a π bond, which therefore constitutes a large energy barrier to rotation (Figure 24.15 "Carbon–Carbon Bonding in Alkenes and Interconversion of "). Consequently, the *cis* and *trans* isomers of alkenes generally behave as distinct compounds with different chemical and physical properties. A four-carbon alkene has four possible isomeric forms: three structural isomers, which differ in their connectivity, plus a pair of geometric isomers from one structural isomer (2-butene). These two geometric isomers are *cis*-2-butene and*trans*-2-butene. The four isomers have significantly different physical properties.



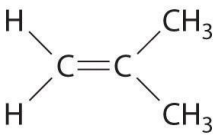
1-Butene
bp 26.2C
mp 2185.3C



***Cis*-2-butene**
bp 3.7C
mp 2138.9C

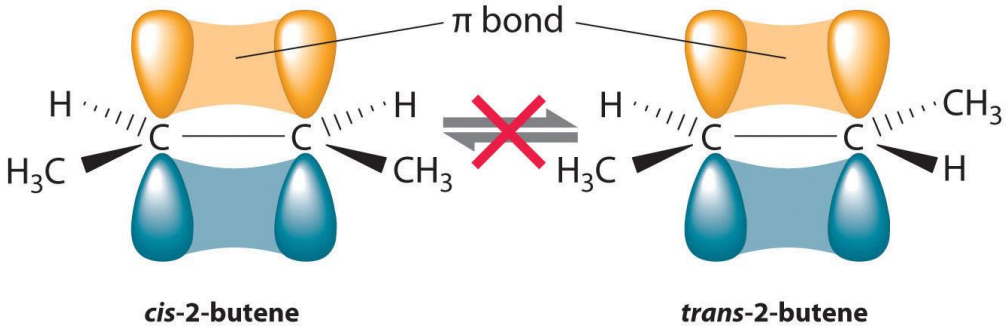


***Trans*-2-butene**
bp 0.8C
mp 2105.5C



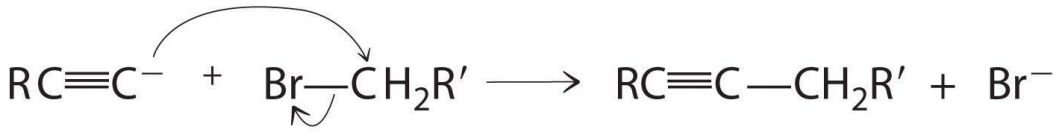
2-Methyl-1-propene
bp 26.9C
mp 2140.4C

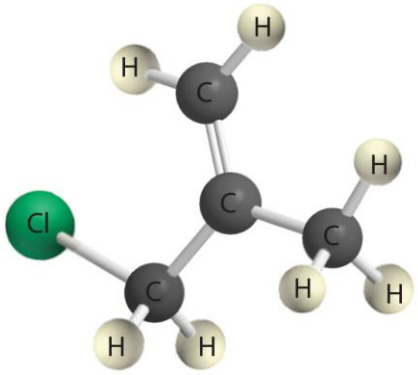
Figure 24.15 *Carbon–Carbon Bonding in Alkenes and Interconversion of Cis andTrans Isomers*



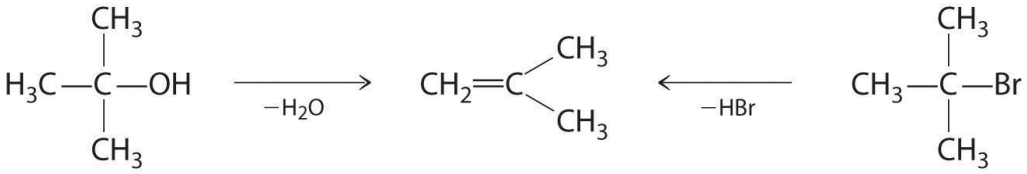
In butane, there is only a small energy barrier to rotation about the C2–C3 σ bond. In the formation of cis- or trans-2-butene from butane, the p orbitals on C2 and C3 overlap to form a π bond. To convert cis-2-butene to trans-2-butene or vice versa through rotation about the double bond, the π bond must be broken. Because this interconversion is energetically unfavorable, cis and trans isomers are distinct compounds that generally have different physical and chemical properties.

Alkynes in which the triple bond is located at one end of a carbon chain are called*terminal alkynes* and contain a hydrogen atom attached directly to a triply bonded carbon: R–C≡C–H. Terminal alkynes are unusual in that the hydrogen atom can be removed relatively easily as H^+, forming an *acetylide ion* ($R–C{\equiv}C^-$). Acetylide ions are potent nucleophiles that are especially useful reactants for making longer carbon chains by a nucleophilic substitution reaction. As in earlier examples of such reactions, the nucleophile attacks the partially positively charged atom in a polar bond, which in the following reaction is the carbon of the Br–C bond:



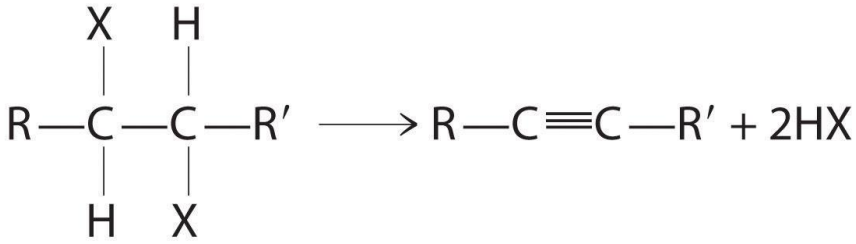


Alkenes and alkynes are most often prepared by elimination reactions (Figure 24.13). A typical example is the preparation of 2-methyl-1-propene, whose derivative, 3-chloro-2-methyl-1-propene, is used as a fumigant and insecticide. The parent compound can be prepared from either 2-hydroxy-2-methylpropane or 2-bromo-2-methylpropane:



2-Hydroxy-2-methylpropane **2-Methyl-1-propene** **2-Bromo-2-methylpropane**

The reaction on the left proceeds by eliminating the elements of water (H^+ plus OH^-), so it is a dehydration reaction. If an alkane contains *two* properly located functional groups, such as –OH or –X, both of them may be removed as H_2O or HX with the formation of a carbon–carbon triple bond:



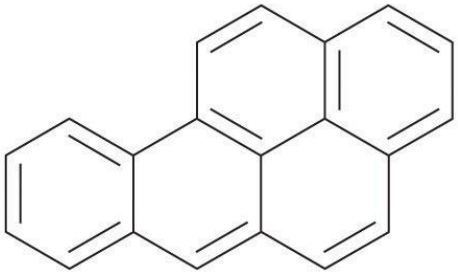
Note the Pattern

Alkenes and alkynes are most often prepared by elimination reactions.

Arenes

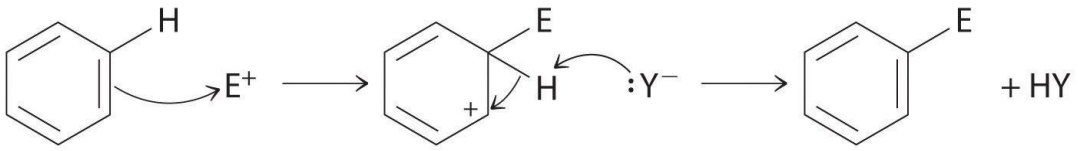
Most arenes that contain a single six-membered ring are volatile liquids, such as benzene and the xylenes, although some arenes with substituents on the ring are solids at room temperature. In the gas phase, the dipole moment of benzene is zero, but the presence of electronegative or electropositive substituents can result in a net dipole moment that increases intermolecular attractive forces and raises the melting and boiling points. For example, 1,4-dichlorobenzene, a compound used as an alternative to naphthalene in the production of mothballs, has a melting point of 52.7°C, which is considerably greater than the melting point of benzene (5.5°C). (For more information on 1,4-dichlorobenzene, see Chapter 11 "Liquids", Section 11.5 "Changes of State".)

Certain aromatic hydrocarbons, such as benzene and benz[a]pyrene, are potent liver toxins and carcinogens. In 1775, a British physician, Percival Pott, described the high incidence of cancer of the scrotum among small boys used as chimney sweeps and attributed it to their exposure to soot. His conclusions were correct: benz[a]pyrene, a component of chimney soot, charcoal-grilled meats, and cigarette smoke, was the first chemical carcinogen to be identified.



Benz[a]pyrene

Although arenes are usually drawn with three C=C bonds, benzene is about 150 kJ/mol more stable than would be expected if it contained three double bonds. This increased stability is due to the delocalization of the π electron density over all the atoms of the ring. (For more information on delocalization, see Chapter 9 "Molecular Geometry and Covalent Bonding Models", Section 9.3 "Delocalized Bonding and Molecular Orbitals".) Compared with alkenes, arenes are poor nucleophiles. Consequently, they do not undergo addition reactions like alkenes; instead, they undergo a variety of electrophilic aromatic substitution reactionsthat involve the replacement of –H on the arene by a group –E, such as $–NO_2$, $–SO_3H$, a halogen, or an alkyl group, in a two-step process. The first step involves addition of the electrophile (E) to the π system of benzene, forming a carbocation. In the second step, a proton is lost from the adjacent carbon on the ring:



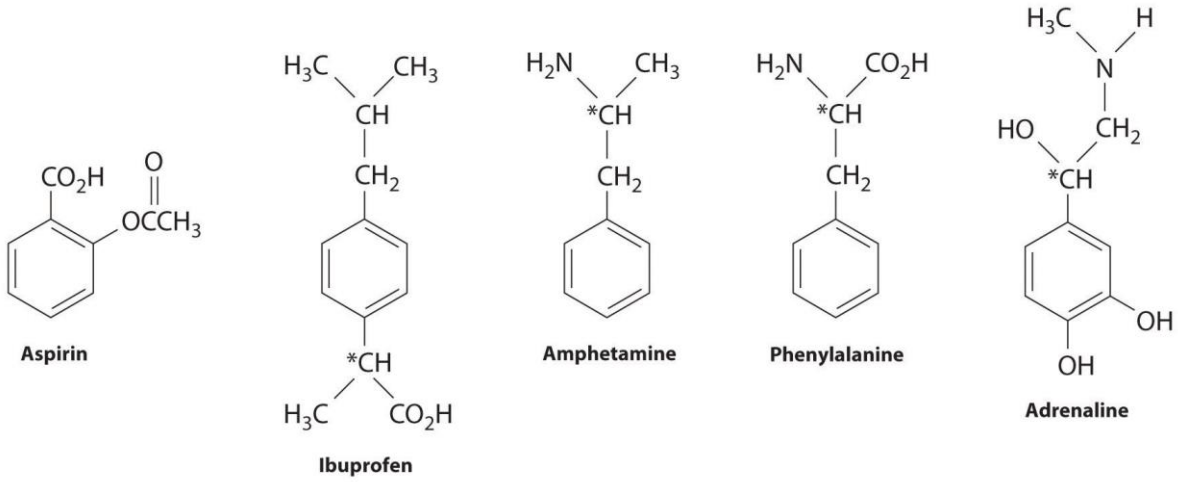
The carbocation formed in the first step is stabilized by resonance.

Note the Pattern

Arenes undergo substitution reactions rather than elimination because of increased stability arising from delocalization of their π electron density.

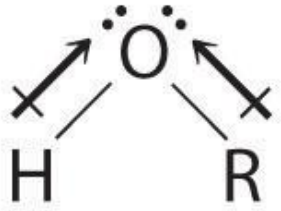
Many substituted arenes have potent biological activity. Some examples include common drugs and antibiotics such as aspirin and ibuprofen, illicit drugs such as amphetamines and peyote, the amino acid phenylalanine, and hormones such as adrenaline (Figure 24.16 "Biologically Active Substituted Arenes").

Figure 24.16 *Biologically Active Substituted Arenes*

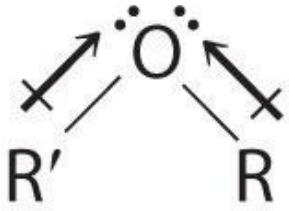


Aspirin (antifever activity), ibuprofen (antifever and anti-inflammatory activity), and amphetamine (stimulant) have pharmacological effects. Phenylalanine is an amino acid. Adrenaline is a hormone that elicits the "fight or flight" response to stress. Chiral centers are indicated with an asterisk.

Alcohols and Ethers



Alcohol



Ether

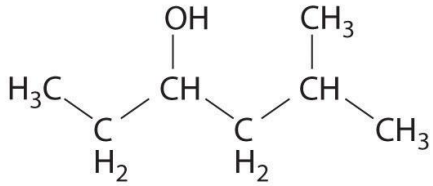
Both alcohols and ethers can be thought of as derivatives of water in which at least one hydrogen atom has been replaced by an organic group, as shown here. Because of the electronegative oxygen atom, the individual O–H bond dipoles in alcohols cannot cancel one another, resulting in a substantial dipole moment that allows alcohols to form hydrogen bonds. Alcohols therefore have significantly higher boiling points than alkanes or alkenes of comparable molecular mass, whereas ethers, without a polar O–H bond, have intermediate boiling points due to the presence of a small dipole moment (Table 24.2 "Boiling Points of Alkanes, Ethers, and Alcohols of Comparable Molecular Mass"). The larger the alkyl group in the molecule, however, the more "alkane-like" the alcohol is in its properties. Because of their polar nature, alcohols and ethers tend to be good solvents for a wide range of organic compounds.

Table 24.2 Boiling Points of Alkanes, Ethers, and Alcohols of Comparable Molecular Mass

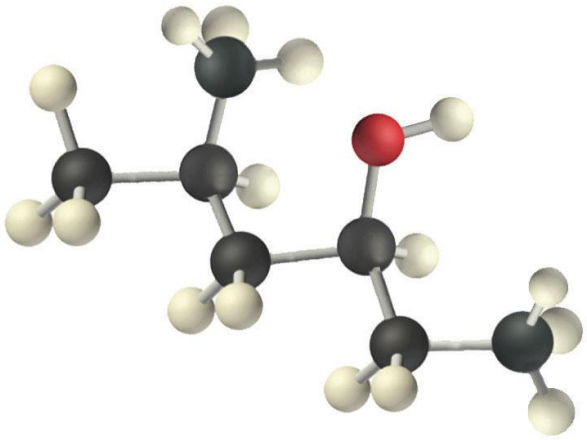
	Name	Formula	Molecular Mass (amu)	Boiling Point (°C)
	propane	C_3H_8	44	−42.1
	n-pentane	C_5H_{12}	72	36.1
alkane	*n*-heptane	C_7H_{16}	100	98.4
	dimethylether	$(CH_3)_2O$	46	−24.8
	diethylether	$(CH_3CH_2)_2O$	74	34.5
ether	di-*n*-propylether	$(CH_3CH_2CH_2)_2O$	102	90.1
	ethanol	CH_3CH_2OH	46	78.3
	n-butanol	$CH_3(CH_2)_3OH$	74	117.7
alcohol	*n*-hexanol	$CH_3(CH_2)_5OH$	102	157.6

Alcohols are usually prepared by adding water across a carbon–carbon double bond or by a nucleophilic substitution reaction of an alkyl halide using hydroxide, a potent nucleophile (Figure 24.12). As you will see in Section 24.6 "The Molecules of Life", alcohols can also be prepared by reducing compounds that contain the carbonyl functional group (C=O; part (a) in Figure 24.14 "The Oxidation State of Carbon in

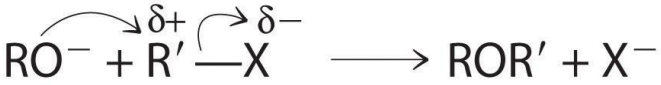
Oxygen- and Nitrogen-Containing Functional Groups"). Alcohols are classified as primary, secondary, or tertiary, depending on whether the –OH group is bonded to a primary, secondary, or tertiary carbon. For example, the compound 5-methyl-3-hexanol is a secondary alcohol.



5-methyl-3-hexanol



Ethers, especially those with two different alkyl groups (ROR′), can be prepared by a substitution reaction in which a nucleophilic alkoxide ion (RO^-) attacks the partially positively charged carbon atom of the polar C–X bond of an alkyl halide (R′X):



Although both alcohols and phenols have an –OH functional group, phenols are 10^6–10^8 more acidic than alcohols. This is largely because simple alcohols have the –OH unit attached to an sp^3 hybridized carbon, whereas phenols have an sp^2 hybridized carbon atom bonded to the oxygen atom. The negative charge of the phenoxide ion can therefore interact with the π electrons in the ring, thereby delocalizing and stabilizing the negative charge through resonance. (For more information on resonance, seeChapter 8 "Ionic versus Covalent Bonding", Section 8.5 "Lewis Structures and Covalent Bonding".) In contrast, the negative charge on an alkoxide ion cannot be stabilized by these types of interactions.

Alcohols undergo two major types of reactions: those involving cleavage of the O–H bond and those involving cleavage of the C–O bond. Cleavage of an O–H bond is a reaction characteristic of an acid, but

alcohols are even weaker acids than water. The acidic strength of phenols, however, is about a million times greater than that of ethanol, making the pK_a of phenol comparable to that of the NH_4^+ ion (9.89 versus 9.25, respectively):

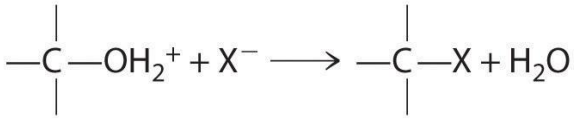
Equation 24.8

$$C6H5OH + H2O \square H3O++ C6H5O-$$

Note the Pattern

Alcohols undergo two major types of reactions: cleavage of the O–H bond and cleavage of the C–O bond.

Cleavage of the C–O bond in alcohols occurs under acidic conditions. The –OH is first protonated, and nucleophilic substitution follows:



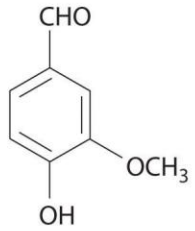
In the absence of a nucleophile, however, elimination can occur, producing an alkene (Figure 24.13).

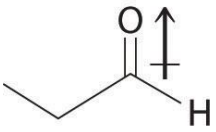
Ethers lack the –OH unit that is central to the reactivity of alcohols, so they are comparatively unreactive. Their low reactivity makes them highly suitable as solvents for carrying out organic reactions.

Aldehydes and Ketones

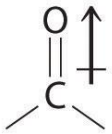
Aromatic aldehydes, which have intense and characteristic flavors and aromas, are the major components of such well-known flavorings as vanilla and cinnamon (Figure 24.17 "Some Familiar Aldehydes and Their Uses"). Many ketones, such as camphor and jasmine, also have intense aromas. Ketones are found in many of the hormones responsible for sex differentiation in humans, such as progesterone and testosterone. (For more information on aldehydes and ketones, see Chapter 4 "Reactions in Aqueous Solution", Section 4.1 "Aqueous Solutions".)

Figure 24.17 Some Familiar Aldehydes and Their Uses

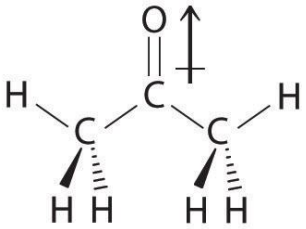
Name	Formula	Use
Formaldehyde	CH_2O	Biological preservative
Cinnamaldehyde	$C_6H_5CH{=}CHCHO$	Cinnamon
Citral	$(CH_3)_2C{=}CHCH_2CH_2C(CH_3){=}CHCHO$	Antiseptic, perfumes
Benzaldehyde	C_6H_5CHO	Manufacture of dyes, almond flavoring
Vanillin		Vanilla flavoring



Propanal



Carbonyl group



2-Propanone

In compounds containing a carbonyl group, nucleophilic attack can occur at the carbon atom of the carbonyl, whereas electrophilic attack occurs at oxygen.

Aldehydes and ketones contain the carbonyl functional group, which has an appreciable dipole moment because of the polar C=O bond. The presence of the carbonyl group results in strong intermolecular interactions that cause aldehydes and ketones to have higher boiling points than alkanes or alkenes of comparable molecular mass (Table 24.3 "Boiling Points of Alkanes, Aldehydes, and Ketones of Comparable Molecular Mass"). As the mass of the molecule increases, the carbonyl group becomes less important to the overall properties of the compound, and the boiling points approach those of the corresponding alkanes.

Table 24.3 Boiling Points of Alkanes, Aldehydes, and Ketones of Comparable Molecular Mass

	Name	Formula	Molecular Mass (amu)	Boiling Point (°C)
alkane	*n*-butane	C_4H_{10}	58	−0.5

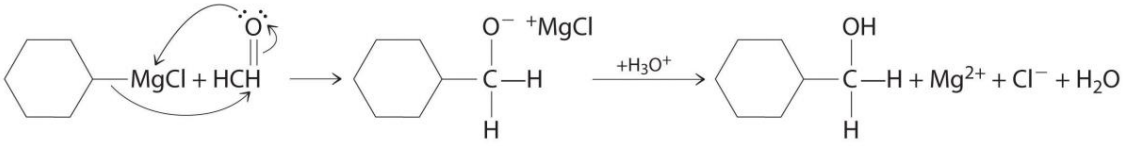
	Name	Formula	Molecular Mass (amu)	Boiling Point (°C)
	n-pentane	C_5H_{12}	72	36.1
aldehyde	propionaldehyde (propanal)	C_3H_6O	58	48.0
	butyraldehyde (butanal)	C_4H_8O	72	74.8
ketone	acetone (2-propanone)	C_3H_6O	58	56.1
	methyl ethyl ketone (2-butanone)	C_4H_8O	72	79.6

Aldehydes and ketones are typically prepared by oxidizing alcohols (part (a) in Figure 24.14 "The Oxidation State of Carbon in Oxygen- and Nitrogen-Containing Functional Groups"). In their reactions, the partially positively charged carbon atom of the carbonyl group is an electrophile that is subject to nucleophilic attack. Conversely, the lone pairs of electrons on the oxygen atom of the carbonyl group allow electrophilic attack to occur. Aldehydes and ketones can therefore undergo both nucleophilic attack (at the carbon atom) and electrophilic attack (at the oxygen atom).

Note the Pattern

Nucleophilic attack occurs at the partially positively charged carbon of a carbonyl functional group. Electrophilic attack occurs at the lone pairs of electrons on the oxygen atom.

Aldehydes and ketones react with many organometallic compounds that contain stabilized carbanions. One of the most important classes of such compounds are theGrignard reagents, organomagnesium compounds with the formula RMgX (X is Cl, Br, or I) that are so strongly polarized that they can be viewed as containing R^- and MgX^+. These reagents are named for the French chemist Victor Grignard (1871–1935), who won a Nobel Prize in Chemistry in 1912 for their development. In a Grignard reaction, the carbonyl functional group is converted to an alcohol, and the carbon chain of the carbonyl compound is lengthened by the addition of the R group from the Grignard reagent. One example is reacting cyclohexylmagnesium chloride, a Grignard reagent, with formaldehyde:

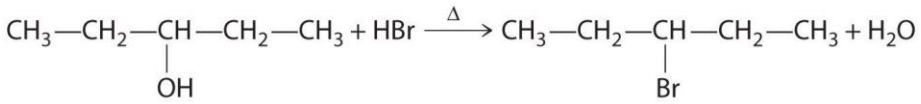


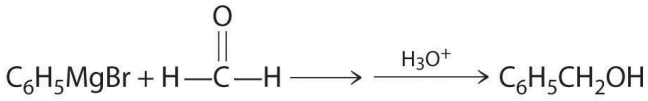
The nucleophilic carbanion of the cyclohexyl ring attacks the electrophilic carbon atom of the carbonyl group. Acidifying the solution results in protonation of the intermediate to give the alcohol. Aldehydes can also be prepared by reducing a carboxylic acid group ($–CO_2H$) (part (a) in Figure 24.14 "The Oxidation State of Carbon in Oxygen- and Nitrogen-

Containing Functional Groups"), and ketones can be prepared by reacting a carboxylic acid derivative with a Grignard reagent. The former reaction requires a powerful reducing agent, such as a metal hydride.

EXAMPLE 7

Explain how each reaction proceeds to form the indicated product.

a. 

b. 

Given: chemical reaction

Asked for: how products are formed

Strategy:

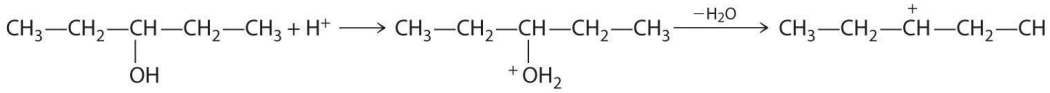
A Identify the functional group and classify the reaction.

B Use the mechanisms described to propose the initial steps in the reaction.

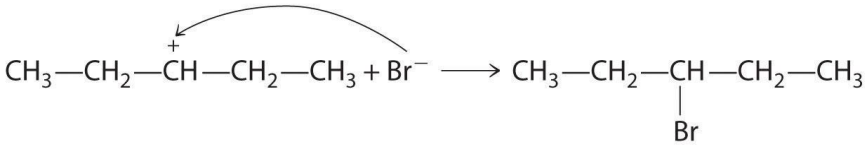
Solution:

a. **A** One reactant is an alcohol that undergoes a substitution reaction.

B In the product, a bromide group is substituted for a hydroxyl group. The first step in this reaction must therefore be protonation of the –OH group of the alcohol by H^+ of HBr, followed by the elimination of water to give the carbocation:

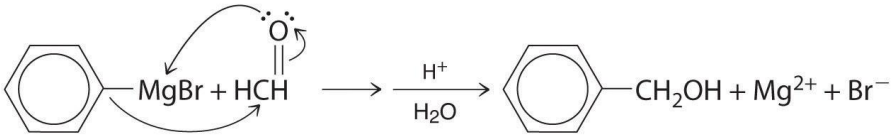


The bromide ion is a good nucleophile that can react with the carbocation to give an alkyl bromide:



A One reactant is a Grignard reagent, and the other contains a carbonyl functional group. Carbonyl compounds act as electrophiles, undergoing nucleophilic attack at the carbonyl carbon.

B The nucleophile is the phenyl carbanion of the Grignard reagent:

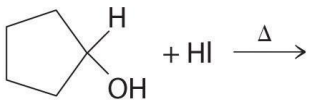


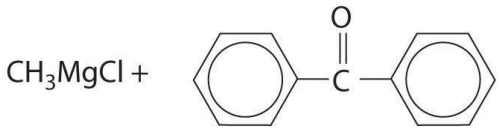
Benzyl alcohol

The product is benzyl alcohol.

Exercise

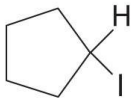
Predict the product of each reaction.

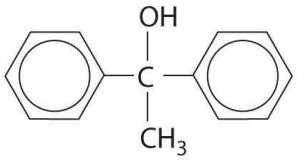
a. 

b. 

(benzophenone), followed by reaction with aqueous acid

Answer:

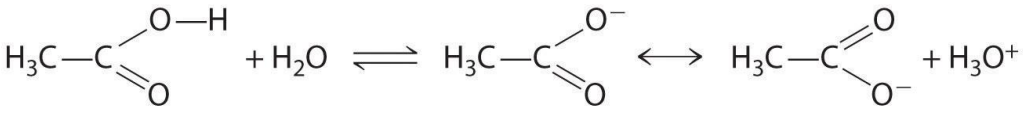
a. 

b. 

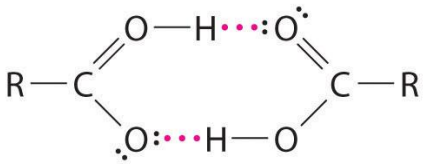
Carboxylic Acids

The pungent odors of many carboxylic acids are responsible for the smells we associate with sources as diverse as Swiss cheese, rancid butter, manure, goats, and sour milk. The boiling points of carboxylic acids tend to be somewhat higher than would be expected from their molecular masses because of strong hydrogen-bonding interactions between molecules. In fact, most simple carboxylic acids form dimers in the liquid and even in the vapor phase. (For more information on the vapor phase, see Chapter 11 "Liquids", Section 11.2 "Intermolecular Forces".) The four lightest carboxylic acids are completely miscible with water, but as the alkyl chain lengthens, they become more “alkane-like,” so their solubility in water decreases.

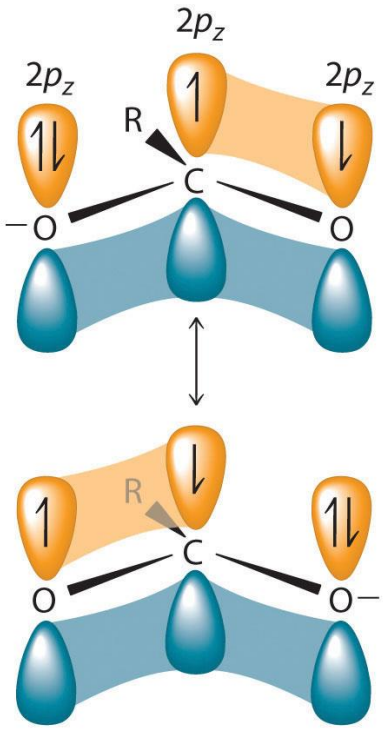
Compounds that contain the carboxyl functional group are acidic because carboxylic acids can easily lose a proton: the negative charge in the carboxylate ion (RCO_2^-) is stabilized by delocalization of the π electrons:



As a result, carboxylic acids are about 10^{10} times more acidic than the corresponding simple alcohols whose anions (RO^-) are not stabilized through resonance.



Hydrogen-bonded carboxylic acid molecules

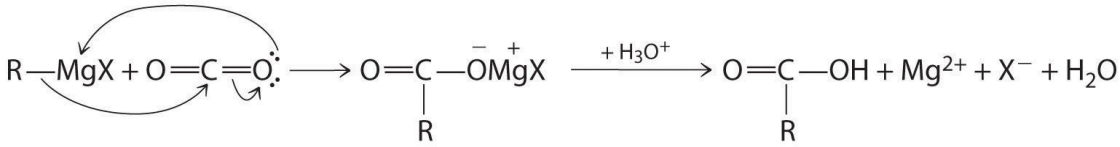


Carboxylic acids are typically prepared by oxidizing the corresponding alcohols and aldehydes (part (a) in Figure 24.14 "The Oxidation State of Carbon in Oxygen- and Nitrogen-Containing Functional Groups"). They can also be prepared by reacting a Grignard reagent with CO_2, followed by acidification:

Equation 24.9

$$CO2 + RMgCl \rightarrow - \rightarrow - - H3O + RCO2H + Mg2 + + Cl - + H2O$$

The initial step in the reaction is nucleophilic attack by the R^- group of the Grignard reagent on the electrophilic carbon of CO_2:



Delocalization of π bonding over three atoms (O–C–O) makes carboxylic acids and their derivatives less susceptible to nucleophilic attack than aldehydes and ketones with their single π bond. The reactions of carboxylic acids are dominated by two factors: their polar $–CO_2H$ group and their acidity. Reaction with strong bases, for example, produce carboxylate salts, such as sodium stearate:

Equation 24.10

$$RCO_2H + NaOH \rightarrow RCO_2^-Na^+ + H_2O$$

where R is $CH_3(CH_2)_{16}$. As you learned in Chapter 13 "Solutions", Section 13.6 "Aggregate Particles in Aqueous Solution", long-chain carboxylate salts are used as soaps.

Note the Pattern

Delocalization of π bonding over three atoms makes carboxylic acids and their derivatives less susceptible to nucleophilic attack as compared with aldehydes and ketones.

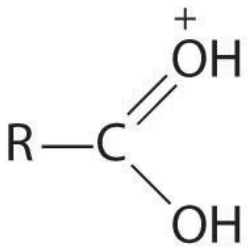
Carboxylic Acid Derivatives

Replacing the –OH of a carboxylic acid with groups that have different tendencies to participate in resonance with the C=O functional group produces derivatives with rather different properties. Resonance structures have significant effects on the reactivity of carboxylic acid derivatives, but their influence varies substantially, being least important for halides and most important for the nitrogen of amides. In this section, we take a brief look at the chemistry of two of the most familiar and important carboxylic acid derivatives: esters and amides.

Esters

Esters have the general formula RCO_2R', where R and R′ can be virtually any alkyl or aryl group. Esters are often prepared by reacting an alcohol (R′OH) with a carboxylic acid (RCO_2H) in the presence of a catalytic amount of strong acid. (For more information on esters and catalysts, see Chapter 3 "Chemical Reactions", Section 3.5 "Classifying Chemical Reactions".) The purpose of the acid (an electrophile) is to

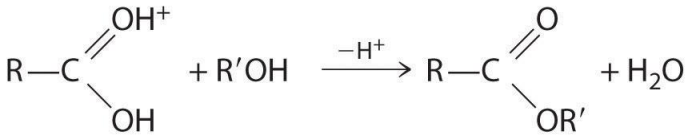
protonate the doubly bonded oxygen atom of the carboxylic acid (a nucleophile) to give a species that is *more* electrophilic than the parent carboxylic acid.



Protonated carboxylic acid

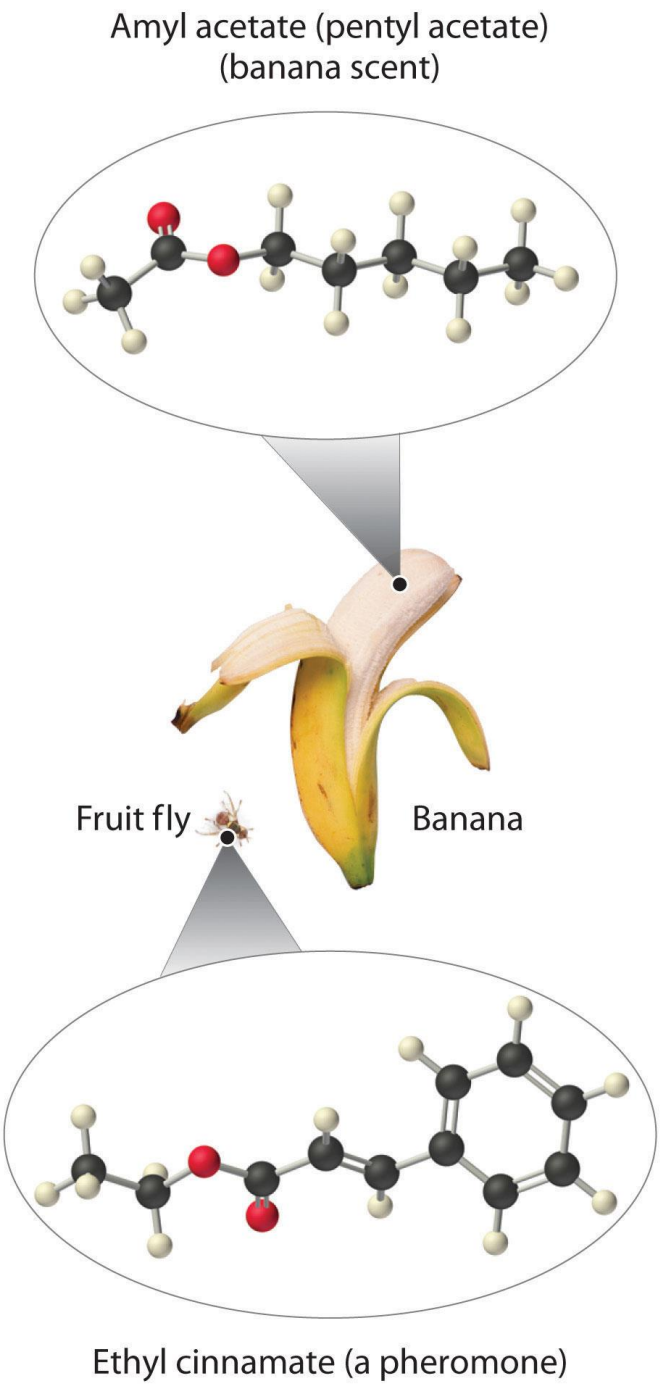
The nucleophilic oxygen atom of the alcohol attacks the electrophilic carbon atom of the protonated carboxylic acid to form a new C–O bond. The overall reaction can be written as follows:

Figure 24.18



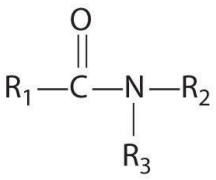
Because water is eliminated, this is a dehydration reaction. If an aqueous solution of an ester and strong acid or base is heated, the reverse reaction will occur, producing the parent alcohol R′OH and either the carboxylic acid RCO_2H (under strongly acidic conditions) or the carboxylate anion RCO_2^- (under basic conditions).

As stated earlier, esters are familiar to most of us as fragrances, such as banana and pineapple. Other esters with intense aromas function as sex attractants, or*pheromones*, such as the pheromone from the oriental fruit fly. Research on using synthetic insect pheromones as a safer alternative to insecticides for controlling insect populations, such as cockroaches, is a rapidly growing field in organic chemistry.



Amides

In the general structure of an amide,



An amide

the two substituents on the amide nitrogen can be hydrogen atoms, alkyl groups, aryl groups, or any combination of those species. Although amides appear to be derived from an acid and an amine, in practice they usually cannot be prepared by this synthetic route. In principle, nucleophilic attack by the lone electron pair of the amine on the carbon of the carboxylic acid could occur, but because carboxylic acids are weak acids and amines are weak bases, an acid–base reaction generally occurs instead:

Equation 24.11

$$RCO_2H + R'NH_2 \rightarrow RCO_2^- + R'NH_3^+$$

Amides are therefore usually prepared by the nucleophilic reaction of amines with more electrophilic carboxylic acid derivatives, such as esters.

The lone pair of electrons on the nitrogen atom of an amide can participate in π bonding with the carbonyl group, thus reducing the reactivity of the amide (Figure 24.19 "The Electronic Structure of an Amide") and inhibiting free rotation about the C–N bond. Amides are therefore the least reactive of the carboxylic acid derivatives. The stability of the amide bond is crucially important in biology because amide bonds form the backbones of peptides and proteins. (For more information on peptides and proteins, see Chapter 12 "Solids", Section 12.8 "Polymeric Solids".) The amide bond is also found in many other biologically active and commercially important molecules, including penicillin; urea, which is used as fertilizer; saccharin, a sugar substitute; and valium, a potent tranquilizer. (For more information on the structure of penicillin, seeChapter 3 "Chemical Reactions", Section 3.2 "Determining Empirical and Molecular Formulas".)

Note the Pattern

Amides are the least reactive of the carboxylic acid derivatives because amides participate in π bonding with the carbonyl group.

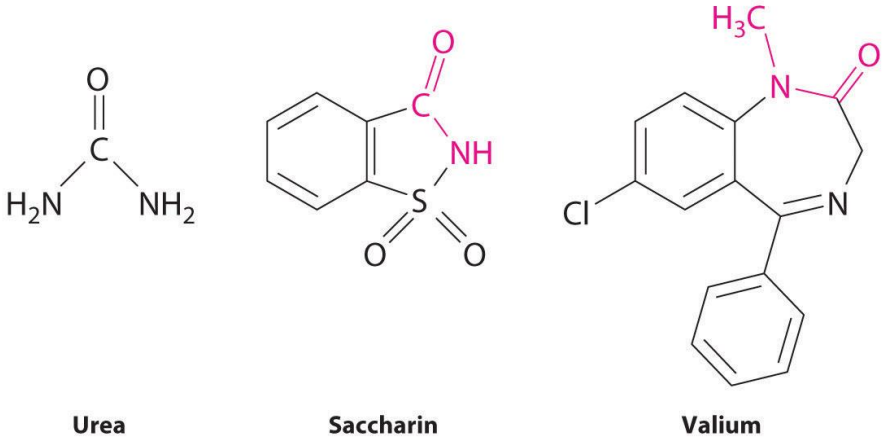
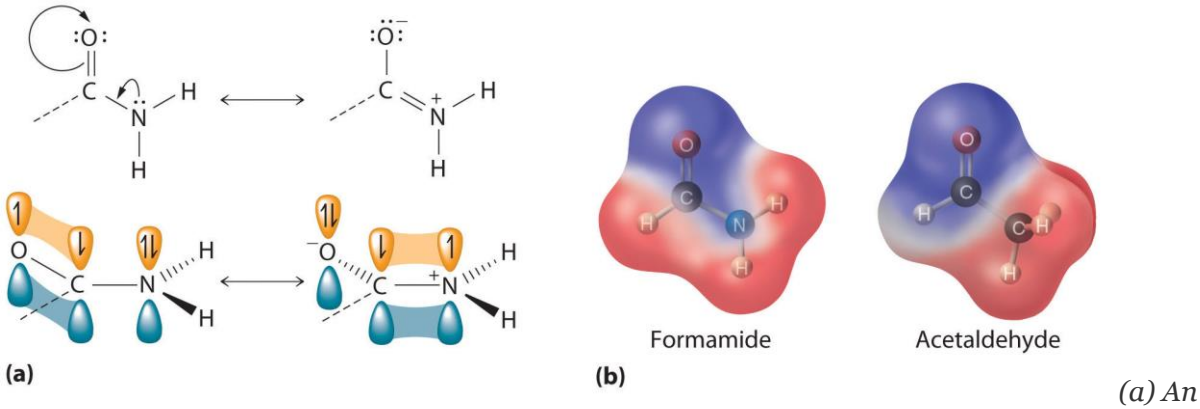


Figure 24.19 *The Electronic Structure of an Amide*



(a) An unhybridized 2p$_z$ orbital on nitrogen, containing a lone electron pair of electrons, can interact with the π orbital of the carbonyl group to give a three-center, four-electron bond. This interaction reduces the reactivity of the amide, making amides the least reactive of the carboxylic acid derivatives. (b) A comparison of the electrostatic potential maps of acetaldehyde and formamide shows that the negative charge (indicated in blue) is more localized on the oxygen atom of acetaldehyde than it is in formamide. Formamide is therefore less reactive.

Amines

Amines are derivatives of ammonia in which one or more hydrogen atoms have been replaced by alkyl or aryl groups. They are therefore analogous to alcohols and ethers. Like alcohols, amines are classified as primary, secondary, or tertiary, but in this case the designation refers to the number of alkyl groups bonded to the nitrogen atom, not to the number of adjacent carbon atoms. In primary amines, the nitrogen is bonded to two hydrogen atoms and one alkyl group; in secondary amines, the nitrogen is

bonded to one hydrogen and two alkyl groups; and in tertiary amines, the nitrogen is bonded to three alkyl groups. With one lone pair of electrons and C–N bonds that are less polar than C–O bonds, ammonia and simple amines have much lower boiling points than water or alcohols with similar molecular masses. Primary amines tend to have boiling points intermediate between those of the corresponding alcohol and alkane. Moreover, secondary and tertiary amines have lower boiling points than primary amines of comparable molecular mass.

Tertiary amines form cations analogous to the ammonium ion (NH_4^+), in which all four H atoms are replaced by alkyl groups. Such substances, calledquaternary ammonium salts, can be chiral if all four substituents are different. (Amines with three different substituents are also chiral because the lone pair of electrons represents a fourth substituent.)

Alkylamines can be prepared by nucleophilic substitution reactions of alkyl halides with ammonia or other amines:

Equation 24.12

$$RCl + NH_3 \rightarrow RNH_2 + HCl$$

Equation 24.13

$$RCl + R'NH_2 \rightarrow RR'NH + HCl$$

Equation 24.14

$$RCl + R'R''NH \rightarrow RR'R''N + HCl$$

The primary amine formed in the first reaction (Equation 24.12) can react with more alkyl halide to generate a secondary amine (Equation 24.13), which in turn can react to form a tertiary amine (Equation 24.14). Consequently, the actual reaction mixture contains primary, secondary, and tertiary amines and even quaternary ammonium salts.

The reactions of amines are dominated by two properties: their ability to act as weak bases and their tendency to act as nucleophiles, both of which are due to the presence of the lone pair of electrons on the nitrogen atom. Amines typically behave as bases by accepting a proton from an acid to form an ammonium salt, as in the reaction of triethylamine (the ethyl group is represented as Et) with aqueous HCl (the lone pair of electrons on nitrogen is shown):

Equation 24.15

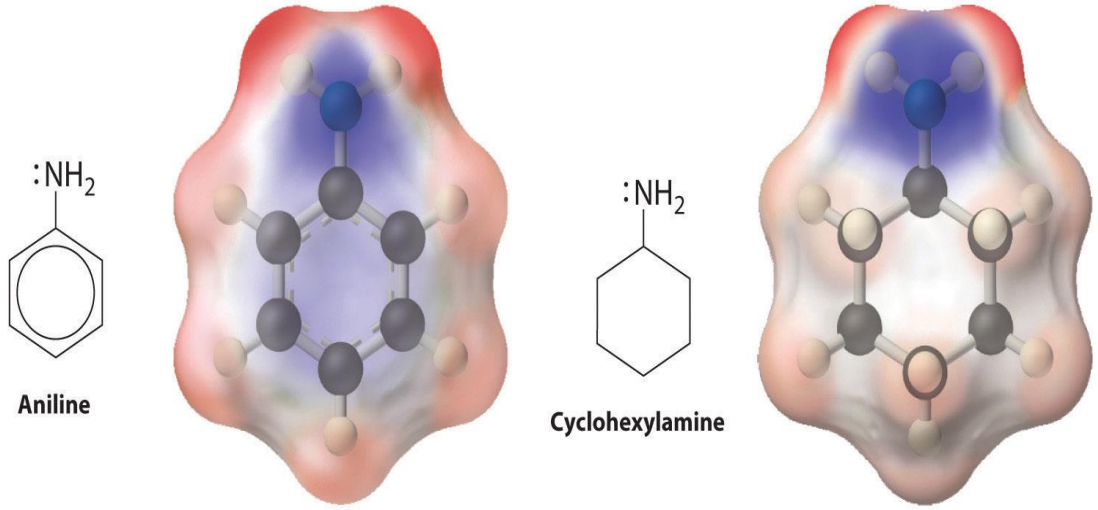
$$Et_3N{:}(l) + HCl(aq) \rightarrow Et_3NH^+Cl^-(aq)$$

which gives triethylammonium chloride. Amines can react with virtually any electrophile, including the carbonyl carbon of an aldehyde, a ketone, or an ester. Aryl amines such as aniline ($C_6H_5NH_2$) are much weaker bases than alkylamines because the lone pair of electrons on nitrogen interacts with the π bonds of the aromatic ring, delocalizing the lone pair through resonance (Figure 24.20 "Structures and Basicity of Aniline and Cyclohexylamine").

Note the Pattern

The reactions of amines are dominated by their ability to act as weak bases and their tendency to act as nucleophiles.

Figure 24.20 *Structures and Basicity of Aniline and Cyclohexylamine*



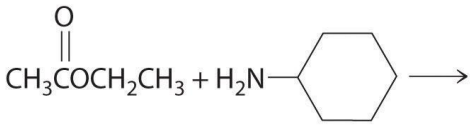
Delocalization of the lone electron pair on N over the benzene ring reduces the basicity of aryl amines, such as aniline, compared with that of alkylamines, such as cyclohexylamine. These electrostatic potential maps show that the electron density on the N of cyclohexylamine is more localized than it is in aniline, which makes cyclohexylamine a stronger base.

EXAMPLE 8

Predict the products formed in each reaction and show the initial site of attack and, for part (b), the final products.

a. $C_6H_5CH_2CO_2H + KOH \rightarrow$

b.



Ethyl acetate **Cyclohexylamine**

Given: reactants

Asked for: products and mechanism of reaction

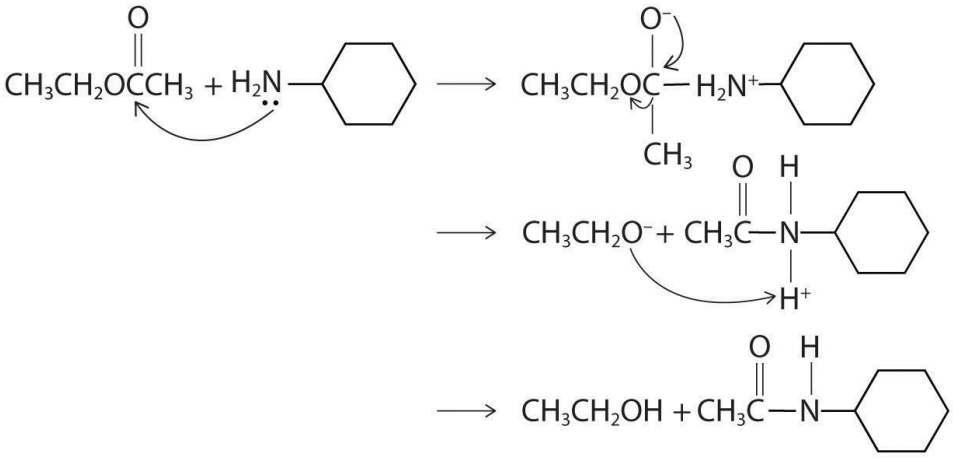
Strategy:

Use the strategy outlined in Example 7.

Solution:

a. The proton on the carboxylic acid functional group is acidic. Thus reacting a carboxylic acid with a strong base is an acid–base reaction, whose products are a salt—in this case, $C_6H_5CH_2CO_2^-K^+$—and water.

b. The nitrogen of cyclohexylamine contains a lone pair of electrons, making it an excellent nucleophile, whereas the carbonyl carbon of ethyl acetate is a good electrophile. We therefore expect a reaction in which nucleophilic attack on the carbonyl carbon of the ester produces an amide and ethanol. The initial site of attack and the reaction products are as follows:



Exercise

Predict the products of each reaction. State the initial site of attack.

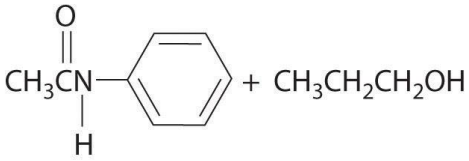
a. acetic acid with 1-propanol

b. aniline ($C_6H_5NH_2$) with propyl acetate [$CH_3C(=O)OCH_2CH_2CH_3$]

Answer:

a. Initial attack occurs with protonation of the oxygen of the carbonyl. The products are:

Initial attack occurs at the carbon of the carbonyl group. The products are:



Reactions like we have discussed in this section and Section 24.4 "Common Classes of Organic Reactions" are used to synthesize a wide range of organic compounds. When chemists plan the synthesis of an organic molecule, however, they must take into consideration various factors, such as the availability and cost of reactants, the need to minimize the formation of undesired products, and the proper sequencing of reactions to maximize the yield of the target molecule and minimize the formation of undesired products. Because the synthesis of many organic molecules requires multiple steps, in designing a synthetic scheme for such molecules, chemists must often work backward from the desired product in a process called *retrosynthesis*. Using this process, they can identify the reaction steps needed to synthesize the desired product from the available reactants.

Summary

There are strong connections among the structure, the physical properties, and the reactivity for compounds that contain the major functional groups. Hydrocarbons that are alkanes undergo catalytic cracking, which can convert straight-chain alkanes to highly branched alkanes. Catalytic cracking is one example of a**pyrolysis reaction**, in which the weakest bond is cleaved at high temperature, producing a mixture of radicals. The multiple bond of an alkene produces geometric isomers (*cis* and *trans*). Terminal alkynes contain a hydrogen atom directly attached to a triply bonded carbon. Removal of the hydrogen forms an acetylide ion, a potent nucleophile used to make longer carbon chains. Arenes undergo substitution rather than elimination because of enhanced stability from delocalization of their π electron density. An alcohol is often prepared by adding the elements of water across a double bond or by a

substitution reaction. Alcohols undergo two major types of reactions: those involving cleavage of the O–H bond and those involving cleavage of the C–O bond. Phenols are acidic because of π interactions between the oxygen atom and the ring. Ethers are comparatively unreactive. Aldehydes and ketones are generally prepared by oxidizing alcohols. Their chemistry is characterized by nucleophilic attack at the carbon atom of the carbonyl functional group and electrophilic attack at the oxygen atom. **Grignard reagents** (RMgX, where X is Cl, Br, or I) convert the carbonyl functional group to an alcohol and lengthen the carbon chain. Compounds that contain the carboxyl functional group are weakly acidic because of delocalization of the π electrons, which causes them to easily lose a proton and form the carboxylate anion. Carboxylic acids are generally prepared by oxidizing alcohols and aldehydes or reacting a Grignard reagent with CO_2. Carboxylic acid derivatives include esters, prepared by reacting a carboxylic acid and an alcohol, and amides, prepared by the nucleophilic reaction of amines with more electrophilic carboxylic acid derivatives, such as esters. Amides are relatively unreactive because of π bonding interactions between the lone pair on nitrogen and the carbonyl group. Amines can also be primary, secondary, or tertiary, depending on the number of alkyl groups bonded to the amine. **Quaternary ammonium salts** have four substituents attached to nitrogen and can be chiral. Amines are often prepared by a nucleophilic substitution reaction between a polar alkyl halide and ammonia or other amines. They are nucleophiles, but their base strength depends on their substituents.

KEY TAKEAWAY

- The physical properties and reactivity of compounds containing the common functional groups are intimately connected to their structures.

CONCEPTUAL PROBLEMS

1. Why do branched-chain alkanes have lower melting points than straight-chain alkanes of comparable molecular mass?
2. Describe alkanes in terms of their orbital hybridization, polarity, and reactivity. What is the geometry about each carbon of a straight-chain alkane?
3. Why do alkenes form *cis* and *trans* isomers, whereas alkanes do not? Do alkynes form *cis*and *trans* isomers? Why or why not?
4. Which compounds can exist as *cis* and *trans* isomers?

a. 2,3-dimethyl-1-butene

b. 3-methyl-1-butene

c. 2-methyl-2-pentene

d. 2-pentene

5. Which compounds can exist as *cis* and *trans* isomers?

a. 3-ethyl-3-hexene

b. 1,1-dichloro-1-propene

c. 1-chloro-2-pentene

d. 3-octene

6. Which compounds have a net dipole moment?

a. *o*-nitrotoluene

b. *p*-bromonitrobenzene

c. *p*-dibromobenzene

7. Why is the boiling point of an alcohol so much greater than that of an alkane of comparable molecular mass? Why are low-molecular-mass alcohols reasonably good solvents for some ionic compounds, whereas alkanes are not?

8. Is an alcohol a nucleophile or an electrophile? What determines the mode of reactivity of an alcohol? How does the reactivity of an alcohol differ from that of an ionic compound containing OH, such as KOH?

9. How does the reactivity of ethers compare with that of alcohols? Why? Ethers can be cleaved under strongly acidic conditions. Explain how this can occur.

10. What functional group is common to aldehydes, ketones, carboxylic acids, and esters? This functional group can react with both nucleophiles and electrophiles. Where does nucleophilic attack on this functional group occur? Where does electrophilic attack occur?

11. What key feature of a Grignard reagent allows it to engage in a nucleophilic attack on a carbonyl carbon?

12. Do you expect carboxylic acids to be more or less water soluble than ketones of comparable molecular mass? Why?

13. Because amides are formally derived from an acid plus an amine, why can they not be prepared by the reaction of an acid with an amine? How are they generally prepared?

14. Is an amide susceptible to nucleophilic attack, electrophilic attack, or both? Specify where the attack occurs.

15. What factors determine the reactivity of amines?

ANSWERS

1.
2.
3.
4.
5. (c) and (d)
6.
7.
8.
9.
10.
11. The presence of a nucleophilic $C^{\delta-}$ resulting from a highly polar interaction with an electropositive Mg
12.
13.
14.
15. Their ability to act as weak bases and their tendency to act as nucleophiles

STRUCTURE AND REACTIVITY

1. What is the product of the reaction of 2-butyne with excess HBr?
2. What is the product of the reaction of 3-hexyne with excess HCl?
3. What elements are eliminated during the dehydrohalogenation of an alkyl halide? What products do you expect from the dehydrohalogenation of 2-chloro-1-pentene?
4. What elements are eliminated during the dehydration of an alcohol? What products do you expect from the dehydration of ethanol?
5. Predict the products of each reaction.

a. sodium phenoxide with ethyl chloride

b. 1-chloropropane with NaOH

6. Show the mechanism and predict the organic product of each reaction.

a. 2-propanol + HCl

b. cyclohexanol + H_2SO_4

7. A Grignard reagent can be used to generate a carboxylic acid. Show the mechanism for the first step in this reaction using CH_3CH_2MgBr as the Grignard reagent. What is the geometry about the carbon of the $–CH_2$ of the intermediate species formed in this first step?
8. Draw a molecular orbital picture showing the bonding in an amide. What orbital is used for the lone pair of electrons on nitrogen?
9. What is the product of the reaction of

a. acetic acid with ammonia?

b. methyl acetate with ethylamine, followed by heat?

10. Develop a synthetic scheme to generate

a. 1,1-dichloroethane from 1,1-dibromoethane.

b. 2-bromo-1-heptene from 1-bromopentane.

ANSWERS

1. 2,2-dibromobutane

2.

3.

4.

5.

a. $C_6H_5OC_2H_5 + NaCl$

b. 1-propanol + NaCl

6.

7.

8.

9.

a. $CH_3CO_2^- NH_4^+$ (an acid-base reaction)

b. $CH_3CONHC_2H_5 + CH_3OH$

24.5 Common Classes of Organic Compounds

LEARNING OBJECTIVE

1. To understand the general properties of functional groups and the differences in their reactivity.

The general properties and reactivity of each class of organic compounds (Figure 24.1 "Major Classes of Organic Compounds") is largely determined by its functional groups. In this section, we describe the relationships between structure, physical properties, and reactivity for the major classes of organic compounds. We also show you how to apply these relationships to understand some common reactions that chemists use to synthesize organic compounds.

Alkanes, Alkenes, and Alkynes

The boiling points of alkanes increase smoothly with increasing molecular mass. They are similar to those of the corresponding alkenes and alkynes because of similarities in molecular mass between analogous structures (Table 24.1 "Boiling Points (in °C) of Alkanes, Alkenes, and Alkynes of Comparable Molecular Mass"). In contrast, the melting points of alkanes, alkenes, and alkynes with similar molecular masses show a much wider variation because the melting point strongly depends on how the molecules stack in the solid state. It is therefore sensitive to relatively small differences in structure, such as the location of a double bond and whether the molecule is *cis* or*trans*.

Table 24.1 Boiling Points (in °C) of Alkanes, Alkenes, and Alkynes of Comparable Molecular Mass

	Length of Carbon Chain		
Class	Two C Atoms	Three C Atoms	Four C Atoms
alkane	−88.6	−42.1	−0.5
alkene	−103.8	−47.7	−6.3
alkyne	−84.7	−23.2	8.1

Because alkanes contain only C–C and C–H bonds, which are strong and not very polar (the electronegativities of C and H are similar; Figure 7.15 "Pauling Electronegativity Values of the "), they are not easily attacked by nucleophiles or electrophiles. Consequently, their reactivity is limited, and often their reactions occur only under extreme conditions. For example, *catalytic cracking* can be used to convert straight-chain alkanes to highly branched alkanes, which are better fuels for internal combustion engines. Catalytic cracking is one example of a pyrolysis reaction (from the Greek *pyros*, meaning “fire,” and *lysis*, meaning “loosening”), in which alkanes are heated to a sufficiently high temperature to induce cleavage of the weakest bonds: the C–C single bonds. The result is a mixture of radicals derived from

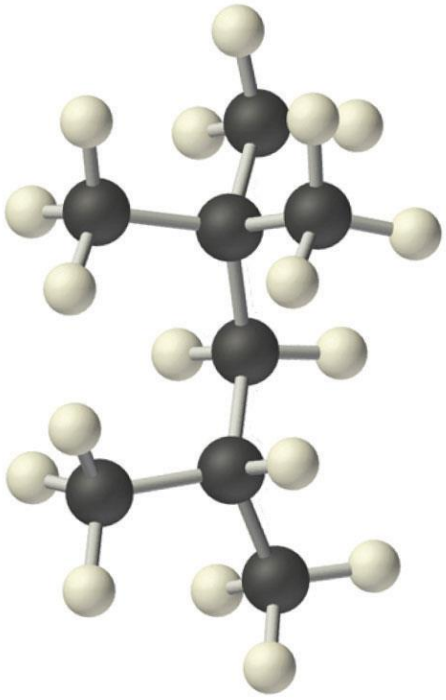
essentially random cleavage of the various C–C bonds in the chain. Pyrolysis of *n*-pentane, for example, is nonspecific and can produce these four radicals:

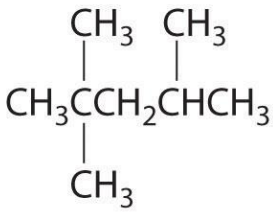
Equation 24.7

$$2CH3CH2CH2CH2CH3 \rightarrow DCH3\cdot + CH2CH2CH2\cdot + CH3CH2\cdot + CH3CH2CH2\cdot$$

Recombination of these radicals (a termination step) can produce ethane, propane, butane, *n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane. Radicals that are formed in the middle of a chain by cleaving a C–H bond tend to produce branched hydrocarbons. In catalytic cracking, lighter alkanes are removed from the mixture by distillation.

Radicals are also produced during the combustion of alkanes, with CO_2 and H_2O as the final products. As discussed in Section 24.3 "Reactivity of Organic Molecules", radicals are stabilized by the presence of multiple carbon substituents that can donate electron density to the electron-deficient carbon. The chemical explanation of octane ratings, as described in Chapter 2 "Molecules, Ions, and Chemical Formulas", Section 2.6 "Industrially Important Chemicals", rests partly on the stability of radicals produced from the different hydrocarbon fuels. Recall that *n*-heptane, which does not burn smoothly, has an octane rating of 0, and 2,2,4-trimethylpentane (“isooctane”), which burns quite smoothly, has a rating of 100 (Figure 2.25 "The Octane Ratings of Some Hydrocarbons and Common Additives"). Isooctane has a branched structure and is capable of forming tertiary radicals that are comparatively stable.

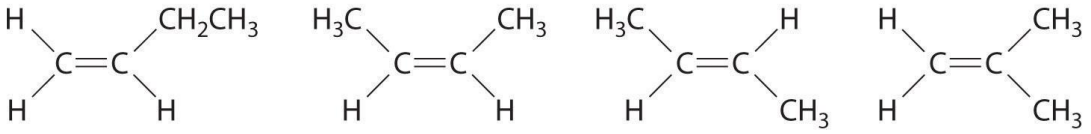




2,2,4-Trimethylpentane ("isooctane")

In contrast, the radicals formed during the combustion of*n*-heptane, whether primary or secondary, are less stable and hence more reactive, which partly explains why burning *n*-heptane causes premature ignition and engine knocking.

In Section 24.2 "Isomers of Organic Compounds", we explained that rotation about the carbon–carbon multiple bonds of alkenes and alkynes cannot occur without breaking a π bond, which therefore constitutes a large energy barrier to rotation (Figure 24.15 "Carbon–Carbon Bonding in Alkenes and Interconversion of "). Consequently, the *cis* and *trans* isomers of alkenes generally behave as distinct compounds with different chemical and physical properties. A four-carbon alkene has four possible isomeric forms: three structural isomers, which differ in their connectivity, plus a pair of geometric isomers from one structural isomer (2-butene). These two geometric isomers are *cis*-2-butene and*trans*-2-butene. The four isomers have significantly different physical properties.



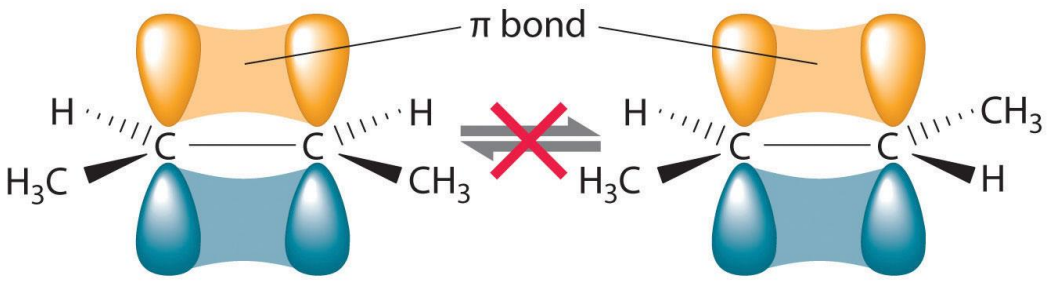
1-Butene
bp 26.2C
mp 2185.3C

Cis-2-butene
bp 3.7C
mp 2138.9C

Trans-2-butene
bp 0.8C
mp 2105.5C

2-Methyl-1-propene
bp 26.9C
mp 2140.4C

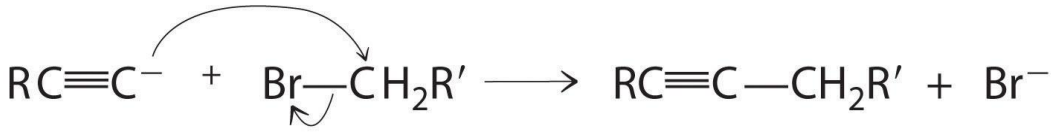
Figure 24.15 Carbon–Carbon Bonding in Alkenes and Interconversion of Cis and Trans Isomers

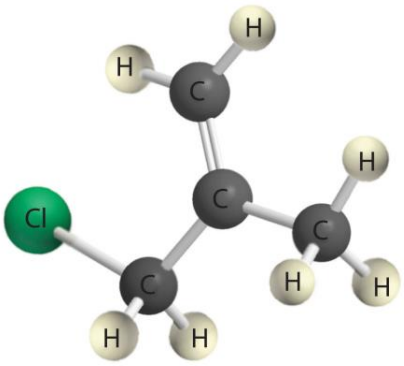


***cis*-2-butene** ***trans*-2-butene**

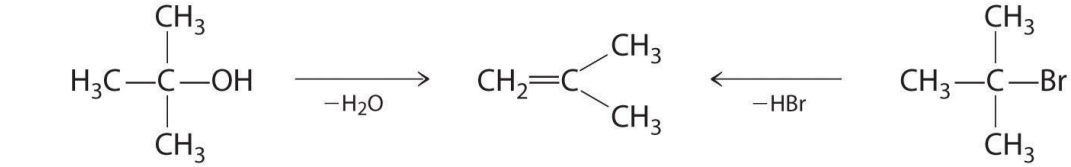
In butane, there is only a small energy barrier to rotation about the C2–C3 σ bond. In the formation of cis- or trans-2-butene from butane, the p orbitals on C2 and C3 overlap to form a π bond. To convert cis-2-butene to trans-2-butene or vice versa through rotation about the double bond, the π bond must be broken. Because this interconversion is energetically unfavorable, cis and trans isomers are distinct compounds that generally have different physical and chemical properties.

Alkynes in which the triple bond is located at one end of a carbon chain are called*terminal alkynes* and contain a hydrogen atom attached directly to a triply bonded carbon: R–C≡C–H. Terminal alkynes are unusual in that the hydrogen atom can be removed relatively easily as H^+, forming an *acetylide ion* (R–C≡C^-). Acetylide ions are potent nucleophiles that are especially useful reactants for making longer carbon chains by a nucleophilic substitution reaction. As in earlier examples of such reactions, the nucleophile attacks the partially positively charged atom in a polar bond, which in the following reaction is the carbon of the Br–C bond:



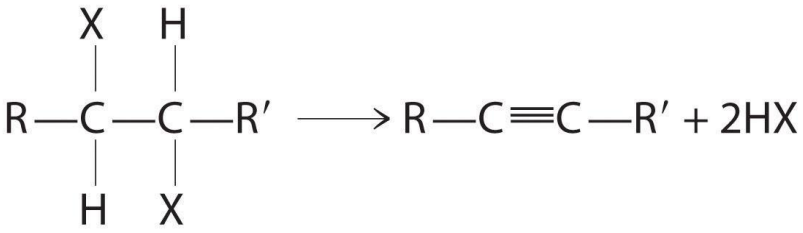


Alkenes and alkynes are most often prepared by elimination reactions (Figure 24.13). A typical example is the preparation of 2-methyl-1-propene, whose derivative, 3-chloro-2-methyl-1-propene, is used as a fumigant and insecticide. The parent compound can be prepared from either 2-hydroxy-2-methylpropane or 2-bromo-2-methylpropane:



2-Hydroxy-2-methylpropane **2-Methyl-1-propene** **2-Bromo-2-methylpropane**

The reaction on the left proceeds by eliminating the elements of water (H^+ plus OH^-), so it is a dehydration reaction. If an alkane contains *two* properly located functional groups, such as –OH or –X, both of them may be removed as H_2O or HX with the formation of a carbon–carbon triple bond:



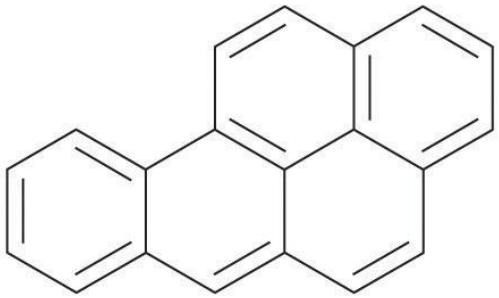
Note the Pattern

Alkenes and alkynes are most often prepared by elimination reactions.

Arenes

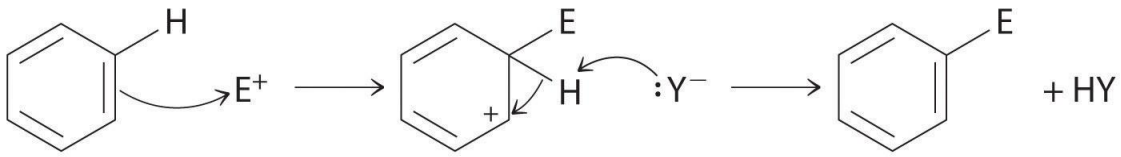
Most arenes that contain a single six-membered ring are volatile liquids, such as benzene and the xylenes, although some arenes with substituents on the ring are solids at room temperature. In the gas phase, the dipole moment of benzene is zero, but the presence of electronegative or electropositive substituents can result in a net dipole moment that increases intermolecular attractive forces and raises the melting and boiling points. For example, 1,4-dichlorobenzene, a compound used as an alternative to naphthalene in the production of mothballs, has a melting point of 52.7°C, which is considerably greater than the melting point of benzene (5.5°C). (For more information on 1,4-dichlorobenzene, see Chapter 11 "Liquids", Section 11.5 "Changes of State".)

Certain aromatic hydrocarbons, such as benzene and benz[a]pyrene, are potent liver toxins and carcinogens. In 1775, a British physician, Percival Pott, described the high incidence of cancer of the scrotum among small boys used as chimney sweeps and attributed it to their exposure to soot. His conclusions were correct: benz[a]pyrene, a component of chimney soot, charcoal-grilled meats, and cigarette smoke, was the first chemical carcinogen to be identified.



Benz[a]pyrene

Although arenes are usually drawn with three C=C bonds, benzene is about 150 kJ/mol more stable than would be expected if it contained three double bonds. This increased stability is due to the delocalization of the π electron density over all the atoms of the ring. (For more information on delocalization, see Chapter 9 "Molecular Geometry and Covalent Bonding Models", Section 9.3 "Delocalized Bonding and Molecular Orbitals".) Compared with alkenes, arenes are poor nucleophiles. Consequently, they do not undergo addition reactions like alkenes; instead, they undergo a variety of electrophilic aromatic substitution reactionsthat involve the replacement of –H on the arene by a group –E, such as $–NO_2$, $–SO_3H$, a halogen, or an alkyl group, in a two-step process. The first step involves addition of the electrophile (E) to the π system of benzene, forming a carbocation. In the second step, a proton is lost from the adjacent carbon on the ring:



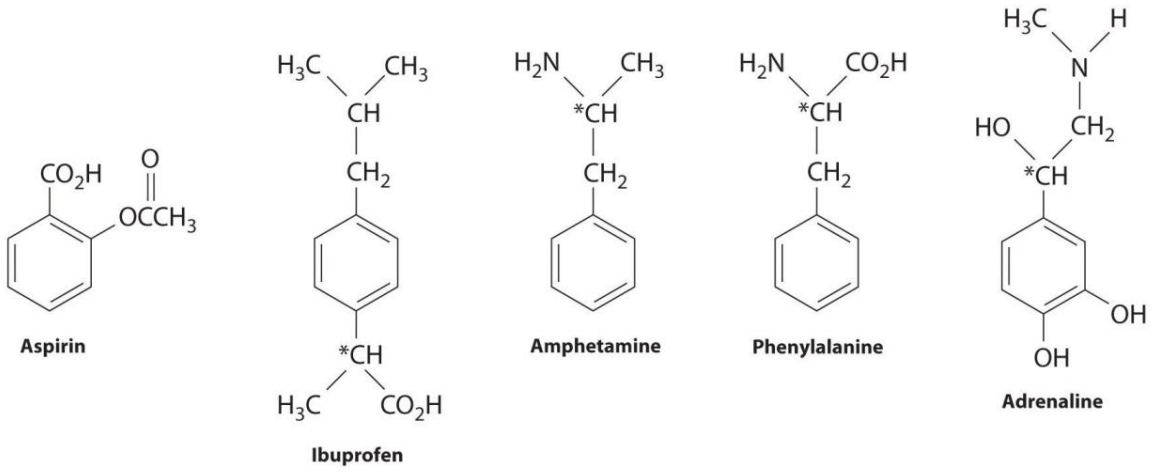
The carbocation formed in the first step is stabilized by resonance.

Note the Pattern

Arenes undergo substitution reactions rather than elimination because of increased stability arising from delocalization of their π electron density.

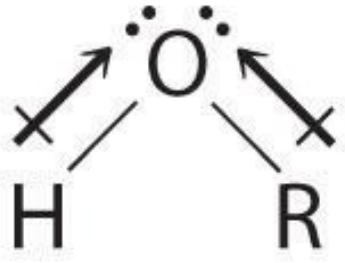
Many substituted arenes have potent biological activity. Some examples include common drugs and antibiotics such as aspirin and ibuprofen, illicit drugs such as amphetamines and peyote, the amino acid phenylalanine, and hormones such as adrenaline (Figure 24.16 "Biologically Active Substituted Arenes").

Figure 24.16 *Biologically Active Substituted Arenes*

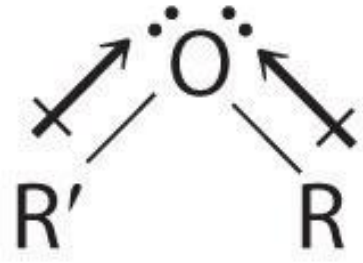


Aspirin (antifever activity), ibuprofen (antifever and anti-inflammatory activity), and amphetamine (stimulant) have pharmacological effects. Phenylalanine is an amino acid. Adrenaline is a hormone that elicits the "fight or flight" response to stress. Chiral centers are indicated with an asterisk.

Alcohols and Ethers



Alcohol



Ether

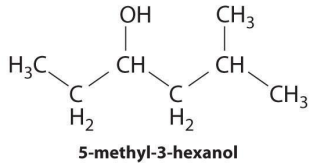
Both alcohols and ethers can be thought of as derivatives of water in which at least one hydrogen atom has been replaced by an organic group, as shown here. Because of the electronegative oxygen atom, the individual O–H bond dipoles in alcohols cannot cancel one another, resulting in a substantial dipole moment that allows alcohols to form hydrogen bonds. Alcohols therefore have significantly higher boiling points than alkanes or alkenes of comparable molecular mass, whereas ethers, without a polar O–H bond, have intermediate boiling points due to the presence of a small dipole moment (Table 24.2 "Boiling Points of Alkanes, Ethers, and Alcohols of Comparable Molecular Mass"). The larger the alkyl group in the molecule, however, the more "alkane-like" the alcohol is in its properties. Because of their polar nature, alcohols and ethers tend to be good solvents for a wide range of organic compounds.

Table 24.2 Boiling Points of Alkanes, Ethers, and Alcohols of Comparable Molecular Mass

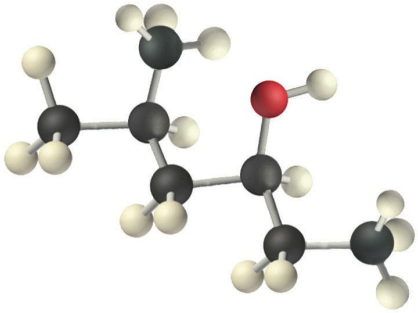
	Name	Formula	Molecular Mass (amu)	Boiling Point (°C)
	propane	C_3H_8	44	−42.1
	n-pentane	C_5H_{12}	72	36.1
alkane	*n*-heptane	C_7H_{16}	100	98.4
	dimethylether	$(CH_3)_2O$	46	−24.8
	diethylether	$(CH_3CH_2)_2O$	74	34.5
ether	di-*n*-propylether	$(CH_3CH_2CH_2)_2O$	102	90.1
	ethanol	CH_3CH_2OH	46	78.3
	n-butanol	$CH_3(CH_2)_3OH$	74	117.7
alcohol	*n*-hexanol	$CH_3(CH_2)_5OH$	102	157.6

Alcohols are usually prepared by adding water across a carbon–carbon double bond or by a nucleophilic substitution reaction of an alkyl halide using hydroxide, a potent nucleophile (Figure 24.12). As you will see in Section 24.6 "The Molecules of Life", alcohols can also be prepared by reducing compounds that

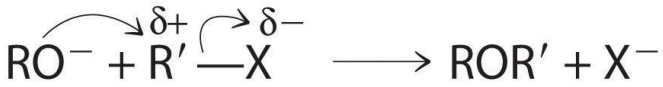
contain the carbonyl functional group (C=O; part (a) in Figure 24.14 "The Oxidation State of Carbon in Oxygen- and Nitrogen-Containing Functional Groups"). Alcohols are classified as primary, secondary, or tertiary, depending on whether the –OH group is bonded to a primary, secondary, or tertiary carbon. For example, the compound 5-methyl-3-hexanol is a secondary alcohol.



5-methyl-3-hexanol



Ethers, especially those with two different alkyl groups (ROR′), can be prepared by a substitution reaction in which a nucleophilic alkoxide ion (RO^-) attacks the partially positively charged carbon atom of the polar C–X bond of an alkyl halide (R′X):



Although both alcohols and phenols have an –OH functional group, phenols are 10^6–10^8 more acidic than alcohols. This is largely because simple alcohols have the –OH unit attached to an sp^3 hybridized carbon, whereas phenols have an sp^2 hybridized carbon atom bonded to the oxygen atom. The negative charge of the phenoxide ion can therefore interact with the π electrons in the ring, thereby delocalizing and stabilizing the negative charge through resonance. (For more information on resonance, seeChapter 8 "Ionic versus Covalent Bonding", Section 8.5 "Lewis Structures and Covalent Bonding".) In contrast, the negative charge on an alkoxide ion cannot be stabilized by these types of interactions.

Alcohols undergo two major types of reactions: those involving cleavage of the O–H bond and those involving cleavage of the C–O bond. Cleavage of an O–H bond is a reaction characteristic of an acid, but alcohols are even weaker acids than water. The acidic strength of phenols, however, is about a million times greater than that of ethanol, making the pK_a of phenol comparable to that of the NH_4^+ ion (9.89 versus 9.25, respectively):

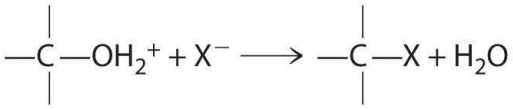
Equation 24.8

$$C6H5OH + H2O \square H3O++ C6H5O-$$

Note the Pattern

Alcohols undergo two major types of reactions: cleavage of the O–H bond and cleavage of the C–O bond.

Cleavage of the C–O bond in alcohols occurs under acidic conditions. The –OH is first protonated, and nucleophilic substitution follows:



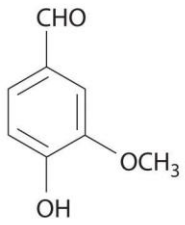
In the absence of a nucleophile, however, elimination can occur, producing an alkene (Figure 24.13).

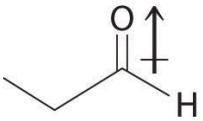
Ethers lack the –OH unit that is central to the reactivity of alcohols, so they are comparatively unreactive. Their low reactivity makes them highly suitable as solvents for carrying out organic reactions.

Aldehydes and Ketones

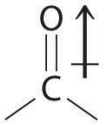
Aromatic aldehydes, which have intense and characteristic flavors and aromas, are the major components of such well-known flavorings as vanilla and cinnamon (Figure 24.17 "Some Familiar Aldehydes and Their Uses"). Many ketones, such as camphor and jasmine, also have intense aromas. Ketones are found in many of the hormones responsible for sex differentiation in humans, such as progesterone and testosterone. (For more information on aldehydes and ketones, see Chapter 4 "Reactions in Aqueous Solution", Section 4.1 "Aqueous Solutions".)

Figure 24.17 *Some Familiar Aldehydes and Their Uses*

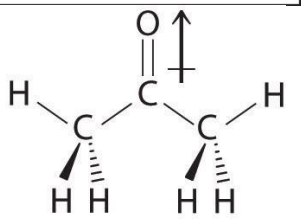
Name	Formula	Use
Formaldehyde	CH_2O	Biological preservative
Cinnamaldehyde	$C_6H_5CH{=}CHCHO$	Cinnamon
Citral	$(CH_3)_2C{=}CHCH_2CH_2C(CH_3){=}CHCHO$	Antiseptic, perfumes
Benzaldehyde	C_6H_5CHO	Manufacture of dyes, almond flavoring
Vanillin		Vanilla flavoring



Propanal



Carbonyl group



2-Propanone

In compounds containing a carbonyl group, nucleophilic attack can occur at the carbon atom of the carbonyl, whereas electrophilic attack occurs at oxygen.

Aldehydes and ketones contain the carbonyl functional group, which has an appreciable dipole moment because of the polar C=O bond. The presence of the carbonyl group results in strong intermolecular interactions that cause aldehydes and ketones to have higher boiling points than alkanes or alkenes of comparable molecular mass (Table 24.3 "Boiling Points of Alkanes, Aldehydes, and Ketones of Comparable Molecular Mass"). As the mass of the molecule increases, the carbonyl group becomes less important to the overall properties of the compound, and the boiling points approach those of the corresponding alkanes.

Table 24.3 Boiling Points of Alkanes, Aldehydes, and Ketones of Comparable Molecular Mass

	Name	Formula	Molecular Mass (amu)	Boiling Point (°C)
alkane	*n*-butane	C_4H_{10}	58	−0.5

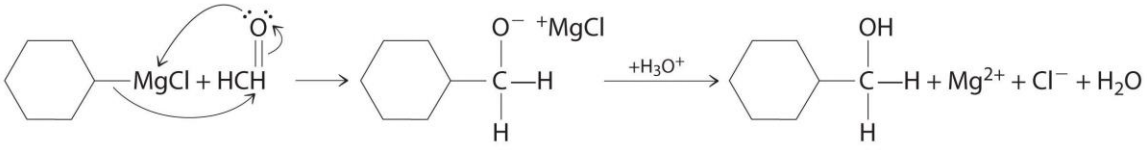
	Name	Formula	Molecular Mass (amu)	Boiling Point (°C)
	n-pentane	C_5H_{12}	72	36.1
aldehyde	propionaldehyde (propanal)	C_3H_6O	58	48.0
	butyraldehyde (butanal)	C_4H_8O	72	74.8
ketone	acetone (2-propanone)	C_3H_6O	58	56.1
	methyl ethyl ketone (2-butanone)	C_4H_8O	72	79.6

Aldehydes and ketones are typically prepared by oxidizing alcohols (part (a) in Figure 24.14 "The Oxidation State of Carbon in Oxygen- and Nitrogen-Containing Functional Groups"). In their reactions, the partially positively charged carbon atom of the carbonyl group is an electrophile that is subject to nucleophilic attack. Conversely, the lone pairs of electrons on the oxygen atom of the carbonyl group allow electrophilic attack to occur. Aldehydes and ketones can therefore undergo both nucleophilic attack (at the carbon atom) and electrophilic attack (at the oxygen atom).

Note the Pattern

Nucleophilic attack occurs at the partially positively charged carbon of a carbonyl functional group. Electrophilic attack occurs at the lone pairs of electrons on the oxygen atom.

Aldehydes and ketones react with many organometallic compounds that contain stabilized carbanions. One of the most important classes of such compounds are theGrignard reagents, organomagnesium compounds with the formula RMgX (X is Cl, Br, or I) that are so strongly polarized that they can be viewed as containing R^- and MgX^+. These reagents are named for the French chemist Victor Grignard (1871–1935), who won a Nobel Prize in Chemistry in 1912 for their development. In a Grignard reaction, the carbonyl functional group is converted to an alcohol, and the carbon chain of the carbonyl compound is lengthened by the addition of the R group from the Grignard reagent. One example is reacting cyclohexylmagnesium chloride, a Grignard reagent, with formaldehyde:

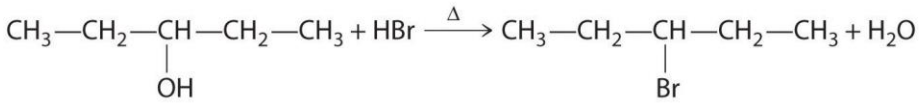


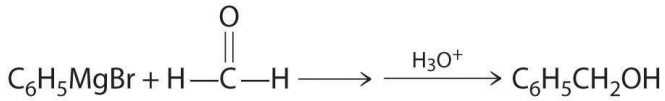
The nucleophilic carbanion of the cyclohexyl ring attacks the electrophilic carbon atom of the carbonyl group. Acidifying the solution results in protonation of the intermediate to give the alcohol. Aldehydes can also be prepared by reducing a carboxylic acid group ($–CO_2H$) (part (a) in Figure 24.14 "The Oxidation State of Carbon in Oxygen- and Nitrogen-

Containing Functional Groups"), and ketones can be prepared by reacting a carboxylic acid derivative with a Grignard reagent. The former reaction requires a powerful reducing agent, such as a metal hydride.

EXAMPLE 7

Explain how each reaction proceeds to form the indicated product.

a. 

b. 

Given: chemical reaction

Asked for: how products are formed

Strategy:

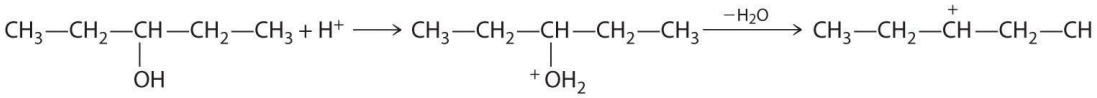
A Identify the functional group and classify the reaction.

B Use the mechanisms described to propose the initial steps in the reaction.

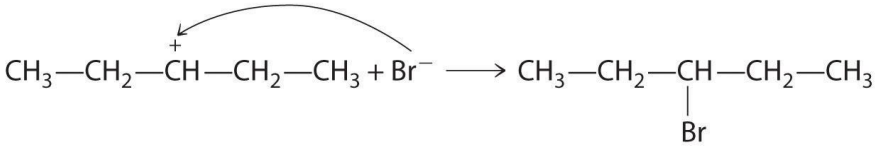
Solution:

a. **A** One reactant is an alcohol that undergoes a substitution reaction.

B In the product, a bromide group is substituted for a hydroxyl group. The first step in this reaction must therefore be protonation of the –OH group of the alcohol by H^+ of HBr, followed by the elimination of water to give the carbocation:



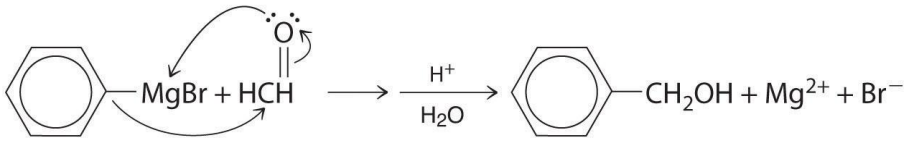
The bromide ion is a good nucleophile that can react with the carbocation to give an alkyl bromide:



b.

A One reactant is a Grignard reagent, and the other contains a carbonyl functional group. Carbonyl compounds act as electrophiles, undergoing nucleophilic attack at the carbonyl carbon.

B The nucleophile is the phenyl carbanion of the Grignard reagent:

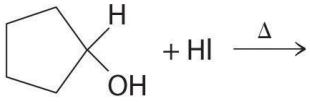


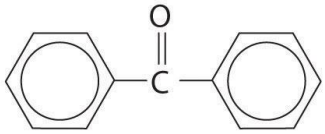
Benzyl alcohol

The product is benzyl alcohol.

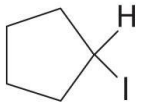
Exercise

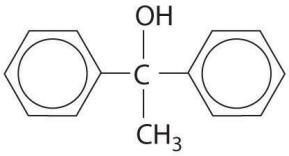
Predict the product of each reaction.

a. 

b. $CH_3MgCl +$  (benzophenone), followed by reaction with aqueous acid

Answer:

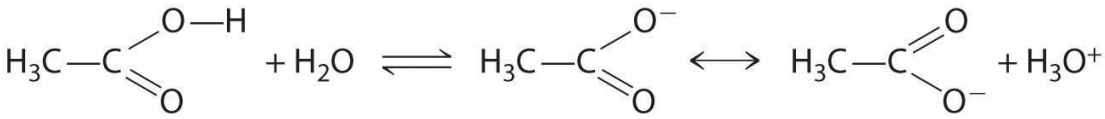
a. 

b. 

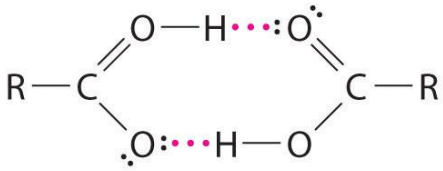
Carboxylic Acids

The pungent odors of many carboxylic acids are responsible for the smells we associate with sources as diverse as Swiss cheese, rancid butter, manure, goats, and sour milk. The boiling points of carboxylic acids tend to be somewhat higher than would be expected from their molecular masses because of strong hydrogen-bonding interactions between molecules. In fact, most simple carboxylic acids form dimers in the liquid and even in the vapor phase. (For more information on the vapor phase, see Chapter 11 "Liquids", Section 11.2 "Intermolecular Forces".) The four lightest carboxylic acids are completely miscible with water, but as the alkyl chain lengthens, they become more “alkane-like,” so their solubility in water decreases.

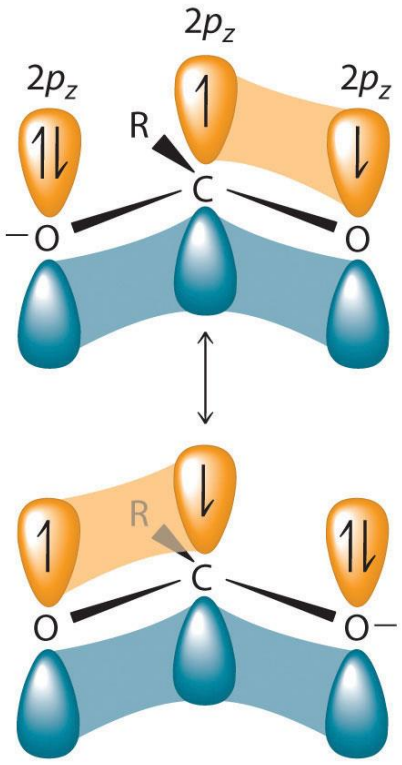
Compounds that contain the carboxyl functional group are acidic because carboxylic acids can easily lose a proton: the negative charge in the carboxylate ion (RCO_2^-) is stabilized by delocalization of the π electrons:



As a result, carboxylic acids are about 10^{10} times more acidic than the corresponding simple alcohols whose anions (RO^-) are not stabilized through resonance.



Hydrogen-bonded carboxylic acid molecules

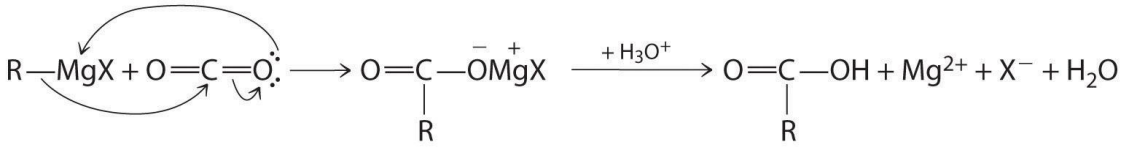


acids are typically prepared by oxidizing the corresponding alcohols and aldehydes (part (a) in Figure 24.14 "The Oxidation State of Carbon in Oxygen- and Nitrogen-Containing Functional Groups"). They can also be prepared by reacting a Grignard reagent with CO_2, followed by acidification:

Equation 24.9

$$CO2 + RMgCl \rightarrow - \rightarrow - - H3O + RCO2H + Mg2 + + Cl - + H2O$$

The initial step in the reaction is nucleophilic attack by the R^- group of the Grignard reagent on the electrophilic carbon of CO_2:



Delocalization of π bonding over three atoms (O–C–O) makes carboxylic acids and their derivatives less susceptible to nucleophilic attack than aldehydes and ketones with their single π bond. The reactions of carboxylic acids are dominated by two factors: their polar $–CO_2H$ group and their acidity. Reaction with strong bases, for example, produce carboxylate salts, such as sodium stearate:

Equation 24.10

$$RCO_2H + NaOH \rightarrow RCO_2^-Na^+ + H_2O$$

where R is $CH_3(CH_2)_{16}$. As you learned in Chapter 13 "Solutions", Section 13.6 "Aggregate Particles in Aqueous Solution", long-chain carboxylate salts are used as soaps.

Note the Pattern

Delocalization of π bonding over three atoms makes carboxylic acids and their derivatives less susceptible to nucleophilic attack as compared with aldehydes and ketones.

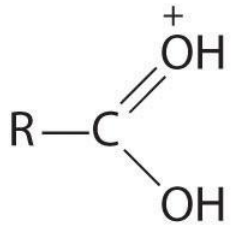
Carboxylic Acid Derivatives

Replacing the –OH of a carboxylic acid with groups that have different tendencies to participate in resonance with the C=O functional group produces derivatives with rather different properties. Resonance structures have significant effects on the reactivity of carboxylic acid derivatives, but their influence varies substantially, being least important for halides and most important for the nitrogen of amides. In this section, we take a brief look at the chemistry of two of the most familiar and important carboxylic acid derivatives: esters and amides.

Esters

Esters have the general formula RCO_2R', where R and R′ can be virtually any alkyl or aryl group. Esters are often prepared by reacting an alcohol (R′OH) with a carboxylic acid (RCO_2H) in the presence of a catalytic amount of strong acid. (For more information on esters and catalysts, see Chapter 3 "Chemical Reactions", Section 3.5 "Classifying Chemical Reactions".) The purpose of the acid (an electrophile) is to

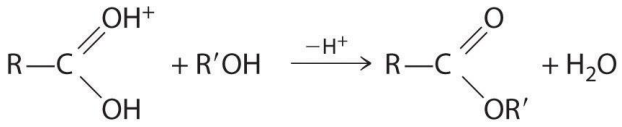
protonate the doubly bonded oxygen atom of the carboxylic acid (a nucleophile) to give a species that is *more* electrophilic than the parent carboxylic acid.



Protonated carboxylic acid

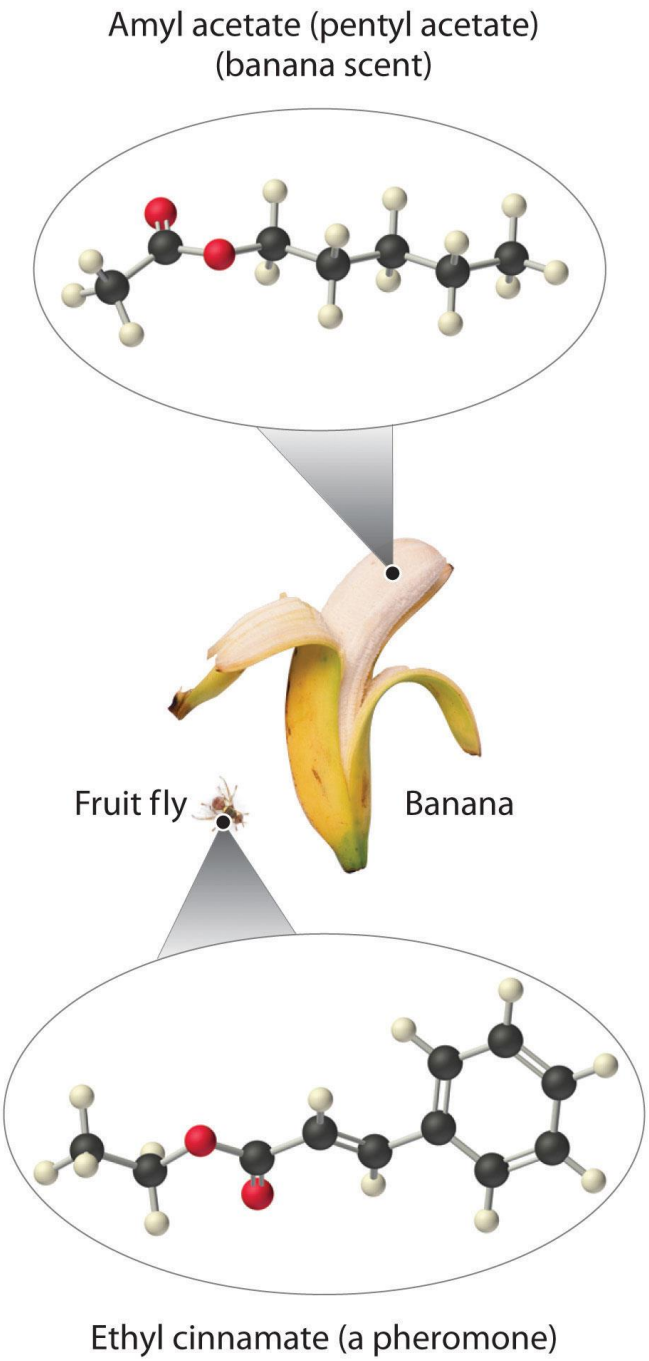
The nucleophilic oxygen atom of the alcohol attacks the electrophilic carbon atom of the protonated carboxylic acid to form a new C–O bond. The overall reaction can be written as follows:

Figure 24.18



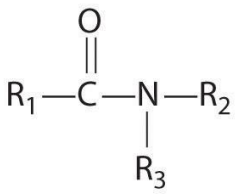
Because water is eliminated, this is a dehydration reaction. If an aqueous solution of an ester and strong acid or base is heated, the reverse reaction will occur, producing the parent alcohol R′OH and either the carboxylic acid RCO_2H (under strongly acidic conditions) or the carboxylate anion RCO_2^- (under basic conditions).

As stated earlier, esters are familiar to most of us as fragrances, such as banana and pineapple. Other esters with intense aromas function as sex attractants, or*pheromones*, such as the pheromone from the oriental fruit fly. Research on using synthetic insect pheromones as a safer alternative to insecticides for controlling insect populations, such as cockroaches, is a rapidly growing field in organic chemistry.



Amides

In the general structure of an amide,



An amide

the two substituents on the amide nitrogen can be hydrogen atoms, alkyl groups, aryl groups, or any combination of those species. Although amides appear to be derived from an acid and an amine, in practice they usually cannot be prepared by this synthetic route. In principle, nucleophilic attack by the lone electron pair of the amine on the carbon of the carboxylic acid could occur, but because carboxylic acids are weak acids and amines are weak bases, an acid–base reaction generally occurs instead:

Equation 24.11

$RCO_2H + R'NH_2 \rightarrow RCO_2^- + R'NH_3^+$

Amides are therefore usually prepared by the nucleophilic reaction of amines with more electrophilic carboxylic acid derivatives, such as esters.

The lone pair of electrons on the nitrogen atom of an amide can participate in π bonding with the carbonyl group, thus reducing the reactivity of the amide (Figure 24.19 "The Electronic Structure of an Amide") and inhibiting free rotation about the C–N bond. Amides are therefore the least reactive of the carboxylic acid derivatives. The stability of the amide bond is crucially important in biology because amide bonds form the backbones of peptides and proteins. (For more information on peptides and proteins, see Chapter 12 "Solids", Section 12.8 "Polymeric Solids".) The amide bond is also found in many other biologically active and commercially important molecules, including penicillin; urea, which is used as fertilizer; saccharin, a sugar substitute; and valium, a potent tranquilizer. (For more information on the structure of penicillin, seeChapter 3 "Chemical Reactions", Section 3.2 "Determining Empirical and Molecular Formulas".)

Note the Pattern

Amides are the least reactive of the carboxylic acid derivatives because amides participate in π bonding with the carbonyl group.

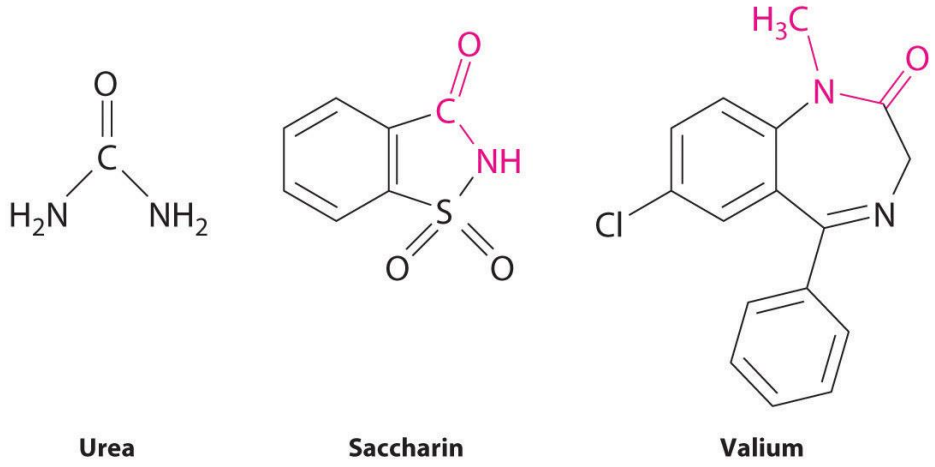
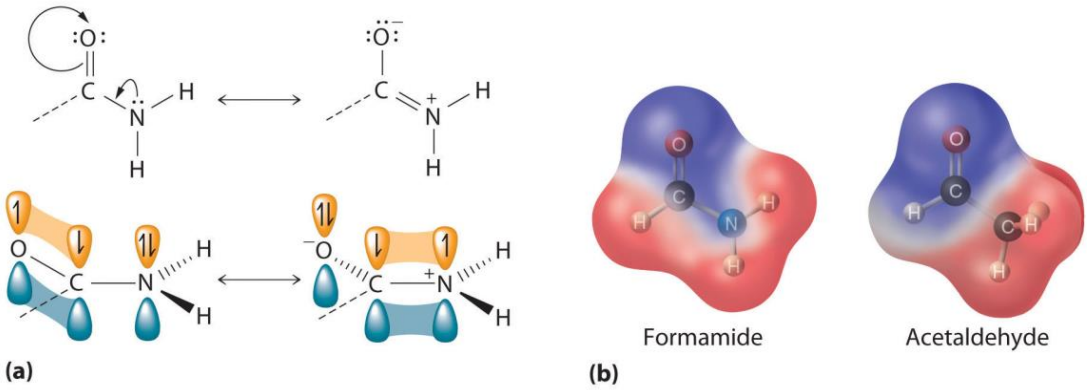


Figure 24.19 *The Electronic Structure of an Amide*



(a) An unhybridized $2p_z$ orbital on nitrogen, containing a lone electron pair of electrons, can interact with the π orbital of the carbonyl group to give a three-center, four-electron bond. This interaction reduces the reactivity of the amide, making amides the least reactive of the carboxylic acid derivatives. (b) A comparison of the electrostatic potential maps of acetaldehyde and formamide shows that the negative charge (indicated in blue) is more localized on the oxygen atom of acetaldehyde than it is in formamide. Formamide is therefore less reactive.

Amines

Amines are derivatives of ammonia in which one or more hydrogen atoms have been replaced by alkyl or aryl groups. They are therefore analogous to alcohols and ethers. Like alcohols, amines are classified as primary, secondary, or tertiary, but in this case the designation refers to the number of alkyl groups bonded to the nitrogen atom, not to the number of adjacent carbon atoms. In primary amines, the nitrogen is bonded to two hydrogen atoms and one alkyl group; in secondary amines, the nitrogen is bonded to one hydrogen and two alkyl groups; and in tertiary amines, the nitrogen is bonded to three alkyl groups. With one lone pair of electrons and C–N bonds that are less polar than C–O bonds, ammonia and simple amines have much lower boiling points than water or alcohols with similar

molecular masses. Primary amines tend to have boiling points intermediate between those of the corresponding alcohol and alkane. Moreover, secondary and tertiary amines have lower boiling points than primary amines of comparable molecular mass.

Tertiary amines form cations analogous to the ammonium ion (NH_4^+), in which all four H atoms are replaced by alkyl groups. Such substances, calledquaternary ammonium salts, can be chiral if all four substituents are different. (Amines with three different substituents are also chiral because the lone pair of electrons represents a fourth substituent.)

Alkylamines can be prepared by nucleophilic substitution reactions of alkyl halides with ammonia or other amines:

Equation 24.12

$$RCl + NH_3 \rightarrow RNH_2 + HCl$$

Equation 24.13

$$RCl + R'NH_2 \rightarrow RR'NH + HCl$$

Equation 24.14

$$RCl + R'R''NH \rightarrow RR'R''N + HCl$$

The primary amine formed in the first reaction (Equation 24.12) can react with more alkyl halide to generate a secondary amine (Equation 24.13), which in turn can react to form a tertiary amine (Equation 24.14). Consequently, the actual reaction mixture contains primary, secondary, and tertiary amines and even quaternary ammonium salts.

The reactions of amines are dominated by two properties: their ability to act as weak bases and their tendency to act as nucleophiles, both of which are due to the presence of the lone pair of electrons on the nitrogen atom. Amines typically behave as bases by accepting a proton from an acid to form an ammonium salt, as in the reaction of triethylamine (the ethyl group is represented as Et) with aqueous HCl (the lone pair of electrons on nitrogen is shown):

Equation 24.15

$$Et_3N{:}(l) + HCl(aq) \rightarrow Et_3NH^+Cl^-(aq)$$

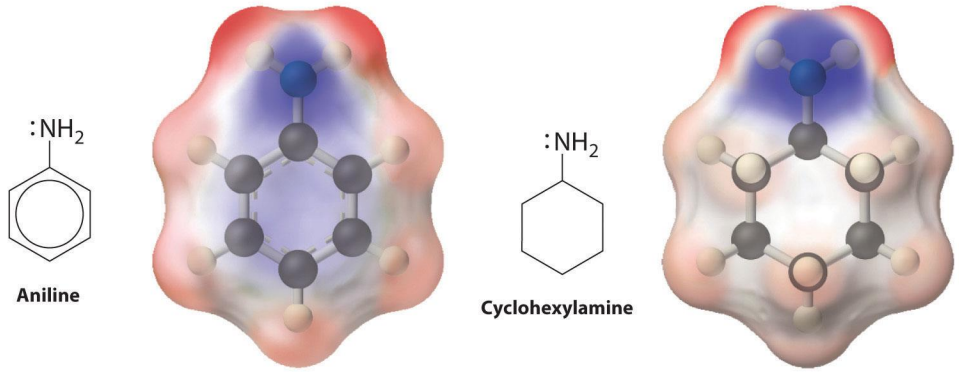
which gives triethylammonium chloride. Amines can react with virtually any electrophile, including the carbonyl carbon of an aldehyde, a ketone, or an ester. Aryl amines such as aniline ($C_6H_5NH_2$) are much weaker bases than alkylamines because the lone pair of electrons on nitrogen interacts with the π bonds of

the aromatic ring, delocalizing the lone pair through resonance (Figure 24.20 "Structures and Basicity of Aniline and Cyclohexylamine").

Note the Pattern

The reactions of amines are dominated by their ability to act as weak bases and their tendency to act as nucleophiles.

Figure 24.20 *Structures and Basicity of Aniline and Cyclohexylamine*



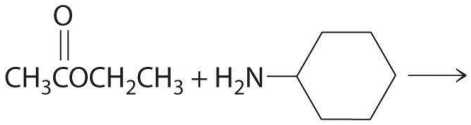
Delocalization of the lone electron pair on N over the benzene ring reduces the basicity of aryl amines, such as aniline, compared with that of alkylamines, such as cyclohexylamine. These electrostatic potential maps show that the electron density on the N of cyclohexylamine is more localized than it is in aniline, which makes cyclohexylamine a stronger base.

EXAMPLE 8

Predict the products formed in each reaction and show the initial site of attack and, for part (b), the final products.

a. $C_6H_5CH_2CO_2H + KOH \rightarrow$

b.



Given: reactants

Asked for: products and mechanism of reaction

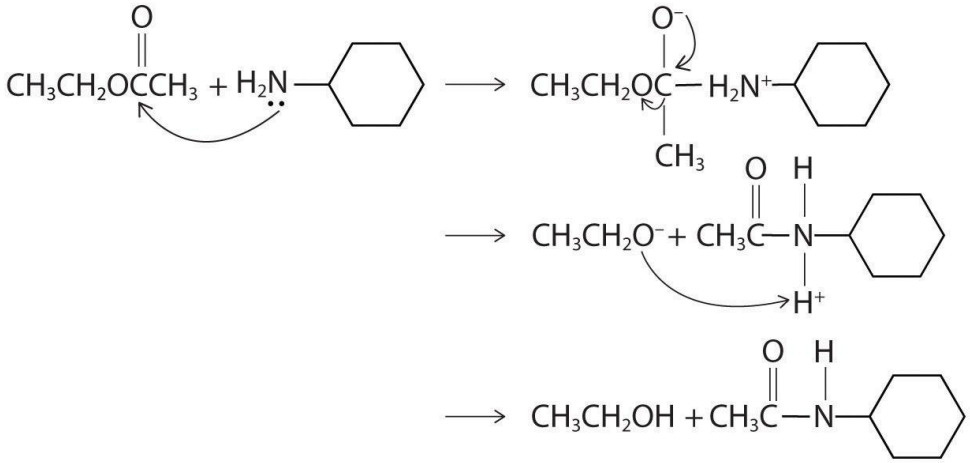
Strategy:

Use the strategy outlined in Example 7.

Solution:

a. The proton on the carboxylic acid functional group is acidic. Thus reacting a carboxylic acid with a strong base is an acid–base reaction, whose products are a salt—in this case, $C_6H_5CH_2CO_2^-K^+$—and water.

b. The nitrogen of cyclohexylamine contains a lone pair of electrons, making it an excellent nucleophile, whereas the carbonyl carbon of ethyl acetate is a good electrophile. We therefore expect a reaction in which nucleophilic attack on the carbonyl carbon of the ester produces an amide and ethanol. The initial site of attack and the reaction products are as follows:



Exercise

Predict the products of each reaction. State the initial site of attack.

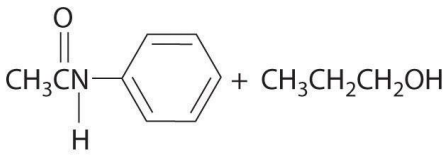
a. acetic acid with 1-propanol

b. aniline ($C_6H_5NH_2$) with propyl acetate [$CH_3C(=O)OCH_2CH_2CH_3$]

Answer:

a. Initial attack occurs with protonation of the oxygen of the carbonyl. The products are:

b. Initial attack occurs at the carbon of the carbonyl group. The products are:



Reactions like we have discussed in this section and Section 24.4 "Common Classes of Organic Reactions" are used to synthesize a wide range of organic compounds. When chemists plan the synthesis of an organic molecule, however, they must take into consideration various factors, such as the availability and cost of reactants, the need to minimize the formation of undesired products, and the proper sequencing of reactions to maximize the yield of the target molecule and minimize the formation of undesired products. Because the synthesis of many organic molecules requires multiple steps, in designing a synthetic scheme for such molecules, chemists must often work backward from the desired product in a process called *retrosynthesis*. Using this process, they can identify the reaction steps needed to synthesize the desired product from the available reactants.

Summary

There are strong connections among the structure, the physical properties, and the reactivity for compounds that contain the major functional groups. Hydrocarbons that are alkanes undergo catalytic cracking, which can convert straight-chain alkanes to highly branched alkanes. Catalytic cracking is one example of a**pyrolysis reaction**, in which the weakest bond is cleaved at high temperature, producing a mixture of radicals. The multiple bond of an alkene produces geometric isomers (*cis* and *trans*). Terminal alkynes contain a hydrogen atom directly attached to a triply bonded carbon. Removal of the hydrogen forms an acetylide ion, a potent nucleophile used to make longer carbon chains. Arenes undergo substitution rather than elimination because of enhanced stability from delocalization of their π electron

density. An alcohol is often prepared by adding the elements of water across a double bond or by a substitution reaction. Alcohols undergo two major types of reactions: those involving cleavage of the O–H bond and those involving cleavage of the C–O bond. Phenols are acidic because of π interactions between the oxygen atom and the ring. Ethers are comparatively unreactive. Aldehydes and ketones are generally prepared by oxidizing alcohols. Their chemistry is characterized by nucleophilic attack at the carbon atom of the carbonyl functional group and electrophilic attack at the oxygen atom. **Grignard reagents** (RMgX, where X is Cl, Br, or I) convert the carbonyl functional group to an alcohol and lengthen the carbon chain. Compounds that contain the carboxyl functional group are weakly acidic because of delocalization of the π electrons, which causes them to easily lose a proton and form the carboxylate anion. Carboxylic acids are generally prepared by oxidizing alcohols and aldehydes or reacting a Grignard reagent with CO_2. Carboxylic acid derivatives include esters, prepared by reacting a carboxylic acid and an alcohol, and amides, prepared by the nucleophilic reaction of amines with more electrophilic carboxylic acid derivatives, such as esters. Amides are relatively unreactive because of π bonding interactions between the lone pair on nitrogen and the carbonyl group. Amines can also be primary, secondary, or tertiary, depending on the number of alkyl groups bonded to the amine. **Quaternary ammonium salts** have four substituents attached to nitrogen and can be chiral. Amines are often prepared by a nucleophilic substitution reaction between a polar alkyl halide and ammonia or other amines. They are nucleophiles, but their base strength depends on their substituents.

KEY TAKEAWAY

- The physical properties and reactivity of compounds containing the common functional groups are intimately connected to their structures.

CONCEPTUAL PROBLEMS

1. Why do branched-chain alkanes have lower melting points than straight-chain alkanes of comparable molecular mass?
2. Describe alkanes in terms of their orbital hybridization, polarity, and reactivity. What is the geometry about each carbon of a straight-chain alkane?
3. Why do alkenes form *cis* and *trans* isomers, whereas alkanes do not? Do alkynes form *cis*and *trans* isomers? Why or why not?
4. Which compounds can exist as *cis* and *trans* isomers?

a. 2,3-dimethyl-1-butene

b. 3-methyl-1-butene

c. 2-methyl-2-pentene

d. 2-pentene

5. Which compounds can exist as *cis* and *trans* isomers?

a. 3-ethyl-3-hexene

b. 1,1-dichloro-1-propene

c. 1-chloro-2-pentene

d. 3-octene

6. Which compounds have a net dipole moment?

a. *o*-nitrotoluene

b. *p*-bromonitrobenzene

c. *p*-dibromobenzene

7. Why is the boiling point of an alcohol so much greater than that of an alkane of comparable molecular mass? Why are low-molecular-mass alcohols reasonably good solvents for some ionic compounds, whereas alkanes are not?

8. Is an alcohol a nucleophile or an electrophile? What determines the mode of reactivity of an alcohol? How does the reactivity of an alcohol differ from that of an ionic compound containing OH, such as KOH?

9. How does the reactivity of ethers compare with that of alcohols? Why? Ethers can be cleaved under strongly acidic conditions. Explain how this can occur.

10. What functional group is common to aldehydes, ketones, carboxylic acids, and esters? This functional group can react with both nucleophiles and electrophiles. Where does nucleophilic attack on this functional group occur? Where does electrophilic attack occur?

11. What key feature of a Grignard reagent allows it to engage in a nucleophilic attack on a carbonyl carbon?

12. Do you expect carboxylic acids to be more or less water soluble than ketones of comparable molecular mass? Why?

13. Because amides are formally derived from an acid plus an amine, why can they not be prepared by the reaction of an acid with an amine? How are they generally prepared?

14. Is an amide susceptible to nucleophilic attack, electrophilic attack, or both? Specify where the attack occurs.

15. What factors determine the reactivity of amines?

ANSWERS

1.

2.

3.

4.

5. (c) and (d)

6.

7.

8.

9.

10.

11. The presence of a nucleophilic $C^{\delta-}$ resulting from a highly polar interaction with an electropositive Mg

12.

13.

14.

15. Their ability to act as weak bases and their tendency to act as nucleophiles

STRUCTURE AND REACTIVITY

1. What is the product of the reaction of 2-butyne with excess HBr?
2. What is the product of the reaction of 3-hexyne with excess HCl?
3. What elements are eliminated during the dehydrohalogenation of an alkyl halide? What products do you expect from the dehydrohalogenation of 2-chloro-1-pentene?
4. What elements are eliminated during the dehydration of an alcohol? What products do you expect from the dehydration of ethanol?
5. Predict the products of each reaction.

a. sodium phenoxide with ethyl chloride

b. 1-chloropropane with NaOH

6. Show the mechanism and predict the organic product of each reaction.

a. 2-propanol + HCl

b. cyclohexanol + H_2SO_4

7. A Grignard reagent can be used to generate a carboxylic acid. Show the mechanism for the first step in this reaction using CH_3CH_2MgBr as the Grignard reagent. What is the geometry about the carbon of the $–CH_2$ of the intermediate species formed in this first step?
8. Draw a molecular orbital picture showing the bonding in an amide. What orbital is used for the lone pair of electrons on nitrogen?
9. What is the product of the reaction of

a. acetic acid with ammonia?

b. methyl acetate with ethylamine, followed by heat?

10. Develop a synthetic scheme to generate

a. 1,1-dichloroethane from 1,1-dibromoethane.

b. 2-bromo-1-heptene from 1-bromopentane.

ANSWERS

1. 2,2-dibromobutane

2.

3.

4.

5.

a. $C_6H_5OC_2H_5$ + NaCl

b. 1-propanol + NaCl

6.

7.

8.

9.

a. $CH_3CO_2^-\ NH_4^+$ (an acid-base reaction)

b. $CH_3CONHC_2H_5 + CH_3OH$

10.

24.6 The Molecules of Life

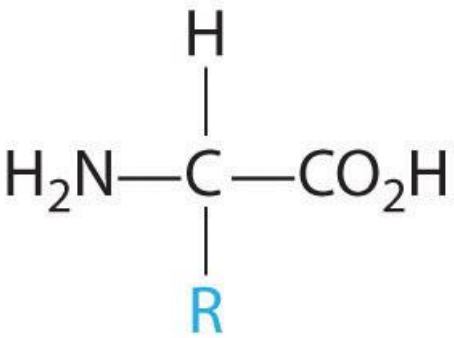
LEARNING OBJECTIVE

1. To identify the common structural units of important biological molecules.

All the functional groups described in this chapter are found in the organic molecules that are constantly synthesized and destroyed by every living organism on Earth. A detailed understanding of the reactions that occur in living organisms is the goal of biochemistry, which deals with a wide variety of organic structures and reactions. The most abundant substances found in living systems belong to four major classes: proteins, carbohydrates, lipids, and nucleic acids. Here we briefly describe the structure and some functions of these biological molecules.

Proteins

In Chapter 12 "Solids", Section 12.8 "Polymeric Solids", we described proteins as biologically active polymers formed from amino acids linked together by amide bonds. In addition to an amine group and a carboxylic acid group, each amino acid contains a characteristic R group (Figure 5.16 "The Structures of 10 Amino Acids"). In the simplest amino acid, glycine, the R group is hydrogen (–H), but in other naturally occurring amino acids, the R group may be an alkyl group or a substituted alkyl group, a carboxylic group, or an aryl group. The nature of the R group determines the particular chemical properties of each amino acid. In Figure 5.16 "The Structures of 10 Amino Acids", all the amino acids found in proteins except glycine are chiral compounds, which suggests that their interactions with other chiral compounds are selective. Some proteins, called enzymes, catalyze biological reactions, whereas many others have structural, contractile, or signaling functions. Because we have described proteins previously, we will not discuss them further.



The general structure of an amino acid. *An amino acid is chiral except when R is an H atom.*

Carbohydrates

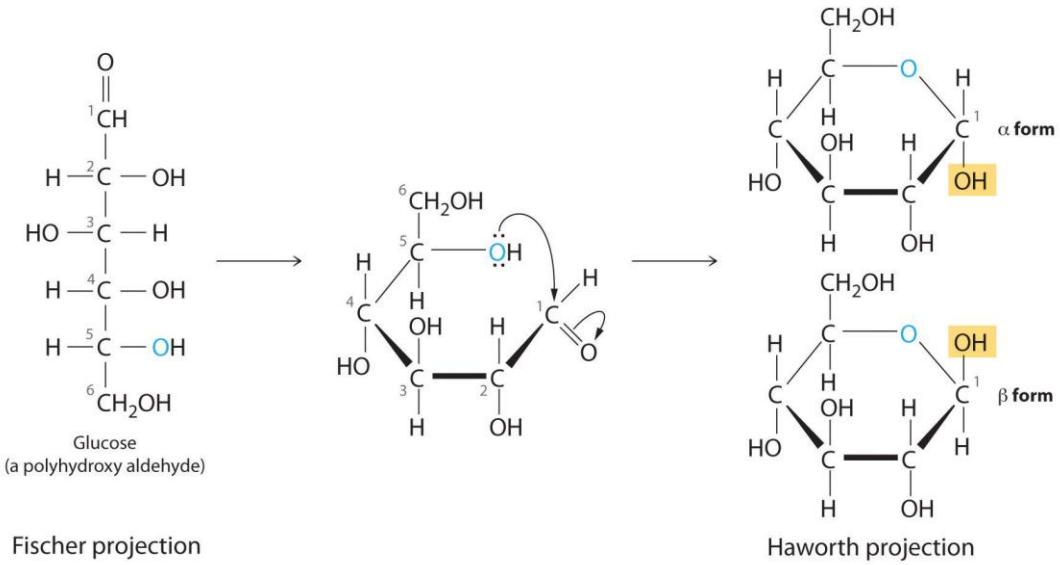
Carbohydrates are the most abundant of the organic compounds found in nature. They constitute a substantial portion of the food we consume and provide us with the energy needed to support life. Table sugar, milk, honey, and fruits all contain low-molecular-mass carbohydrates that are easily assimilated by the human body. In contrast, the walls of plant cells and wood contain high-molecular-mass carbohydrates that we cannot digest.

Once thought to be hydrates of carbon with the general formula $C_n(H_2O)_m$,carbohydrates are actually polyhydroxy aldehydes or polyhydroxy ketones (i.e., aldehydes or ketones with several –OH groups attached to the parent hydrocarbon). The simplest carbohydrates consist of unbranched chains of three to eight carbon atoms: one carbon atom is part of a carbonyl group, and some or all of the others are bonded to hydroxyl groups. The structure of a carbohydrate can be drawn either as a hydrocarbon chain, using a *Fischer projection*, or as a ring, using a *Haworth projection* (Figure 24.21 "Fischer Projection and Haworth Projection of Glucose"). The Haworth projection is named after the British chemist Sir Walter Norman Haworth, who was awarded a Nobel Prize in Chemistry in 1937 for his discovery that sugars exist mainly in their cyclic forms, as well as for his collaboration on the synthesis of vitamin C. The cyclic form is the product of nucleophilic attack by the oxygen of a hydroxyl group on the electrophilic carbon of the carbonyl group within the same molecule, producing a stable ring structure composed of five or six carbons that minimizes bond strain (Figure 24.21 "Fischer Projection and Haworth Projection of Glucose"). The substituents on the right side of the carbon chain in a Fischer projection are in the “down” position in the corresponding Haworth projection. Attack by the hydroxyl group on either side of the carbonyl group leads to the formation of two cyclic forms, called *anomers*: an α form, with the –OH in the “down” position, and a β form, with the –OH in the “up” position.

Walter Norman Haworth (1883–1950)

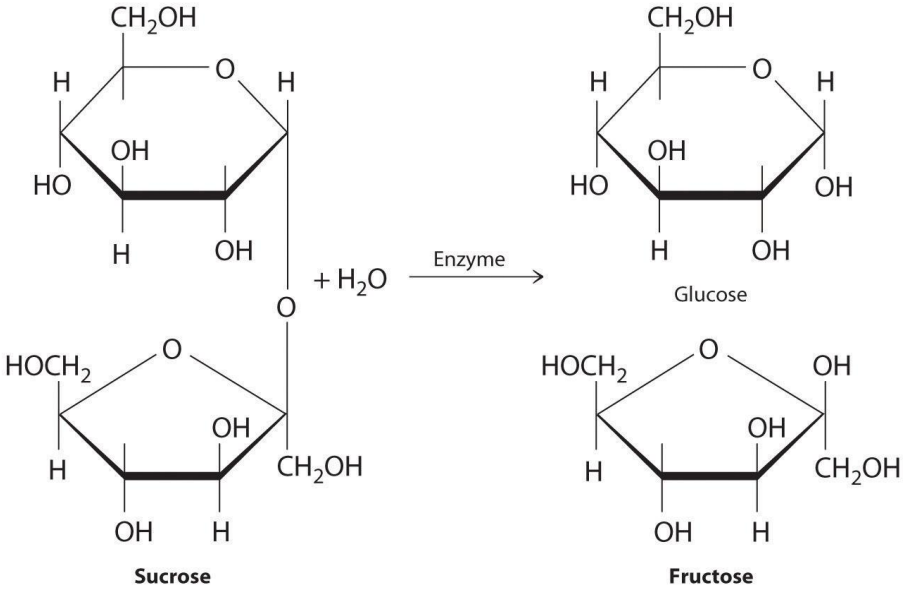
At age 14, Walter Norman Haworth left school to join his father to learn linoleum design and manufacturing, but he became interested in chemistry through his use of dyes. Private tutoring enabled him to pass the entrance exam of the University of Manchester, where he received his doctorate in 1911. During World War I, Haworth organized the laboratories at St. Andrews for the production of chemicals and drugs, returning to the investigation of carbohydrates after the war.

Figure 24.21 *Fischer Projection and Haworth Projection of Glucose*



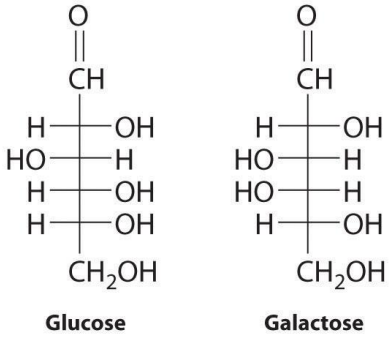
In solution, simple sugars exist predominantly in the ring form, the product of nucleophilic attack by the oxygen of a hydroxyl group on the electrophilic carbon of the carbonyl group. The α and β forms, called anomers, differ in the configuration at C1.

Carbohydrates are classified according to the number of single *saccharide*, or sugar, units they contain (from the Latin *saccharum*, meaning "sugar"). The simplest are*monosaccharides*; a *disaccharide* consists of two linked monosaccharide units; a*trisaccharide* has three linked monosaccharide units; and so forth. Glucose is a monosaccharide, and sucrose (common table sugar) is a disaccharide. The hydrolysis of sucrose produces glucose and another monosaccharide, fructose, in a reaction catalyzed by an enzyme or by acid:

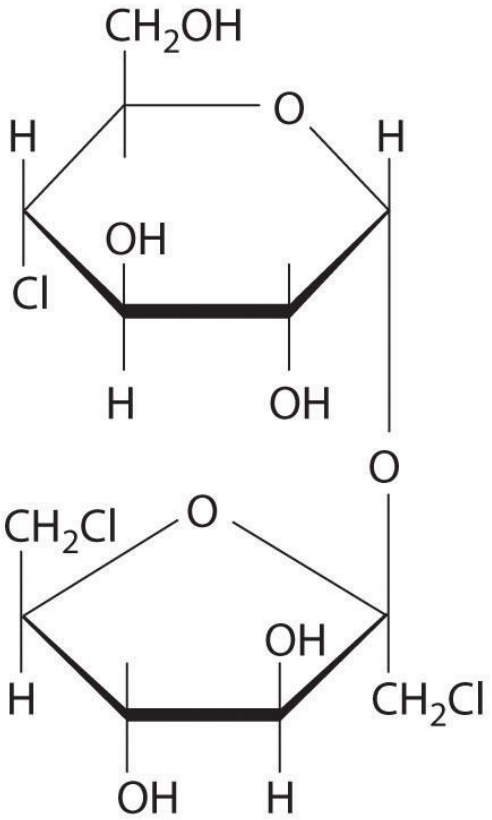


Polysaccharides hydrolyze to produce more than 10 monosaccharide units.

The common monosaccharides contain several chiral carbons and exist in several isomeric forms. One isomer of glucose, for example, is galactose, which differs from glucose in the position of the –OH bond at carbon-4:



Because carbons-2, -3, -4, and -5 of glucose are chiral, changing the position of the –OH on carbon-4 does not produce an enantiomer of glucose but a different compound, galactose, with distinct physical and chemical properties. Galactose is a hydrolysis product of lactose, a disaccharide found in milk. People who suffer from *galactosemia*lack the enzyme needed to convert galactose to glucose, which is then metabolized to CO_2 and H_2O, releasing energy. Galactose accumulates in their blood and tissues, leading to mental retardation, cataracts, and cirrhosis of the liver.



Sucralose, an artificial sweetner

Because carbohydrates have a carbonyl functional group and several hydroxyl groups, they can undergo a variety of biochemically important reactions. The carbonyl group, for example, can be oxidized to form a carboxylic acid or reduced to form an alcohol. The hydroxyl groups can undergo substitution reactions, resulting in derivatives of the original compound. One such derivative is Sucralose, an artificial sweetener that is six times sweeter than sucrose; it is made by replacing two of the hydroxyl groups on sucrose with chlorine. Carbohydrates can also eliminate hydroxyl groups, producing alkenes.

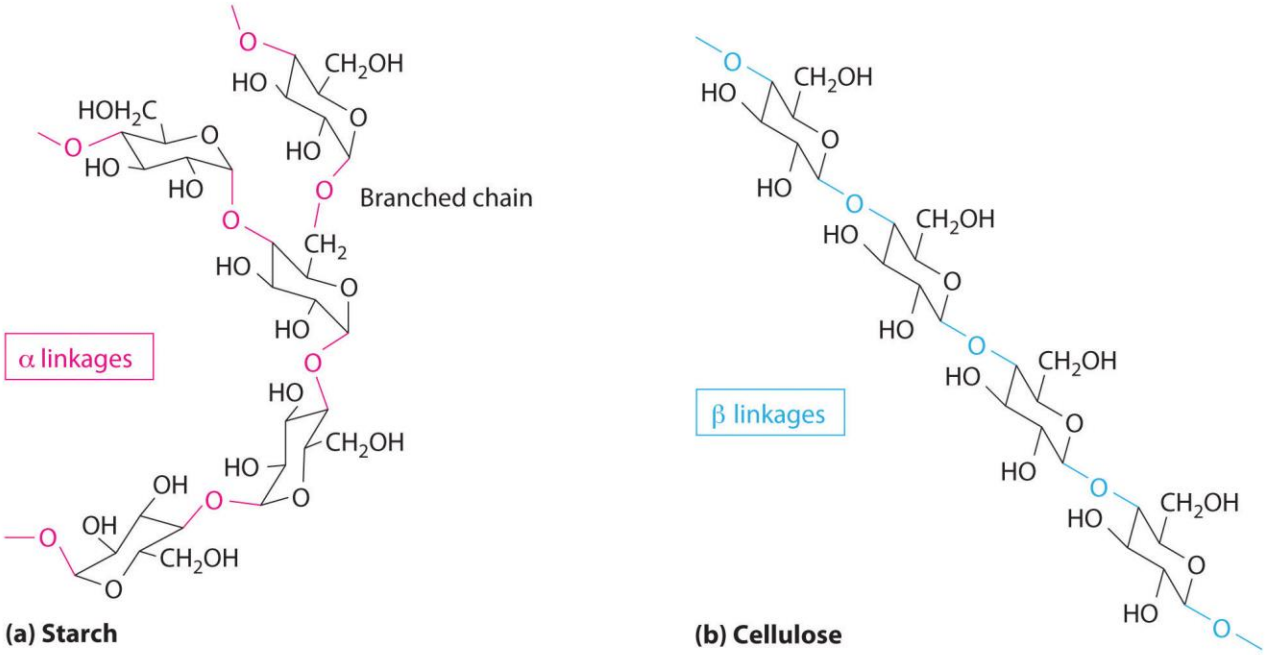
Note the Pattern

Because carbohydrates have a carbonyl functional group and several hydroxyl groups, they can undergo a variety of reactions.

Two familiar polysaccharides are *starch* and *cellulose*, which both hydrolyze to produce thousands of glucose units. They differ only in the connection between glucose units and the amount of branching in the molecule (Figure 24.22 "The Polysaccharides Starch and Cellulose"). Starches can be coiled or branched and are hydrolyzed by the enzymes in our saliva and pancreatic juices. Animal starch, called *glycogen*, is stored in the liver and muscles. It consists of branched glucose units linked by bonds

that produce a coiled structure. The glucose units in cellulose, in contrast, are linked to give long, unbranched chains. The chains in cellulose stack in parallel rows held together by hydrogen bonds between hydroxyl groups. This arrangement produces a rigid structure that is insoluble in water.

Figure 24.22 *The Polysaccharides Starch and Cellulose*

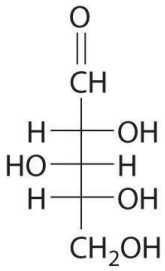


Starches (a) and cellulose (b) differ in the connection between glucose units and the amount of branching in the molecule. Starches can be coiled or branched, whereas cellulose, the primary structural material of plants, has long, unbranched chains held together by hydrogen bonds.

Cellulose is the primary structural material of plants and one of the most abundant organic substances on Earth. Because our enzymes are not able to hydrolyze the bonds between the glucose units in cellulose, we are unable to digest it. A recently marketed product containing a high percentage of cellulose was sold as a dietetic substance for rapid weight loss, but those who consumed it experienced severe intestinal discomfort because the cellulose could not be digested. The product was quickly removed from the market.

EXAMPLE 9

The Fischer projection of xylose, found in many varieties of apples, is shown. Draw the ring form (Haworth projection) of xylose.



Given: Fischer projection of a sugar

Asked for: cyclic structure

Strategy:

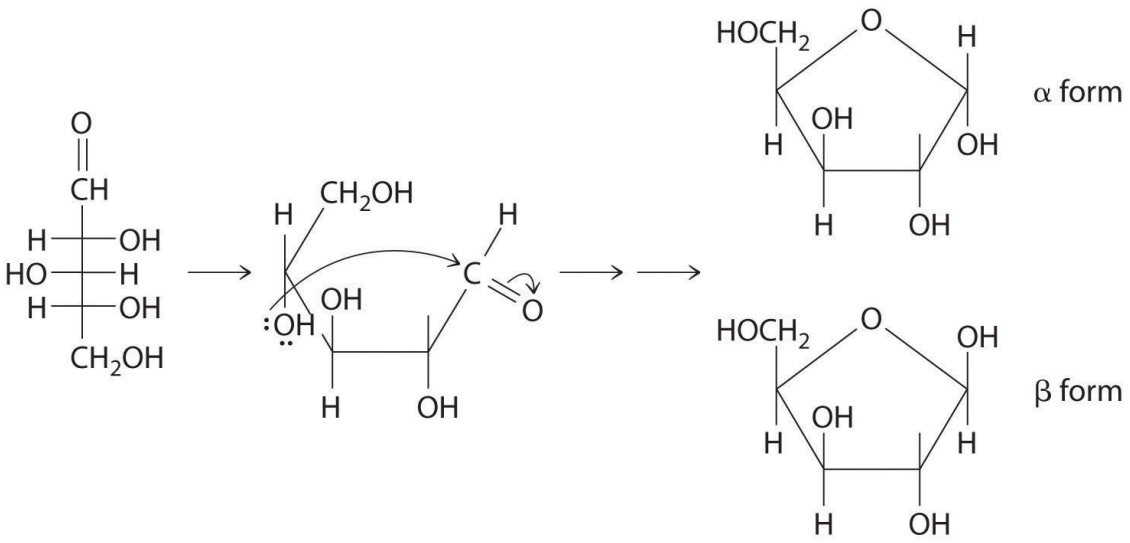
A Identify the nucleophile and the electrophile. Indicate the point of attack, remembering that cyclic structures are most stable when they contain at least five atoms in the ring to prevent bond strain from bond angles that are too small.

B Draw the cyclic form of the structure.

Solution:

A The carbonyl carbon (C1) is a good electrophile, and each oxygen is a good nucleophile. Nucleophilic attack occurs from the –OH group on C4, producing a stable five-membered ring.

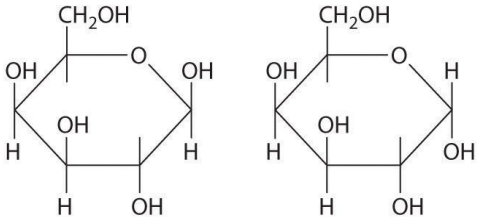
B Because of rotation about the bond between C1 and C2, ring formation gives both a and b anomers, with the following structures (H atoms have been omitted for clarity):



Exercise

Draw the cyclic form(s) of galactose, whose Fischer projection is shown in the previous discussion.

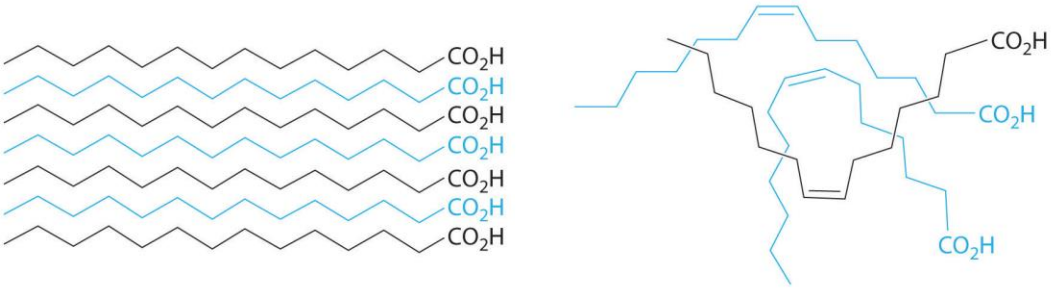
Answer:



Lipids

Lipids (from the Greek *lipos*, meaning “fat” or “lard”) are characterized by their insolubility in water. They form a family of compounds that includes fats, waxes, some vitamins, and steroids. *Fatty acids*, the simplest lipids, have a long hydrocarbon chain that ends with a carboxylic acid functional group. In saturated fatty acids, the hydrocarbon chains contain only C–C bonds, so they can stack in a regular array (part (a) in Figure 24.23 "Fatty Acids, the Simplest Class of Lipids"). In contrast, unsaturated fatty acids have a single double bond in the hydrocarbon chain (monounsaturated) or more than one double bond (polyunsaturated). These double bonds give fatty acid chains a kinked structure, which prevents the molecules from packing tightly (part (b) in Figure 24.23 "Fatty Acids, the Simplest Class of Lipids"). As a result of reduced van der Waals interactions, the melting point of an unsaturated fatty acid is lower than that of a saturated fatty acid of comparable molecule mass, thus producing an oil rather than a solid. (For more information on van der Waals interactions, see Chapter 11 "Liquids", Section 11.2 "Intermolecular Forces".) Fish oils and vegetable oils, for example, have a higher concentration of unsaturated fatty acids than does butter.

Figure 24.23 *Fatty Acids, the Simplest Class of Lipids*



(a) Saturated fatty acids **(b) Unsaturated (cis) fatty acids**

Fatty acids are composed of a long chain that terminates in a carboxylic acid functional group. (a) Molecules of saturated fatty acids, which contain no carbon–carbon double bonds, can stack in a regular array. (b) Molecules of unsaturated fatty acids, which contain one or more cis carbon–carbon double bonds, have kinked structures that cannot pack closely together.

The double bonds of unsaturated fatty acids can by hydrogenated in an addition reaction that produces a saturated fatty acid:

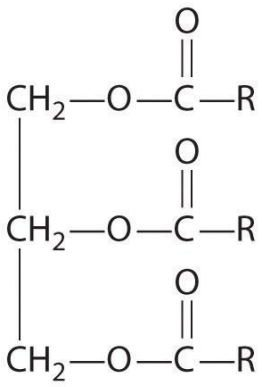
Equation 24.16

$$\text{—}CH = CH\text{—}\ unsaturated\ \ fatty\ \ acid + H2 \rightarrow Ni\text{—}CH2CH2 saturated\ \ fatty\ \ acid\text{—}$$

They can also be oxidized to produce an aldehyde or carboxylic acid. (For more information on hydrogenation, see Chapter 14 "Chemical Kinetics", Section 14.8 "Catalysis".)

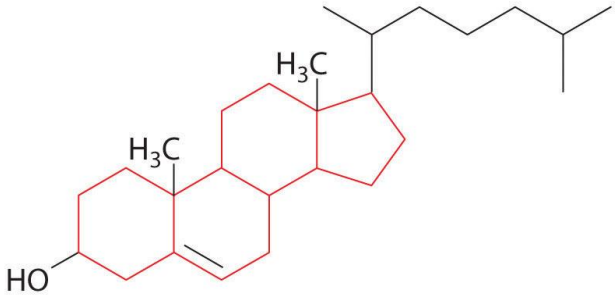
Unsaturated fatty acids are the starting compounds for the biosynthesis of*prostaglandins*. These hormone-like substances are involved in regulating blood pressure, tissue inflammation, and contracting and relaxing smooth muscles. Drugs such as aspirin and ibuprofen inhibit the production of prostaglandins, thereby reducing inflammation.

Waxes are esters produced by the nucleophilic attack of an alcohol on the carbonyl carbon of a long-chain carboxylic acid (Figure 24.18). For example, the wax used in shoe polish and wax paper, which is derived from beeswax, is formed from a straight-chain alcohol with 15 carbon atoms and a fatty acid with 31 carbon atoms.*Triacylglycerols* are a particularly important type of ester in living systems; they are used by the body to store fats and oils. These compounds are formed from one molecule of glycerol (1,2,3-trihydroxypropane) and three fatty acid molecules. During warmer months of the year, animals that hibernate consume large quantities of plants, seeds, and nuts that have a high fat and oil content. They convert the fatty acids to triacylglycerols and store them. Hydrolysis of stored triacylglycerols during hibernation (the reverse of Figure 24.18) releases alcohols and carboxylic acids that the animal uses to generate energy for maintaining cellular activity, respiration, and heart rate. Derivatives of triacylglycerols with a phosphate group are major components of all cell membranes.

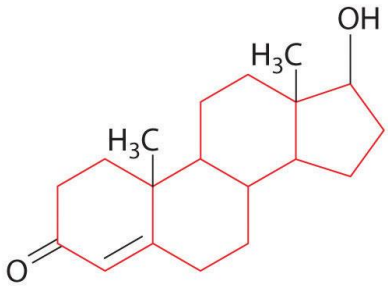


General structure of a triacylglycerol

Steroids are lipids whose structure is composed of three cyclohexane rings and one cyclopentane ring fused together. The presence of various substituents, including double bonds, on the basic steroid ring structure produces a large family of steroid compounds with different biological activities. For example, *cholesterol*, a steroid found in cellular membranes, contains a double bond in one ring and four substituents: a hydroxyl group, two methyl groups, and a hydrocarbon chain.



Cholesterol



Testosterone

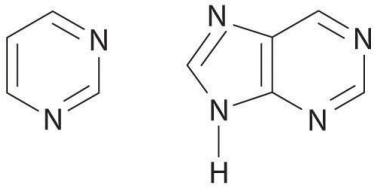
The structure in red is derived from cholesterol.

Cholesterol is the starting point for the biosynthesis of steroid hormones, including testosterone, the primary male sex hormone, and progesterone, which helps maintain pregnancy. These cholesterol derivatives lack the long hydrocarbon side chain, and most contain one or more ketone groups.

Cholesterol is synthesized in the human body in a multistep pathway that begins with a derivative of acetic acid. We also consume cholesterol in our diets: eggs, meats, fish, and diary products all contain cholesterol, but vegetables and other plant-derived foods do not contain cholesterol. Excess cholesterol in the human body can cause gallstones, which are composed of nearly 100% cholesterol, or lipid deposits called plaque in arteries. A buildup of plaque can block a coronary artery and result in a heart attack (Figure 24.24 "Plaque in an Artery").

Nucleic Acids

Nucleic acids are the basic structural components of DNA (deoxyribonucleic acid) and RNA (ribonucleic acid), the biochemical substances found in the nuclei of all cells that transmit the information needed to direct cellular growth and reproduction. Their structures are derived from cyclic nitrogen-containing compounds called *pyrimidines* and *purines*, which can engage in hydrogen bonding through the lone electron pair on nitrogen (in pyrimidine and purine) or through the hydrogen of the amine (in purine):



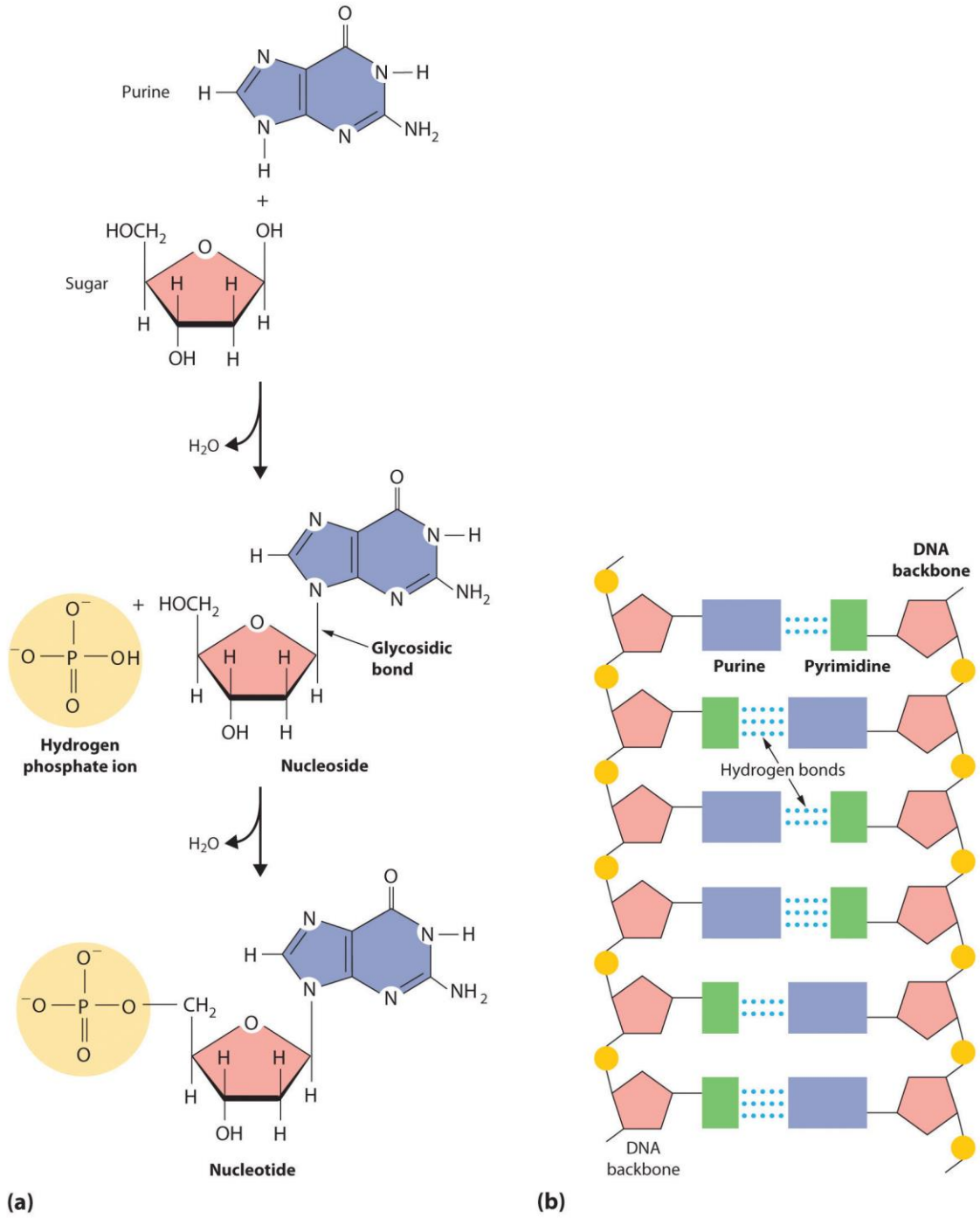
Pyrimidine **Purine**

The same cyclic structures are found in substances such as caffeine, a purine that is a stimulant, and the antifungal agent flucytosine, a pyrimidine. (For more information on the structure of caffeine, see Chapter 3 "Chemical Reactions", Section 3.2 "Determining Empirical and Molecular Formulas".)

When a pyrimidine or a purine is linked to a sugar by a bond called a *glycosidic bond*, a*nucleoside* is formed. Adding a phosphoric acid group to the sugar then produces a*nucleotide* (part (a) in Figure 24.25 "The Formation of Nucleic Acids"). The linkage of nucleotides forms a polymeric chain that consists of alternating sugar and phosphate groups, which is the backbone of DNA and RNA (part (b) in Figure 24.25 "The Formation of Nucleic Acids").

While the function of DNA is to preserve genetic information, RNA translates the genetic information in DNA and carries that information to cellular sites where proteins are synthesized. Many antibiotics function by interfering with the synthesis of proteins in one or more kinds of bacteria. Chloramphenicol, for example, is used against infections of the eye or outer ear canal; it inhibits the formation of peptide bonds between amino acids in a protein chain. Puromycin, which is used against herpes simplex type I, interrupts extension of a peptide chain, causing the release of an incomplete protein and the subsequent death of the virus.

Figure 24.25 The Formation of Nucleic Acids



(a)

When pyrimidine or purine and a sugar react to form a glycosidic bond, a nucleoside is produced. Adding a phosphoric acid group to the sugar of a nucleoside produces a nucleotide. (b) Nucleotides link together to form long polymeric chains. A DNA molecule consists of two such chains held together by hydrogen bonding between the purine and pyrimidine components on different chains.

Mutations in the DNA of an organism may lead to the synthesis of defective proteins.*Phenylketonuria* (*PKU*), for example, is a condition caused by a defective enzyme. Left

untreated, it produces severe brain damage and mental retardation. *Albinism* is caused by a defective enzyme that is unable to produce melanin, the pigment responsible for the color of skin and hair. *Cystic fibrosis*, the most common inherited disease in the United States, blocks pancreatic function and causes thick mucus secretions that make breathing difficult. An area of intense research in combating cancer involves the synthesis of drugs that stop uncontrolled cell growth by interfering with DNA replication.

KEY TAKEAWAY

The four major classes of organic compounds found in biology are proteins, carbohydrates, lipids, and nucleic acids. Their structures and reactivity are determined by the functional groups present.

Summary

Proteins are biologically active polymers formed from amino acids linked together by amide bonds. All the amino acids in proteins are chiral compounds except glycine. The most common organic compounds found in nature are the**carbohydrates**, polyhydroxy aldehydes or polyhydroxy ketones in unbranched chains of three to eight carbons. They are classified according to the number of sugar, or saccharide, units, and they can be drawn as a chain in a Fischer projection or in a cyclic form called a Haworth projection. The two cyclic forms in a Haworth projection are called anomers. Many sugars contain at least one chiral center. With their carbonyl and hydroxyl functional groups, carbohydrates can undergo a variety of biochemically relevant reactions. Starch and cellulose differ only in the connectivity between glucose units. Starches can be branched or unbranched, but cellulose, the structural material of plants, is unbranched, and cannot be digested by humans. **Lipids** are insoluble in water. The simplest lipids, fatty acids, have a long hydrocarbon chain ending in a carboxylic acid functional group. Their physical properties depend on the number of double bonds in the chain. Prostaglandins, hormone-like substances, are formed from unsaturated fatty acids, and waxes are long-chain esters of saturated fatty acids. Triacylglycerols, which the body uses to store fats and oils, consist of glycerol esterified to three fatty acid molecules. Steroids, which include cholesterol and the steroid hormones, are characterized by three cyclohexane rings and one cyclopentane ring fused together. The basic structural units of DNA and RNA are the **nucleic acids**, whose structures are derived from nitrogen-containing cyclic compounds called pyrimidines and purines. These structures are linked to a sugar through a glycosidic bond, forming a nucleoside. Adding a phosphoric acid group produces a nucleotide. Nucleotides link to form a polymeric chain that is the backbone of DNA and RNA.

KEY TAKEAWAY

- An understanding of the reactivity of functional groups is necessary to understanding the reactions that occur in living systems.

CONCEPTUAL PROBLEMS

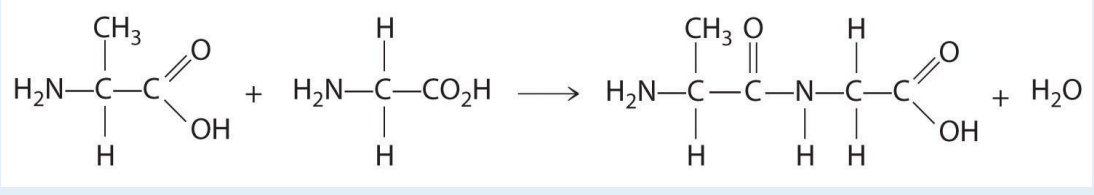
1. What are the strengths and limitations of using a Haworth projection? of using a Fischer projection?
2. Nutritionists will often state that a leafy salad contains no calories. Do you agree?
3. Would you expect margarine, a polyunsaturated fat, to have a higher or lower melting point than butter, a saturated fat?

STRUCTURE AND REACTIVITY

1. Propose a method for synthesizing the dipeptide alanylglycine (Ala-Gly), starting with the individual amino acids (Figure 5.16 "The Structures of 10 Amino Acids").
2. Are all the naturally occurring amino acids chiral compounds? Do you expect proteins to contain both enantiomers of alanine and other amino acids? Explain your answer.
3. The structures of cholesterol and testosterone were shown in this section. Identify the functional groups in each.
4. The structures of glucose and purine were shown in this section. Identify the functional groups in each.

ANSWER

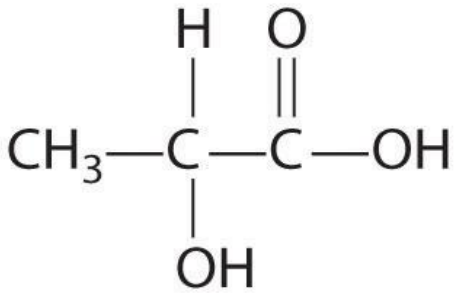
1. Use a condensation reaction:



24.7 End-of-Chapter Material

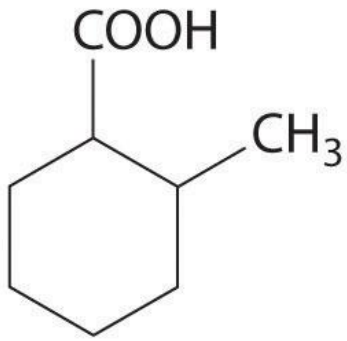
APPLICATION PROBLEMS

1. After exercise, the concentration of lactic acid increases in both muscle tissue and blood. In fact, it is responsible for muscle cramps that may develop after vigorous exercise. Using the structure of lactic acid shown here, draw the conformational isomers of lactic acid as viewed along the C2–C3 axis, where C3 is the carbon of the methyl group. Which would you predict to be the most stable conformation? Why?

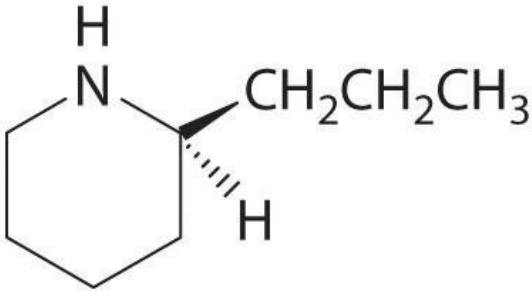


Lactic acid

2. Cyclohexanecarboxylic acid is a liquid used in insecticide formulations. A derivative of this compound, 2-methylcyclohexanecarboxylic acid is shown here. Sketch the *cis* and*trans* isomers of this derivative. Arrange the conformations of its geometric isomers in order of increasing energy.



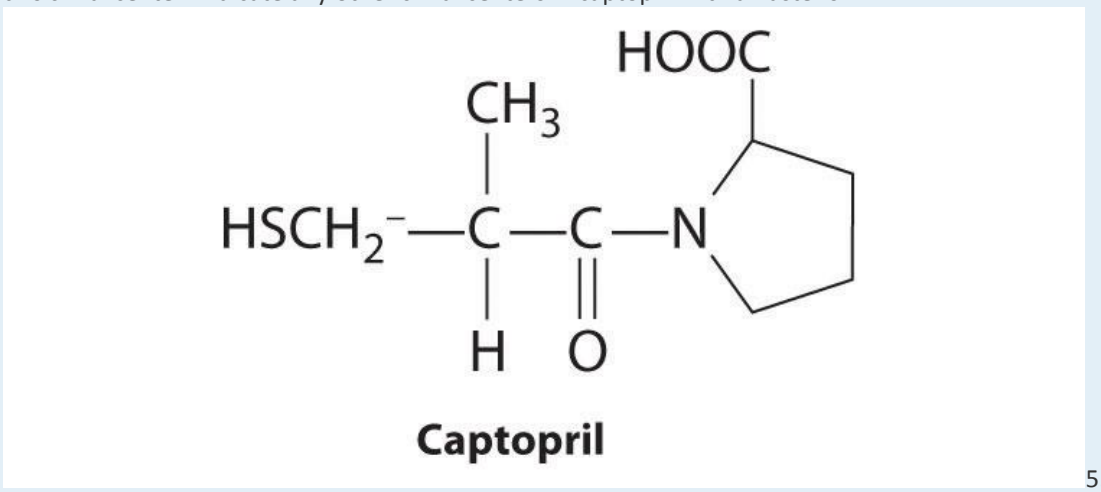
3. Coniine is a naturally occurring compound with insect-paralyzing properties. Ingestion of this compound causes weakness, vomiting, labored respiration, and eventual death. Does coniine have a chiral carbon? If so, indicate the carbon with an asterisk.



Coniine

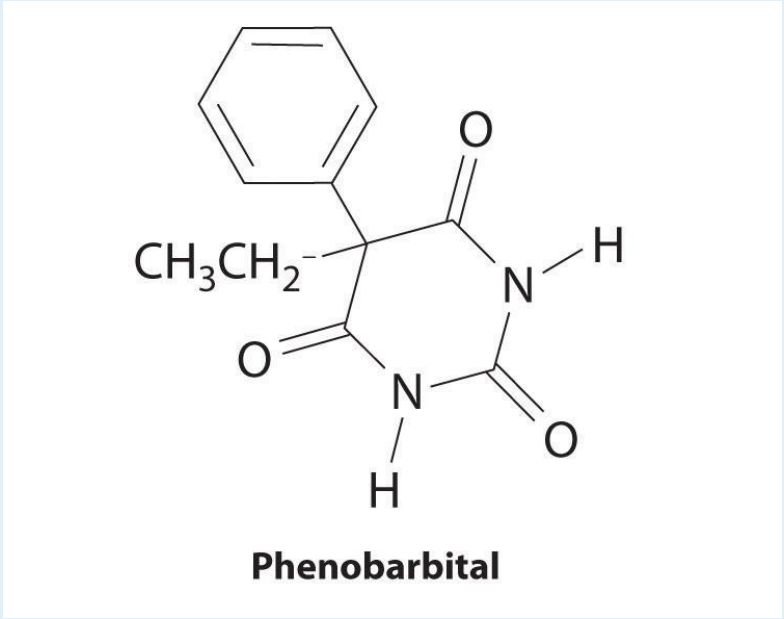
4. A compound that has been found to be an effective hypertensive is captopril, sold commercially as Hypertil and

Tensoprel, among other names. Captopril has a chiral center at C2. Draw the enantiomers that result from this chiral center. Indicate any other chiral centers in captopril with an asterisk.



Captopril

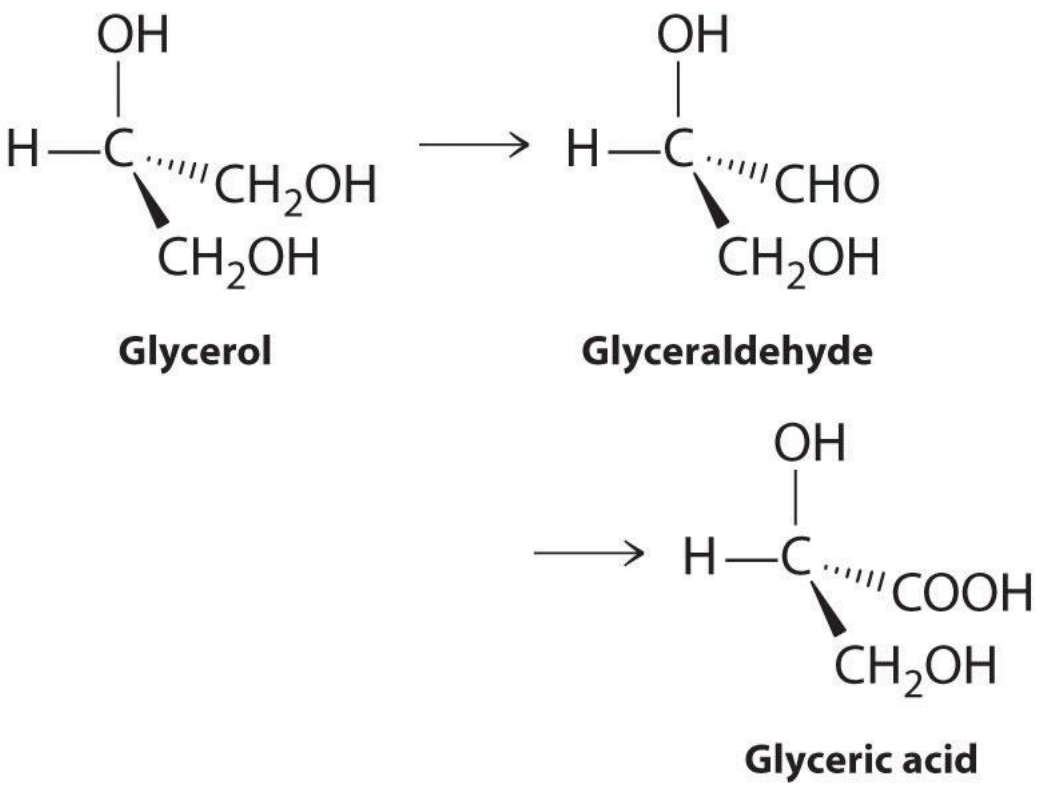
5. The structure of phenobarbital, a compound used to treat epilepsy, is shown here. Identify the functional groups.



Phenobarbital

6. The compound 2-amino-2-methyl-1-propanol is used not only in the synthesis of pharmaceuticals but also in cosmetic creams, polishes, and cleaning compounds. Is it a chiral compound?

7. Glycerol (1,2,3-propanetriol, or 1,2,3-trihydroxypropane) is produced from sugars by fermentation. It also is obtained from oils and fats as a by-product during the manufacture of soaps. Glycerol can be converted to glyceric acid by the following sequence:



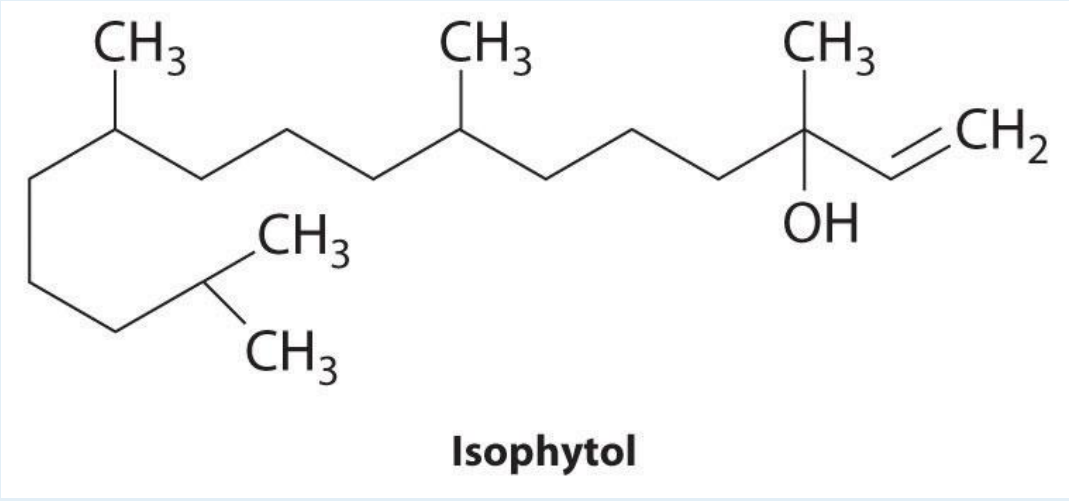
Both glyceraldehyde and glyceric acid are derivatives of biochemical intermediates in sugar metabolism.

a. Is the conversion of glycerol to glyceric acid an oxidative process or a reductive process?
b. How many of these compounds are chiral? Indicate any chiral centers with an asterisk.

2. When exposed to light or heat, peroxides (ROOR) can undergo radical reactions. The first step is the dissociation of the peroxide into two alkoxy radicals. Each alkoxy radical then reacts with a species such as HBr to form an alcohol.

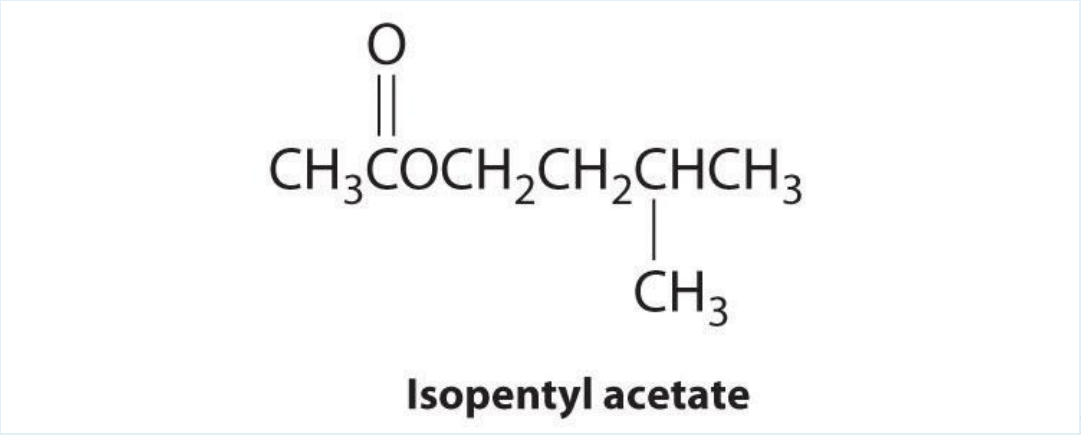
a. Write chemical equations for these reactions.
b. One of the products of the second step can react with an alkene to generate another radical. Show a chemical equation for this reaction, using ethylene as the alkene.
c. The product of part (b) can then react with HBr to form two products. What are those products?
d. Identify any propagation reactions in part (b) or part (c). Show all possible termination reactions.

3. The structure of isophytol is shown here. This compound is used to prepare vitamins E and K. Does isophytol form *cis* and *trans* isomers? If so, draw these isomers.



Isophytol

10. Isopentyl acetate, also known as “oil of banana,” has the structure shown here. Show the first step in the mechanism for reaction of isopentyl acetate with C_6H_5MgBr, which gives the first ionic adduct.



Isopentyl acetate

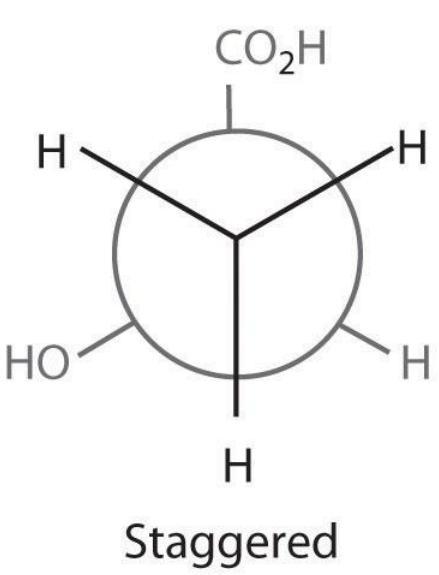
11. An enkephalin is a pentapeptide that controls pain in humans. Enkephalins function by binding to the same specific sites in brain cells that are known to bind morphine and heroin. Methionine enkephalin has the structure Tyr-Gly-Gly-Phe-Met.

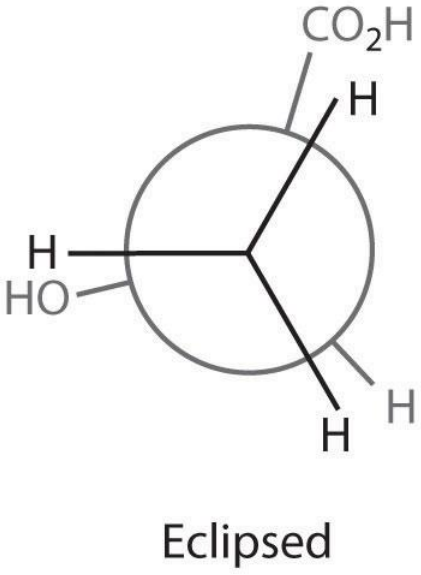
a. Use Figure 5.16 "The Structures of 10 Amino Acids" to draw the structure of methionine enkephalin.

b. Rotation about the amide bond that connects residues 3 and 4 is restricted because of electron delocalization. Draw the *cis* and *trans* isomers.

ANSWERS

1. The first staggered conformation minimizes electrostatic repulsions between adjacent atoms:





Chapter 25

Appendix A: Standard Thermodynamic Quantities for Chemical Substances at 25°C

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Aluminum:			
Al(s)	0.0	0.0	28.3
Al(g)	330.0	289.4	164.6
$AlCl_3$(s)	−704.2	−628.8	109.3
Al_2O_3(s)	−1675.7	−1582.3	50.9
Barium:			
Ba(s)	0.0	0.0	62.5
Ba(g)	180.0	146.0	170.2
BaO(s)	−548.0	−520.3	72.1
$BaCO_3$(s)	−1213.0	−1134.4	112.1
$BaSO_4$(s)	−1473.2	−1362.2	132.2
Beryllium:			
Be(s)	0.0	0.0	9.5

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Be(g)	324.0	286.6	136.3
$Be(OH)_2$(s)	−902.5	−815.0	45.5
BeO(s)	−609.4	−580.1	13.8
Bismuth:			
Bi(s)	0.0	0.0	56.7
Bi(g)	207.1	168.2	187.0
Bromine:			
Br(g)	111.9	82.4	175.0
Br_2(l)	0.0	0.0	152.2
Br^-(aq)	−121.6	−104.0	82.4
Br_2(g)	30.9	3.1	245.5
HBr(g)	−36.3	−53.4	198.7
HBr(aq)	−121.6	−104.0	82.4
Cadmium:			
Cd(s)	0.0	0.0	51.8
Cd(g)	111.8	—	167.7
$CdCl_2$(s)	−391.5	−343.9	115.3
CdS(s)	−161.9	−156.5	64.9
Calcium:			
Ca(s)	0.0	0.0	41.6
Ca(g)	177.8	144.0	154.9
$CaCl_2$(s)	−795.4	−748.8	108.4
CaF_2(s)	−1228.0	−1175.6	68.5
$Ca(OH)_2$(s)	−985.2	−897.5	83.4
CaO(s)	−634.9	−603.3	38.1
$CaSO_4$(s)	−1434.5	−1322.0	106.5
$CaCO_3$(s, calcite)	−1207.6	−1129.1	91.7
$CaCO_3$(s, aragonite)	−1207.8	−1128.2	88.0
Carbon:			
C(s, graphite)	0.0	0.0	5.7

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
C(s, diamond)	1.9	2.9	2.4
C(s, fullerene—C_{60})	2327.0	2302.0	426.0
C(s, fullerene—C_{70})	2555.0	2537.0	464.0
C(g)	716.7	671.3	158.1
C(g, fullerene—C_{60})	2502.0	2442.0	544.0
C(g, fullerene—C_{70})	2755.0	2692.0	614.0
CBr_4(s)	29.4	47.7	212.5
CBr_4(g)	83.9	67.0	358.1
CCl_2F_2(g)	−477.4	−439.4	300.8
CCl_2O(g)	−219.1	−204.9	283.5
CCl_4(l)	−128.2	−62.6	216.2
CCl_4(g)	−95.7	−53.6	309.9
CF_4(g)	−933.6	−888.3	261.6
$CHCl_3$(l)	−134.1	−73.7	201.7
$CHCl_3$(g)	−102.7	6.0	295.7
CH_2Cl_2(l)	−124.2	—	177.8
CH_2Cl_2(g)	−95.4	−68.9	270.2
CH_3Cl(g)	−81.9	−58.5	234.6
CH_4(g)	−74.6	−50.5	186.3
CH_3COOH(l)	−484.3	−389.9	159.8
CH_3OH(l)	−239.2	−166.6	126.8
CH_3OH(g)	−201.0	−162.3	239.9
CH_3NH_2(l)	−47.3	35.7	150.2
CH_3NH_2(g)	−22.5	32.7	242.9
CH_3CN(l)	40.6	86.5	149.6
CH_3CN(g)	74.0	91.9	243.4
CO(g)	−110.5	−137.2	197.7
CO_2(g)	−393.5	−394.4	213.8
CS_2(l)	89.0	64.6	151.3
CS_2(g)	116.7	67.1	237.8

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
$C_2H_2(g)$	227.4	209.9	200.9
$C_2H_4(g)$	52.4	68.4	219.3
$C_2H_6(g)$	−84.0	−32.0	229.2
$C_3H_8(g)$	−103.8	−23.4	270.3
$C_3H_6O_3(s)$ (lactic acid)	−694.1	−522.9	142.3
$C_6H_6(l)$	49.1	124.5	173.4
$C_6H_6(g)$	82.9	129.7	269.2
$C_6H_{12}O_6(s)$ (glucose)	−1273.3	−910.4	212.1
$C_2H_5OH(l)$	−277.6	−174.8	160.7
$C_2H_5OH(g)$	−234.8	−167.9	281.6
$(CH_3)_2O(l)$	−203.3	—	—
$(CH_3)_2O(g)$	−184.1	−112.6	266.4
$CH_3CO_2^-(aq)$	−486.0	−369.3	86.6
n-$C_{12}H_{26}(l)$ (dodecane)	−350.9	28.1	490.6
Cesium:			
Cs(s)	0.0	0.0	85.2
Cs(g)	76.5	49.6	175.6
CsCl(s)	−443.0	−414.5	101.2
Chlorine:			
Cl(g)	121.3	105.3	165.2
$Cl_2(g)$	0.0	0.0	223.1
$Cl^-(aq)$	−167.2	−131.2	56.5
HCl(g)	−92.3	−95.3	186.9
HCl(aq)	−167.2	−131.2	56.5
$ClF_3(g)$	−163.2	−123.0	281.6
Chromium:			
Cr(s)	0.0	0.0	23.8
Cr(g)	396.6	351.8	174.5
$CrCl_3(s)$	−556.5	−486.1	123.0
$CrO_3(g)$	−292.9	—	266.2

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
$Cr_2O_3(s)$	−1139.7	−1058.1	81.2
Cobalt:			
Co(s)	0.0	0.0	30.0
Co(g)	424.7	380.3	179.5
$CoCl_2(s)$	−312.5	−269.8	109.2
Copper:			
Cu(s)	0.0	0.0	33.2
Cu(g)	337.4	297.7	166.4
CuCl(s)	−137.2	−119.9	86.2
$CuCl_2(s)$	−220.1	−175.7	108.1
CuO(s)	−157.3	−129.7	42.6
$Cu_2O(s)$	−168.6	−146.0	93.1
CuS(s)	−53.1	−53.6	66.5
$Cu_2S(s)$	−79.5	−86.2	120.9
CuCN(s)	96.2	111.3	84.5
Fluorine:			
F(g)	79.4	62.3	158.8
$F^-(aq)$	−332.6	−278.8	−13.8
$F_2(g)$	0.0	0.0	202.8
HF(g)	−273.3	−275.4	173.8
HF(aq)	−332.6	−278.8	−13.8
Hydrogen:			
H(g)	218.0	203.3	114.7
$H_2(g)$	0.0	0.0	130.7
$H^+(aq)$	0.0	0.0	0.0
Iodine:			
I(g)	106.8	70.2	180.8
$I^-(aq)$	−55.2	−51.6	111.3
$I_2(s)$	0.0	0.0	116.1
$I_2(g)$	62.4	19.3	260.7

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
HI(g)	26.5	1.7	206.6
HI(aq)	−55.2	−51.6	111.3
Iron:			
Fe(s)	0.0	0.0	27.3
Fe(g)	416.3	370.7	180.5
Fe^{2+}(aq)	−89.1	−78.9	−137.7
Fe^{3+}(aq)	−48.5	−4.7	−315.9
$FeCl_2$(s)	−341.8	−302.3	118.0
$FeCl_3$(s)	−399.5	−334.0	142.3
FeO(s)	−272.0	−251.4	60.7
Fe_2O_3(s)	−824.2	−742.2	87.4
Fe_3O_4(s)	−1118.4	−1015.4	146.4
FeS_2(s)	−178.2	−166.9	52.9
$FeCO_3$(s)	−740.6	−666.7	92.9
Lead:			
Pb(s)	0.0	0.0	64.8
Pb(g)	195.2	162.2	175.4
PbO(s, red or litharge)	−219.0	−188.9	66.5
PbO(s, yellow or massicot)	−217.3	−187.9	68.7
PbO_2(s)	−277.4	−217.3	68.6
$PbCl_2$(s)	−359.4	−314.1	136.0
PbS(s)	−100.4	−98.7	91.2
$PbSO_4$(s)	−920.0	−813.0	148.5
$PbCO_3$(s)	−699.1	−625.5	131.0
$Pb(NO_3)_2$(s)	−451.9	—	—
$Pb(NO_3)_2$(aq)	−416.3	−246.9	303.3
Lithium:			
Li(s)	0.0	0.0	29.1
Li(g)	159.3	126.6	138.8
Li^+(aq)	−278.5	−293.3	13.4

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
LiCl(s)	−408.6	−384.4	59.3
Li_2O(s)	−597.9	−561.2	37.6
Magnesium:			
Mg(s)	0.0	0.0	32.7
Mg(g)	147.1	112.5	148.6
$MgCl_2$(s)	−641.3	−591.8	89.6
MgO(s)	−601.6	−569.3	27.0
$Mg(OH)_2$(s)	−924.5	−833.5	63.2
$MgSO_4$(s)	−1284.9	−1170.6	91.6
MgS(s)	−346.0	−341.8	50.3
Manganese:			
Mn(s)	0.0	0.0	32.0
Mn(g)	280.7	238.5	173.7
$MnCl_2$(s)	−481.3	−440.5	118.2
MnO(s)	−385.2	−362.9	59.7
MnO_2(s)	−520.0	−465.1	53.1
$KMnO_4$(s)	−837.2	−737.6	171.7
MnO_4^-(aq)	−541.4	−447.2	191.2
Mercury:			
Hg(l)	0.0	0.0	75.9
Hg(g)	61.4	31.8	175.0
$HgCl_2$(s)	−224.3	−178.6	146.0
Hg_2Cl_2(s)	−265.4	−210.7	191.6
HgO(s)	−90.8	−58.5	70.3
HgS(s, red)	−58.2	−50.6	82.4
Hg_2(g)	108.8	68.2	288.1
Molybdenum:			
Mo(s)	0.0	0.0	28.7
Mo(g)	658.1	612.5	182.0
MoO_2(s)	−588.9	−533.0	46.3

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
$MoO_3(s)$	−745.1	−668.0	77.7
Nickel:			
Ni(s)	0.0	0.0	29.9
Ni(g)	429.7	384.5	182.2
$NiCl_2(s)$	−305.3	−259.0	97.7
$Ni(OH)_2(s)$	−529.7	−447.2	88.0
Nitrogen:			
N(g)	472.7	455.5	153.3
$N_2(g)$	0.0	0.0	191.6
$NH_3(g)$	−45.9	−16.4	192.8
$NH_4^+(aq)$	−132.5	−79.3	113.4
$N_2H_4(l)$	50.6	149.3	121.2
$N_2H_4(g)$	95.4	159.4	238.5
$NH_4Cl(s)$	−314.4	−202.9	94.6
$NH_4OH(l)$	−361.2	−254.0	165.6
$NH_4NO_3(s)$	−365.6	−183.9	151.1
$(NH_4)_2SO_4(s)$	−1180.9	−901.7	220.1
NO(g)	91.3	87.6	210.8
$NO_2(g)$	33.2	51.3	240.1
$N_2O(g)$	81.6	103.7	220.0
$N_2O_4(l)$	−19.5	97.5	209.2
$N_2O_4(g)$	11.1	99.8	304.4
$HNO_2(g)$	−79.5	−46.0	254.1
$HNO_3(l)$	−174.1	−80.7	155.6
$HNO_3(g)$	−133.9	−73.5	266.9
$HNO_3(aq)$	−207.4	−111.3	146.4
$NF_3(g)$	−132.1	−90.6	260.8
HCN(l)	108.9	125.0	112.8
HCN(g)	135.1	124.7	201.8
Osmium:			

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Os(s)	0.0	0.0	32.6
Os(g)	791.0	745.0	192.6
OsO_4(s)	−394.1	−304.9	143.9
OsO_4(g)	−337.2	−292.8	293.8
Oxygen:			
O(g)	249.2	231.7	161.1
O_2(g)	0.0	0.0	205.2
O_3(g)	142.7	163.2	238.9
OH^-(aq)	−230.0	−157.2	−10.8
H_2O(l)	−285.8	−237.1	70.0
H_2O(g)	−241.8	−228.6	188.8
H_2O_2(l)	−187.8	−120.4	109.6
H_2O_2(g)	−136.3	−105.6	232.7
Phosphorus:			
P(s, white)	0.0	0.0	41.1
P(s, red) −17.6	−17.6	−12.5	22.8
P(s, black)	−39.3	—	—
P(g, white)	316.5	280.1	163.2
P_2(g)	144.0	103.5	218.1
P_4(g)	58.9	24.4	280.0
PCl_3(l)	−319.7	−272.3	217.1
PCl_3(g)	−287.0	−267.8	311.8
$POCl_3$(l)	−597.1	−520.8	222.5
$POCl_3$(g)	−558.5	−512.9	325.5
PCl_5(g)	−374.9	−305.0	364.6
PH_3(g)	5.4	13.5	210.2
H_3PO_4(s)	−1284.4	−1124.3	110.5
H_3PO_4(l)	−1271.7	−1123.6	150.8
Potassium:			
K(s)	0.0	0.0	64.7

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
K(g)	89.0	60.5	160.3
KBr(s)	−393.8	−380.7	95.9
KCl(s)	−436.5	−408.5	82.6
$KClO_3$(s)	−397.7	−296.3	143.1
K_2O(s)	−361.5	−322.1	94.1
K_2O_2(s)	−494.1	−425.1	102.1
KNO_2(s)	−369.8	−306.6	152.1
KNO_3(s)	−494.6	−394.9	133.1
KSCN(s)	−200.2	−178.3	124.3
K_2CO_3(s)	−1151.0	−1063.5	155.5
K_2SO_4(s)	−1437.8	−1321.4	175.6
Rubidium:			
Rb(s)	0.0	0.0	76.8
Rb(g)	80.9	53.1	170.1
RbCl(s)	−435.4	−407.8	95.9
Selenium:			
Se(s, gray)	0.0	0.0	42.4
Se(g, gray)	227.1	187.0	176.7
H_2Se(g)	29.7	15.9	219.0
Silicon:			
Si(s)	0.0	0.0	18.8
Si(g)	450.0	405.5	168.0
$SiCl_4$(l)	−687.0	−619.8	239.7
$SiCl_4$(g)	−657.0	−617.0	330.7
SiH_4(g)	34.3	56.9	204.6
SiC(s, cubic)	−65.3	−62.8	16.6
SiC(s, hexagonal)	−62.8	−60.2	16.5
Silver:			
Ag(s)	0.0	0.0	42.6
Ag(g)	284.9	246.0	173.0

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
$Ag^+(aq)$	105.6	77.1	72.7
AgBr(s)	−100.4	−96.9	107.1
AgCl(s)	−127.0	−109.8	96.3
$AgNO_3(s)$	−124.4	−33.4	140.9
$Ag_2O(s)$	−31.1	−11.2	121.3
$Ag_2S(s)$	−32.6	−40.7	144.0
Sodium:			
Na(s)	0.0	0.0	51.3
Na(g)	107.5	77.0	153.7
$Na^+(aq)$	−240.1	−261.9	59.0
NaF(s)	−576.6	−546.3	51.1
NaF(aq)	−572.8	−540.7	45.2
NaCl(s)	−411.2	−384.1	72.1
NaCl(aq)	−407.3	−393.1	115.5
NaBr(s)	−361.1	−349.0	86.8
NaBr(g)	−143.1	−177.1	241.2
NaBr(aq)	−361.7	−365.8	141.4
$NaO_2(s)$	−260.2	−218.4	115.9
$Na_2O(s)$	−414.2	−375.5	75.1
$Na_2O_2(s)$	−510.9	−447.7	95.0
NaCN(s)	−87.5	−76.4	115.6
$NaNO_3(aq)$	−447.5	−373.2	205.4
$NaNO_3(s)$	−467.9	−367.0	116.5
$NaN_3(s)$	21.7	93.8	96.9
$Na_2CO_3(s)$	−1130.7	−1044.4	135.0
$Na_2SO_4(s)$	−1387.1	−1270.2	149.6
Sulfur:			
S(s, rhombic)	0.0	0.0	32.1
S(g, rhombic)	277.2	236.7	167.8
$SO_2(g)$	−296.8	−300.1	248.2

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
$SO_3(g)$	−395.7	−371.1	256.8
$SO_4^{2-}(aq)$	−909.3	−744.5	20.1
$SOCl_2(g)$	−212.5	−198.3	309.8
$H_2S(g)$	−20.6	−33.4	205.8
$H_2SO_4(aq)$	−909.3	−744.5	20.1
Tin:			
Sn(s, white)	0.0	0.0	51.2
Sn(s, gray)	−2.1	0.1	44.1
Sn(g, white)	301.2	266.2	168.5
$SnCl_4(l)$	−511.3	−440.1	258.6
$SnCl_4(g)$	−471.5	−432.2	365.8
$SnO_2(s)$	−557.6	−515.8	49.0
Titanium:			
Ti(s)	0.0	0.0	30.7
Ti(g)	473.0	428.4	180.3
$TiCl_2(s)$	−513.8	−464.4	87.4
$TiCl_3(s)$	−720.9	−653.5	139.7
$TiCl_4(l)$	−804.2	−737.2	252.3
$TiCl_4(g)$	−763.2	−726.3	353.2
$TiO_2(s)$	−944.0	−888.8	50.6
Uranium:			
U(s)	0.0	0.0	50.2
U(g)	533.0	488.4	199.8
$UO_2(s)$	−1085.0	−1031.8	77.0
$UO_2(g)$	−465.7	−471.5	274.6
$UF_4(s)$	−1914.2	−1823.3	151.7
$UF_4(g)$	−1598.7	−1572.7	368.0
$UF_6(s)$	−2197.0	−2068.5	227.6
$UF_6(g)$	−2147.4	−2063.7	377.9
Vanadium:			

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
V(s)	0.0	0.0	28.9
V(g)	514.2	754.4	182.3
VCl_3(s)	−580.7	−511.2	131.0
VCl_4(l)	−569.4	−503.7	255.0
VCl_4(g)	−525.5	−492.0	362.4
V_2O_5(s)	−1550.6	−1419.5	131.0
Zinc:			
Zn(s)	0.0	0.0	41.6
Zn(g)	130.4	94.8	161.0
$ZnCl_2$(s)	−415.1	−369.4	111.5
$Zn(NO_3)_2$(s)	−483.7	—	—
ZnS(s, sphalerite)	−206.0	−201.3	57.7
$ZnSO_4$(s)	−982.8	−871.5	110.5
Zirconium:			
Zr(s)	0.0	0.0	39.0
Zr(g)	608.8	566.5	181.4
$ZrCl_2$(s)	−502.0	−386	110
$ZrCl_4$(s)	−980.5	−889.9	181.6

Source of data: *CRC Handbook of Chemistry and Physics*, 84th Edition (2004).

Chapter 26

Appendix B: Solubility-Product Constants (K_{sp}) for Compounds at 25°C

Compound Name	Compound Formula	K_{sp}
Aluminum phosphate	$AlPO_4$	9.84×10^{-21}
Barium bromate	$Ba(BrO_3)_2$	2.43×10^{-4}
Barium carbonate	$BaCO_3$	2.58×10^{-9}
Barium chromate	$BaCrO_4$	1.17×10^{-10}
Barium fluoride	BaF_2	1.84×10^{-7}
Barium iodate	$Ba(IO_3)_2$	4.01×10^{-9}
Barium nitrate	$Ba(NO_3)_2$	4.64×10^{-3}
Barium sulfate	$BaSO_4$	1.08×10^{-10}
Barium sulfite	$BaSO_3$	5.0×10^{-10}
Beryllium hydroxide	$Be(OH)_2$	6.92×10^{-22}
Bismuth arsenate	$BiAsO_4$	4.43×10^{-10}
Bismuth iodide	BiI_3	7.71×10^{-19}
Cadmium carbonate	$CdCO_3$	1.0×10^{-12}
Cadmium fluoride	CdF_2	6.44×10^{-3}
Cadmium hydroxide	$Cd(OH)_2$	7.2×10^{-15}
Cadmium iodate	$Cd(IO_3)_2$	2.5×10^{-8}
Cadmium phosphate	$Cd_3(PO_4)_2$	2.53×10^{-33}
Cadmium sulfide	CdS	8.0×10^{-27}
Calcium carbonate	$CaCO_3$	3.36×10^{-9}
Calcium fluoride	CaF_2	3.45×10^{-11}
Calcium hydroxide	$Ca(OH)_2$	5.02×10^{-6}
Calcium iodate	$Ca(IO_3)_2$	6.47×10^{-6}
Calcium phosphate	$Ca_3(PO_4)_2$	2.07×10^{-33}
Calcium sulfate	$CaSO_4$	4.93×10^{-5}
Cesium perchlorate	$CsClO_4$	3.95×10^{-3}
Cesium periodate	$CsIO_4$	5.16×10^{-6}
Cobalt(II) arsenate	$Co_3(AsO_4)_2$	6.80×10^{-29}

Compound Name	Compound Formula	K_{sp}
Cobalt(II) hydroxide	$Co(OH)_2$	5.92×10^{-15}
Cobalt(II) phosphate	$Co_3(PO_4)_2$	2.05×10^{-35}
Copper(I) bromide	CuBr	6.27×10^{-9}
Copper(I) chloride	CuCl	1.72×10^{-7}
Copper(I) cyanide	CuCN	3.47×10^{-20}
Copper(I) iodide	CuI	1.27×10^{-12}
Copper(I) thiocyanate	CuSCN	1.77×10^{-13}
Copper(II) arsenate	$Cu_3(AsO_4)_2$	7.95×10^{-36}
Copper(II) oxalate	CuC_2O_4	4.43×10^{-10}
Copper(II) phosphate	$Cu_3(PO_4)_2$	1.40×10^{-37}
Copper(II) sulfide	CuS	6.3×10^{-36}
Europium(III) hydroxide	$Eu(OH)_3$	9.38×10^{-27}
Gallium(III) hydroxide	$Ga(OH)_3$	7.28×10^{-36}
Iron(II) carbonate	$FeCO_3$	3.13×10^{-11}
Iron(II) fluoride	FeF_2	2.36×10^{-6}
Iron(II) hydroxide	$Fe(OH)_2$	4.87×10^{-17}
Iron(III) hydroxide	$Fe(OH)_3$	2.79×10^{-39}
Iron(III) sulfide	FeS	6.3×10^{-18}
Lanthanum iodate	$La(IO_3)_3$	7.50×10^{-12}
Lead(II) bromide	$PbBr_2$	6.60×10^{-6}
Lead(II) carbonate	$PbCO_3$	7.40×10^{-14}
Lead(II) chloride	$PbCl_2$	1.70×10^{-5}
Lead(II) fluoride	PbF_2	3.3×10^{-8}
Lead(II) hydroxide	$Pb(OH)_2$	1.43×10^{-20}
Lead(II) iodate	$Pb(IO_3)_2$	3.69×10^{-13}
Lead(II) iodide	PbI_2	9.8×10^{-9}
Lead(II)selenite	$PbSeO_4$	1.37×10^{-7}
Lead(II) sulfate	$PbSO_4$	2.53×10^{-8}
Lead(II) sulfide	PbS	8.0×10^{-28}
Lithium carbonate	Li_2CO_3	8.15×10^{-4}

Compound Name	Compound Formula	K_{sp}
Lithium fluoride	LiF	1.84×10^{-3}
Lithium phosphate	Li_3PO_4	2.37×10^{-11}
Magnesium carbonate	$MgCO_3$	6.82×10^{-6}
Magnesium fluoride	MgF_2	5.16×10^{-11}
Magnesium hydroxide	$Mg(OH)_2$	5.61×10^{-12}
Magnesium phosphate	$Mg_3(PO_4)_2$	1.04×10^{-24}
Manganese(II) carbonate	$MnCO_3$	2.24×10^{-11}
Manganese(II) iodate	$Mn(IO_3)_2$	4.37×10^{-7}
Mercury(I) bromide	Hg_2Br_2	6.40×10^{-23}
Mercury(I) carbonate	Hg_2CO_3	3.6×10^{-17}
Mercury(I) chloride	Hg_2Cl_2	1.43×10^{-18}
Mercury(I) fluoride	Hg_2F_2	3.10×10^{-6}
Mercury(I) iodide	Hg_2I_2	5.2×10^{-29}
Mercury(I) oxalate	$Hg_2C_2O_4$	1.75×10^{-13}
Mercury(I) sulfate	Hg_2SO_4	6.5×10^{-7}
Mercury(I) thiocyanate	$Hg_2(SCN)_2$	3.2×10^{-20}
Mercury(II) bromide	$HgBr_2$	6.2×10^{-20}
Mercury (II) iodide	HgI_2	2.9×10^{-29}
Mercury(II) sulfide (red)	HgS	4×10^{-53}
Mercury(II) sulfide (black)	HgS	1.6×10^{-52}
Neodymium carbonate	$Nd_2(CO_3)_3$	1.08×10^{-33}
Nickel(II) carbonate	$NiCO_3$	1.42×10^{-7}
Nickel(II) hydroxide	$Ni(OH)_2$	5.48×10^{-16}
Nickel(II) iodate	$Ni(IO_3)_2$	4.71×10^{-5}
Nickel(II) phosphate	$Ni_3(PO_4)_2$	4.74×10^{-32}
Palladium(II) thiocyanate	$Pd(SCN)_2$	4.39×10^{-23}
Potassium hexachloroplatinate	K_2PtCl_6	7.48×10^{-6}
Potassium perchlorate	$KClO_4$	1.05×10^{-2}
Potassium periodate	KIO_4	3.71×10^{-4}
Praseodymium hydroxide	$Pr(OH)_3$	3.39×10^{-24}

Compound Name	Compound Formula	K_{sp}
Rubidium perchlorate	$RbClO_4$	3.00×10^{-3}
Scandium fluoride	ScF_3	5.81×10^{-24}
Scandium hydroxide	$Sc(OH)_3$	2.22×10^{-31}
Silver(I) acetate	$AgCH_3CO_2$	1.94×10^{-3}
Silver(I) arsenate	Ag_3AsO_4	1.03×10^{-22}
Silver(I) bromate	$AgBrO_3$	5.38×10^{-5}
Silver(I) bromide	$AgBr$	5.35×10^{-13}
Silver(I) carbonate	Ag_2CO_3	8.46×10^{-12}
Silver(I) chloride	$AgCl$	1.77×10^{-10}
Silver(I) chromate	Ag_2CrO_4	1.12×10^{-12}
Silver(I) cyanide	$AgCN$	5.97×10^{-17}
Silver(I) iodate	$AgIO_3$	3.17×10^{-8}
Silver(I) iodide	AgI	8.52×10^{-17}
Silver(I) oxalate	$Ag_2C_2O_4$	5.40×10^{-12}
Silver(I) phosphate	Ag_3PO_4	8.89×10^{-17}
Silver(I) sulfate	Ag_2SO_4	1.20×10^{-5}
Silver(I) sulfide	Ag_2S	6.3×10^{-50}
Silver(I) sulfite	Ag_2SO_3	1.50×10^{-14}
Silver(I) thiocyanate	$AgSCN$	1.03×10^{-12}
Strontium arsenate	$Sr_3(AsO_4)_2$	4.29×10^{-19}
Strontium carbonate	$SrCO_3$	5.60×10^{-10}
Strontium fluoride	SrF_2	4.33×10^{-9}
Strontium iodate	$Sr(IO_3)_2$	1.14×10^{-7}
Strontium sulfate	$SrSO_4$	3.44×10^{-7}
Thallium(I) bromate	$TlBrO_3$	1.10×10^{-4}
Thallium(I) bromide	$TlBr$	3.71×10^{-6}
Thallium(I) chloride	$TlCl$	1.86×10^{-4}
Thallium(I) chromate	Tl_2CrO_4	8.67×10^{-13}
Thallium(I) iodate	$TlIO_3$	3.12×10^{-6}
Thallium(I) iodide	TlI	5.54×10^{-8}

Compound Name	Compound Formula	K_{sp}
Thallium(I) thiocyanate	TlSCN	1.57×10^{-4}
Thallium(III) hydroxide	$Tl(OH)_3$	1.68×10^{-44}
Tin(II) hydroxide	$Sn(OH)_2$	5.45×10^{-27}
Tin(II) sulfide	SnS	1.0×10^{-25}
Yttrium carbonate	$Y_2(CO_3)_3$	1.03×10^{-31}
Yttrium fluoride	YF_3	8.62×10^{-21}
Yttrium hydroxide	$Y(OH)_3$	1.00×10^{-22}
Yttrium iodate	$Y(IO_3)_3$	1.12×10^{-10}
Zinc arsenate	$Zn_3(AsO_4)_2$	2.8×10^{-28}
Zinc carbonate	$ZnCO_3$	1.46×10^{-10}
Zinc fluoride	ZnF_2	3.04×10^{-2}
Zinc hydroxide	$Zn(OH)_2$	3×10^{-17}
Zinc selenide	ZnSe	3.6×10^{-26}
Zinc sulfide (wurtzite)	ZnS	1.6×10^{-24}
Zinc sulfide (sphalerite)	ZnS	2.5×10^{-22}

Source of data: *CRC Handbook of Chemistry and Physics*, 84th Edition (2004); sulfide data from *Lange's Handbook of Chemistry*, 15th Edition (1999).

Chapter 27

Appendix C: Dissociation Constants and pK_a Values for Acids at 25°C

Name	Formula	K_{a1}	pK_{a1}	K_{a2}	pK_{a2}	K_{a3}	pK_{a3}	K_{a4}	pK_{a4}
Acetic acid	CH_3CO_2H	1.75×10^{-5}	4.756						
Arsenic acid	H_3AsO_4	5.5×10^{-3}	2.26	1.7×10^{-7}	6.76	5.1×10^{-12}	11.29		
Benzoic acid	$C_6H_5CO_2H$	6.25×10^{-5}	4.204						
Boric acid	H_3BO_3	5.4×10^{-10}*	9.27*	>1×10^{-14}*	>14*				
Bromoacetic acid	CH_2BrCO_2H	1.3×10^{-3}	2.90						
Carbonic acid	H_2CO_3	4.5×10^{-7}	6.35	4.7×10^{-11}	10.3				

Name	Formula	K_{a1}	pK_{a1}	K_{a2}	pK_{a2}	K_{a3}	pK_{a3}	K_{a4}	pK_{a4}
					3				
Chloroacetic acid	CH_2ClCO_2H	1.3×10^{-3}	2.87						
Chlorous acid	$HClO_2$	1.1×10^{-2}	1.94						
Chromic acid	H_2CrO_4	1.8×10^{-1}	0.74	3.2×10^{-7}	6.49				
Citric acid	$C_6H_8O_7$	7.4×10^{-4}	3.13	1.7×10^{-5}	4.76	4.0×10^{-7}	6.40		
Cyanic acid	HCNO	3.5×10^{-4}	3.46						
Dichloroacetic acid	$CHCl_2CO_2H$	4.5×10^{-2}	1.35						
Fluoroacetic acid	CH_2FCO_2H	2.6×10^{-3}	2.59						
Formic acid	CH_2O_2	1.8×10^{-4}	3.75						
Hydrazoic acid	HN_3	2.5×10^{-5}	4.6						
Hydrocyanic acid	HCN	6.2×10^{-10}	9.21						
Hydrofluoric acid	HF	6.3×10^{-4}	3.20						
Hydrogen selenide	H_2Se	1.3×10^{-4}	3.89	1.0×10^{-11}	11.0				
Hydrogen sulfide	H_2S	8.9×10^{-8}	7.05	1×10^{-19}	19				
Hydrogen telluride	H_2Te	2.5×10^{-3}‡	2.6‡	1×10^{-11}	11				
Hypobromous acid	HBrO	2.8×10^{-9}	8.55						
Hypochlorous acid	HClO	4.0×10^{-8}	7.40						
Hypoiodous acid	HIO	3.2×10^{-11}	10.5						
Iodic acid	HIO_3	1.7×10^{-1}	0.78						
Iodoacetic acid	CH_2ICO_2H	6.6×10^{-4}	3.18						
Nitrous acid	HNO_2	5.6×10^{-4}	3.25						
Oxalic acid	$C_2H_2O_4$	5.6×10^{-2}	1.25	1.5×10^{-4}	3.81				
Periodic acid	HIO_4	2.3×10^{-2}	1.64						

Name	Formula	K_{a1}	pK_{a1}	K_{a2}	pK_{a2}	K_{a3}	pK_{a3}	K_{a4}	pK_{a4}
Phenol	C_6H_5OH	1.0×10^{-10}	9.99						
Phosphoric acid	H_3PO_4	6.9×10^{-3}	2.16	6.2×10^{-8}	7.21	4.8×10^{-13}	12.32		
Phosphorous acid	H_3PO_3	5.0×10^{-2}*	1.3*	2.0×10^{-7}*	6.70*				
Pyrophosphoric acid	$H_4P_2O_7$	1.2×10^{-1}	0.91	7.9×10^{-3}	2.10	2.0×10^{-7}	6.70	4.8×10^{-10}	9.32
Resorcinol	$C_6H_4(OH)_2$	4.8×10^{-10}	9.32	7.9×10^{-12}	11.1				
Selenic acid	H_2SeO_4	Strong	Strong	2.0×10^{-2}	1.7				
Selenious acid	H_2SeO_3	2.4×10^{-3}	2.62	4.8×10^{-9}	8.32				
Sulfuric acid	H_2SO_4	Strong	Strong	1.0×10^{-2}	1.99				
Sulfurous acid	H_2SO_3	1.4×10^{-2}	1.85	6.3×10^{-8}	7.2				
meso-Tartaric acid	$C_4H_6O_6$	6.8×10^{-4}	3.17	1.2×10^{-5}	4.91				
Telluric acid	H_2TeO_4	2.1×10^{-8}‡	7.68‡	1.0×10^{-11}‡	11.0‡				
Tellurous acid	H_2TeO_3	5.4×10^{-7}	6.27	3.7×10^{-9}	8.43				
Trichloroacetic acid	CCl_3CO_2H	2.2×10^{-1}	0.66						
Trifluoroacetic acid	CF_3CO_2H	3.0×10^{-1}	0.52						
*** Measured at 20°C, not 25°C.**									
‡ Measured at 18°C, not 25°C.									

Source of data: *CRC Handbook of Chemistry and Physics*, 84th Edition (2004).

Chapter 27

Appendix C: Dissociation Constants and pK_a Values for Acids at 25°C

Name	Formula	K_{a1}	pK_{a1}	K_{a2}	pK_{a2}	K_{a3}	pK_{a3}	K_{a4}	pK_{a4}
Acetic acid	CH_3CO_2H	1.75×10^{-5}	4.756						
Arsenic acid	H_3AsO_4	5.5×10^{-3}	2.26	1.7×10^{-7}	6.76	5.1×10^{-12}	11.29		
Benzoic acid	$C_6H_5CO_2H$	6.25×10^{-5}	4.204						
Boric acid	H_3BO_3	5.4×10^{-10}*	9.27*	$>1 \times 10^{-14}$*	>14*				
Bromoacetic acid	CH_2BrCO_2H	1.3×10^{-3}	2.90						
Carbonic acid	H_2CO_3	4.5×10^{-7}	6.35	4.7×10^{-11}	10.33				
Chloroacetic acid	CH_2ClCO_2H	1.3×10^{-3}	2.87						
Chlorous acid	$HClO_2$	1.1×10^{-2}	1.94						
Chromic acid	H_2CrO_4	1.8×10^{-1}	0.74	3.2×10^{-7}	6.49				
Citric acid	$C_6H_8O_7$	7.4×10^{-4}	3.13	1.7×10^{-5}	4.76	4.0×10^{-7}	6.40		
Cyanic acid	HCNO	3.5×10^{-4}	3.46						
Dichloroacetic acid	$CHCl_2CO_2H$	4.5×10^{-2}	1.35						
Fluoroacetic acid	CH_2FCO_2H	2.6×10^{-3}	2.59						
Formic acid	CH_2O_2	1.8×10^{-4}	3.75						
Hydrazoic acid	HN_3	2.5×10^{-5}	4.6						
Hydrocyanic acid	HCN	6.2×10^{-10}	9.21						
Hydrofluoric acid	HF	6.3×10^{-4}	3.20						
Hydrogen selenide	H_2Se	1.3×10^{-4}	3.89	1.0×10^{-11}	11.0				
Hydrogen sulfide	H_2S	8.9×10^{-8}	7.05	1×10^{-19}	19				
Hydrogen telluride	H_2Te	2.5×10^{-3}‡	2.6‡	1×10^{-11}	11				

Name	Formula	K_{a1}	pK_{a1}	K_{a2}	pK_{a2}	K_{a3}	pK_{a3}	K_{a4}	pK_{a4}
Hypobromous acid	HBrO	2.8×10^{-9}	8.55						
Hypochlorous acid	HClO	4.0×10^{-8}	7.40						
Hypoiodous acid	HIO	3.2×10^{-11}	10.5						
Iodic acid	HIO_3	1.7×10^{-1}	0.78						
Iodoacetic acid	CH_2ICO_2H	6.6×10^{-4}	3.18						
Nitrous acid	HNO_2	5.6×10^{-4}	3.25						
Oxalic acid	$C_2H_2O_4$	5.6×10^{-2}	1.25	1.5×10^{-4}	3.81				
Periodic acid	HIO_4	2.3×10^{-2}	1.64						
Phenol	C_6H_5OH	1.0×10^{-10}	9.99						
Phosphoric acid	H_3PO_4	6.9×10^{-3}	2.16	6.2×10^{-8}	7.21	4.8×10^{-13}	12.32		
Phosphorous acid	H_3PO_3	5.0×10^{-2}*	1.3*	2.0×10^{-7}*	6.70*				
Pyrophosphoric acid	$H_4P_2O_7$	1.2×10^{-1}	0.91	7.9×10^{-3}	2.10	2.0×10^{-7}	6.70	4.8×10^{-10}	9.32
Resorcinol	$C_6H_4(OH)_2$	4.8×10^{-10}	9.32	7.9×10^{-12}	11.1				
Selenic acid	H_2SeO_4	Strong	Strong	2.0×10^{-2}	1.7				
Selenious acid	H_2SeO_3	2.4×10^{-3}	2.62	4.8×10^{-9}	8.32				
Sulfuric acid	H_2SO_4	Strong	Strong	1.0×10^{-2}	1.99				
Sulfurous acid	H_2SO_3	1.4×10^{-2}	1.85	6.3×10^{-8}	7.2				
meso-Tartaric acid	$C_4H_6O_6$	6.8×10^{-4}	3.17	1.2×10^{-5}	4.91				
Telluric acid	H_2TeO_4	2.1×10^{-8}‡	7.68‡	1.0×10^{-11}‡	11.0‡				
Tellurous acid	H_2TeO_3	5.4×10^{-7}	6.27	3.7×10^{-9}	8.43				
Trichloroacetic acid	CCl_3CO_2H	2.2×10^{-1}	0.66						
Trifluoroacetic acid	CF_3CO_2H	3.0×10^{-1}	0.52						

*** Measured at 20°C, not 25°C.**

Name	Formula	K_{a1}	pK_{a1}	K_{a2}	pK_{a2}	K_{a3}	pK_{a3}	K_{a4}	pK_{a4}
‡ Measured at 18°C, not 25°C.									

Source of data: *CRC Handbook of Chemistry and Physics,* 84th Edition (2004).

Chapter 28

Appendix D: Dissociation Constants and pK_b Values for Bases at 25°C

Name	Formula	K_b	pK_b
Ammonia	NH_3	1.8×10^{-5}	4.75
Aniline	$C_6H_5NH_2$	7.4×10^{-10}	9.13
n-Butylamine	$C_4H_9NH_2$	4.0×10^{-4}	3.40
sec-Butylamine	$(CH_3)_2CHCH_2NH_2$	3.6×10^{-4}	3.44
tert-Butylamine	$(CH_3)_3CNH_2$	4.8×10^{-4}	3.32
Dimethylamine	$(CH_3)_2NH$	5.4×10^{-4}	3.27
Ethylamine	$C_2H_5NH_2$	4.5×10^{-4}	3.35
Hydrazine	N_2H_4	1.3×10^{-6}	5.9
Hydroxylamine	NH_2OH	8.7×10^{-9}	8.06
Methylamine	CH_3NH_2	4.6×10^{-4}	3.34
Propylamine	$C_3H_7NH_2$	3.5×10^{-4}	3.46
Pyridine	C_5H_5N	1.7×10^{-9}	8.77
Trimethylamine	$(CH_3)_3N$	6.3×10^{-5}	4.20

Source of data: *CRC Handbook of Chemistry and Physics*, 84th Edition (2004).

Chapter 29

Appendix E: Standard Reduction Potentials at 25°C

Half-Reaction	E° (V)
$Ac^{3+} + 3e^- \rightarrow Ac$	−2.20
$Ag^+ + e^- \rightarrow Ag$	0.7996
$AgBr + e^- \rightarrow Ag + Br^-$	0.07133
$AgCl + e^- \rightarrow Ag + Cl^-$	0.22233
$Ag_2CrO_4 + 2e^- \rightarrow 2Ag + CrO_4^{2-}$	0.4470
$AgI + e^- \rightarrow Ag + I^-$	−0.15224
$Ag_2S + 2e^- \rightarrow 2Ag + S^{2-}$	−0.691
$Ag_2S + 2H^+ + 2e^- \rightarrow 2Ag + H_2S$	−0.0366
$AgSCN + e^- \rightarrow Ag + SCN^-$	0.08951
$Al^{3+} + 3e^- \rightarrow Al$	−1.662
$Al(OH)_4^- + 3e^- \rightarrow Al + 4OH^-$	−2.328
$Am^{3+} + 3e^- \rightarrow Am$	−2.048
$As + 3H^+ + 3e^- \rightarrow AsH_3$	−0.608
$H_3AsO_4 + 2H^+ + 2e^- \rightarrow HAsO_2 + 2H_2O$	0.560
$Au^+ + e^- \rightarrow Au$	1.692
$Au^{3+} + 3e^- \rightarrow Au$	1.498
$H_3BO_3 + 3H^+ + 3e^- \rightarrow B + 3H_2O$	−0.8698
$Ba^{2+} + 2e^- \rightarrow Ba$	−2.912
$Be^{2+} + 2e^- \rightarrow Be$	−1.847
$Bi^{3+} + 3e^- \rightarrow Bi$	0.308
$BiO^+ + 2H^+ + 3e^- \rightarrow Bi + H_2O$	0.320
$Br_2(aq) + 2e^- \rightarrow 2Br^-$	1.0873
$Br_2(l) + 2e^- \rightarrow 2Br^-$	1.066
$BrO_3^- + 6H^+ + 5e^- \rightarrow 12Br_2 + 3H_2O$	1.482
$BrO_3^- + 6H^+ + 6e^- \rightarrow Br^- + 3H_2O$	1.423

Half-Reaction	E° (V)
$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H$	−0.199
$Ca^{2+} + 2e^- \rightarrow Ca$	−2.868
$Ca(OH)_2 + 2e^- \rightarrow Ca + 2OH^-$	−3.02
$Cd^{2+} + 2e^- \rightarrow Cd$	−0.4030
$CdSO_4 + 2e^- \rightarrow Cd + SO_4^{2-}$	−0.246
$Cd(OH)_4^{2-} + 2e^- \rightarrow Cd + 4OH^-$	−0.658
$Ce^{3+} + 3e^- \rightarrow Ce$	−2.336
$Ce^{4-} + e^- \rightarrow Ce^{3+}$	1.72
$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	1.35827
$HClO + H^+ + e^- \rightarrow 12Cl_2 + H_2C$	1.611
$HClO + H^+ + 2e^- \rightarrow Cl^- + H_2O$	1.482
$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$	0.81
$ClO_3^- + 6H^+ + 5e^- \rightarrow 12Cl_2 + 3H_2O$	1.47
$ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O$	1.451
$ClO_4^- + 8H^+ + 7e^- \rightarrow 12Cl_2 + 4H_2O$	1.39
$ClO_4^- + 8H^+ + 8e^- \rightarrow Cl^- + 4H_2O$	1.389
$Co^{2+} + 2e^- \rightarrow Co$	−0.28
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.92
$Cr^{2+} + 2e^- \rightarrow Cr$	−0.913
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.407
$Cr^{3+} + 3e^- \rightarrow Cr$	−0.744
$Cr_2O_7^- + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.232
$CrO_4^{2-} + 4H_2O + 3e^- \rightarrow Cr(OH)_3 + 5OH^-$	−0.13
$Cs^+ + e^- \rightarrow Cs$	−3.026
$Cu^+ + e^- \rightarrow Cu$	0.521
$Cu^{2+} + e^- \rightarrow Cu^+$	0.153

Half-Reaction	E° (V)
$Cu^{2+} + 2e^- \rightarrow Cu$	0.3419
$CuI_2^- + e^- \rightarrow Cu + 2I^-$	0.00
$Cu_2O + H_2O + 2e^- \rightarrow 2Cu + 2OH^-$	−0.360
$Dy^{3+} + 3e^- \rightarrow Dy$	−2.295
$Er^{3+} + 3e^- \rightarrow Er$	−2.331
$Es^{3+} + 3e^- \rightarrow Es$	−1.91
$Eu^{2+} + 2e^- \rightarrow Eu$	−2.812
$Eu^{3+} + 3e^- \rightarrow Eu$	−1.991
$F_2 + 2e^- \rightarrow 2F^-$	2.866
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.447
$Fe^{3+} + 3e^- \rightarrow Fe$	−0.037
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.771
$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$	0.358
$Fe(OH)_3 + e^- \rightarrow Fe(OH)_2 + OH^-$	−0.56
$Fm^{3+} + 3e^- \rightarrow Fm$	−1.89
$Fm^{2+} + 2e^- \rightarrow Fm$	−2.30
$Ga^{3+} + 3e^- \rightarrow Ga$	−0.549
$Gd^{3+} + 3e^- \rightarrow Gd$	−2.279
$Ge^{2+} + 2e^- \rightarrow Ge$	0.24
$Ge^{4+} + 4e^- \rightarrow Ge$	0.124
$2H^+ + 2e^- \rightarrow H_2$	0.00000
$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.8277
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.776
$Hf^{4+} + 4e^- \rightarrow Hf$	−1.55
$Hg^{2+} + 2e^- \rightarrow Hg$	0.851
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.920
$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.26808

Half-Reaction	E° (V)
$Ho^{2+} + 2e^- \rightarrow Ho$	−2.1
$Ho^{3+} + 3e^- \rightarrow Ho$	−2.33
$I_2 + 2e^- \rightarrow 2I^-$	0.5355
$I_3^- + 2e^- \rightarrow 3I^-$	0.536
$2IO_3^- + 12H^+ + 10e^- \rightarrow I_2 + 6H_2O$	1.195
$IO_3^- + 6H^+ + 6e^- \rightarrow I^- + 3H_2O$	1.085
$In^+ + e^- \rightarrow In$	−0.14
$In^{3+} + 2e^- \rightarrow In^+$	−0.443
$In^{3+} + 3e^- \rightarrow In$	−0.3382
$Ir^{3+} + 3e^- \rightarrow Ir$	1.156
$K^+ + e^- \rightarrow K$	−2.931
$La^{3+} + 3e^- \rightarrow La$	−2.379
$Li^+ + e^- \rightarrow Li$	−3.0401
$Lr^{3+} + 3e^- \rightarrow Lr$	−1.96
$Lu^{3+} + 3e^- \rightarrow Lu$	−2.28
$Md^{3+} + 3e^- \rightarrow Md$	−1.65
$Md^{2+} + 2e^- \rightarrow Md$	−2.40
$Mg^{2+} + 2e^- \rightarrow Mg$	−2.372
$Mn^{2+} + 2e^- \rightarrow Mn$	−1.185
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.224
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.507
$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$	0.595
$Mo^{3+} + 3e^- \rightarrow Mo$	−0.200
$N_2 + 2H_2O + 6H^+ + 6e^- \rightarrow 2NH_4OH$	0.092
$HNO_2 + H^+ + e^- \rightarrow NO + H_2O$	0.983
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.957
$Na^+ + e^- \rightarrow Na$	−2.71
$Nb^{3+} + 3e^- \rightarrow Nb$	−1.099

Half-Reaction	E° (V)
$Nd^{3+} + 3e^- \rightarrow Nd$	−2.323
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.257
$No^{3+} + 3e^- \rightarrow No$	−1.20
$No^{2+} + 2e^- \rightarrow No$	−2.50
$Np^{3+} + 3e^- \rightarrow Np$	−1.856
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.695
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.229
$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$	−0.146
$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	2.076
$OsO_4 + 8H^+ + 8e^- \rightarrow Os + 4H_2O$	0.838
$P + 3H_2O + 3e^- \rightarrow PH_3(g) + 3OH^-$	−0.87
$PO_4^{3-} + 2H_2O + 2e^- \rightarrow HPO_3^{2-} + 3OH^-$	−1.05
$Pa^{3+} + 3e^- \rightarrow Pa$	−1.34
$Pa^{4+} + 4e^- \rightarrow Pa$	−1.49
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.1262
$PbO + H_2O + 2e^- \rightarrow Pb + 2OH^-$	−0.580
$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.6913
$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.3588
$Pd^{2+} + 2e^- \rightarrow Pd$	0.951
$Pm^{3+} + 3e^- \rightarrow Pm$	−2.30
$Po^{4+} + 4e^- \rightarrow Po$	0.76
$Pr^{3+} + 3e^- \rightarrow Pr$	−2.353
$Pt^{2+} + 2e^- \rightarrow Pt$	1.18
$[PtCl_4]^{2-} + 2e^- \rightarrow Pt + 4Cl^-$	0.755
$Pu^{3+} + 3e^- \rightarrow Pu$	−2.031
$Ra^{2+} + 2e^- \rightarrow Ra$	−2.8
$Rb^+ + e^- \rightarrow Rb$	−2.98
$Re^{3+} + 3e^- \rightarrow Re$	0.300

Half-Reaction	E° (V)
$Rh^{3+} + 3e^- \rightarrow Rh$	0.758
$Ru^{3+} + e^- \rightarrow Ru^{2+}$	0.2487
$S + 2e^- \rightarrow S^{2-}$	−0.47627
$S + 2H^+ + 2e^- \rightarrow H_2S(aq)$	0.142
$2S + 2e^- \rightarrow S_2^{2-}$	−0.42836
$H_2SO_3 + 4H^+ + 4e^- \rightarrow S + 3H_2O$	0.449
$SO_4^{2-} + H_2O + 2e^- \rightarrow SO_3^{2-} + 2OH^-$	−0.93
$Sb + 3H^+ + 3e^- \rightarrow SbH_3$	−0.510
$Sc^{3+} + 3e^- \rightarrow Sc$	−2.077
$Se + 2e^- \rightarrow Se^{2-}$	−0.924
$Se + 2H^+ + 2e^- \rightarrow H_2Se$	−0.082
$SiF_6^{2-} + 4e^- \rightarrow Si + 6F^-$	−1.24
$Sm^{3+} + 3e^- \rightarrow Sm$	−2.304
$Sn^{2+} + 2e^- \rightarrow Sn$	−0.1375
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	0.151
$Sr^{2+} + 2e^- \rightarrow Sr$	−2.899
$Ta^{3+} + 3e^- \rightarrow Ta$	−0.6
$TcO_4^- + 4H^+ + 3e^- \rightarrow TcO_2 + 2H_2O$	0.782
$TcO_4^- + 8H^+ + 7e^- \rightarrow Tc + 4H_2O$	0.472
$Tb^{3+} + 3e^- \rightarrow Tb$	−2.28
$Te + 2e^- \rightarrow Te^{2-}$	−1.143
$Te^{4+} + 4e^- \rightarrow Te$	0.568
$Th^{4+} + 4e^- \rightarrow Th$	−1.899
$Ti^{2+} + 2e^- \rightarrow Ti$	−1.630
$Tl^+ + e^- \rightarrow Tl$	−0.336
$Tl^{3+} + 2e^- \rightarrow Tl^+$	1.252
$Tl^{3+} + 3e^- \rightarrow Tl$	0.741
$Tm^{3+} + 3e^- \rightarrow Tm$	−2.319

Half-Reaction	E° (V)
$U^{3+} + 3e^- \rightarrow U$	−1.798
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	0.991
$V_2O_5 + 6H^+ + 2e^- \rightarrow 2VO^{2+} + 3H_2O$	0.957
$W_2O_5 + 2H^+ + 2e^- \rightarrow 2WO_2 + H_2O$	−0.031
$XeO_3 + 6H^+ + 6e^- \rightarrow Xe + 3H_2O$	2.10
$Y^{3+} + 3e^- \rightarrow Y$	−2.372
$Yb^{3+} + 3e^- \rightarrow Yb$	−2.19
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.7618
$Zn(OH)_4^{2-} + 2e^- \rightarrow Zn + 4OH^-$	−1.199
$Zn(OH)_2 + 2e^- \rightarrow Zn + 2OH^-$	−1.249
$ZrO_2 + 4H^+ + 4e^- \rightarrow Zr + 2H_2O$	−1.553
$Zr^{4+} + 4e^- \rightarrow Zr$	−1.45

Source of data: CRC Handbook of Chemistry and Physics, 84th Edition (2004).

Chapter 30

Appendix F: Properties of Water

Density: 0.99984 g/cm^3 at 0°C
0.99970 g/cm^3 at 10°C
0.99821 g/cm^3 at 20°C
0.98803 g/cm^3 at 50°C
0.95840 g/cm^3 at 100°C
Enthalpy (heat) of vaporization: 45.054 kJ/mol at 0°C
43.990 kJ/mol at 25°C
42.482 kJ/mol at 60°C
40.657 kJ/mol at 100°C
Surface tension: 74.23 J/m^2 at 10°C
71.99 J/m^2 at 25°C
67.94 J/m^2 at 50°C
58.91 J/m^2 at 100°C
Viscosity: 1.793 mPa · s at 0°C
0.890 mPa_s at 25°C
0.547 mPa_s at 50°C
0.282 mPa_s at 100°C
Ion-product constant,*K*w: 1.15 × 10^{-15} at 0°C
1.01 × 10^{-14} at 25°C
5.31 × 10^{-14} at 50°C
5.43 × 10^{-13} at 100°C
Specific heat (*C*s): 4.2176 J/(g-°C) at 0°C
4.1818 J/(g-°C) at 20°C
4.1806 J/(g-°C) at 50°C
4.2159 J/(g-°C) at 100°C

Vapor pressure of water (kP$_a$)

T(°C)	P(kP$_a$)	T(°C)	P(kP$_a$)	T(°C)	P(kP$_a$)	T(°C)	P(kP$_a$)
0	0.61129	30	4.2455	60	19.932	90	70.117
5	0.87260	35	5.6267	65	25.022	95	84.529

10	1.2281	40	7.3814	70	31.176	100	101.32
15	1.7056	45	9.5898	75	38.563	105	120.79
20	2.3388	50	12.344	80	47.373	110	143.24
25	3.1690	55	15.752	85	57.815	115	169.02

Vapor pressure of water (mmHg)

T(°C)	P(mmHg)	T(°C)	P(mmHg)	T(°C)	P(mmHg)	T(°C)	P(mmHg)
0	4.585	30	31.844	60	149.50	90	525.91
5	6.545	35	42.203	65	187.68	95	634.01
10	9.211	40	55.364	70	233.84	100	759.95
15	12.793	45	71.929	75	289.24	105	905.99
20	17.542	50	92.59	80	355.32	110	1074.38
25	23.769	55	118.15	85	433.64	115	1267.74

Source of data: *CRC Handbook of Chemistry and Physics*, 84th Edition (2004).

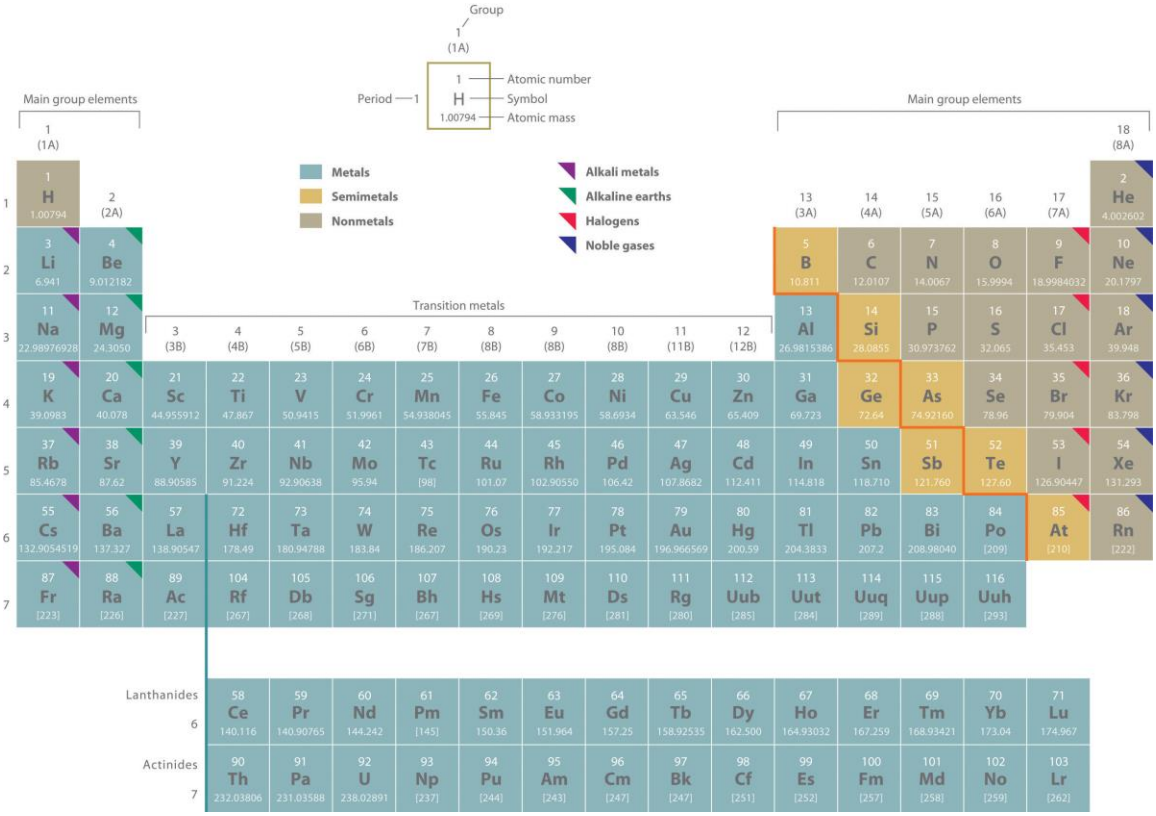
Chapter 31

Appendix G: Physical Constants and Conversion Factors

Selected Physical Constants	
Atomic mass unit	1 amu = $1.6605389 \times 10^{-24}$ g
	1 g = 6.022142×10^{23} amu
Avogadro's number	$N = 6.022142 \times 10^{23}$/mol
Boltzmann's constant	$k = 1.380651 \times 10^{-23}$ J/K
Charge on electron	$e = 1.6021765 \times 10^{-19}$ C
Faraday's constant	$F = 9.6485338 \times 10^{4}$ C/mol
Gas constant	$R = 0.0820575$ (L atm)/(mol K)
	= 8.31447 J/(mol K)
Mass of electron	$m_e = 5.485799 \times 10^{-4}$ amu
	$= 9.109383 \times 10^{-28}$ g
Mass of neutron	$m_n = 1.0086649$ amu
	$= 1.6749273 \times 10^{-24}$ g
Mass of proton	$m_p = 1.0072765$ amu
	$= 1.6726217 \times 10^{-24}$ g
Pi	$\pi = 3.1415927$
Planck's constant	$h = 6.626069 \times 10^{-34}$ J s
Speed of light (in vacuum)	$c = 2.99792458 \times 10^{8}$ m/s (exact)
Useful Conversion Factors and Relationships	
Length	**Energy (derived)**
Si unit: meter (m)	*Si unit: joule (J)*
Mass	**Pressure (derived)**
SI unit: kilogram (kg)	*SI unit: pascal (Pa)*
Temperature	**Volume (derived)**
Si unit: kelvin (K)	*SI unit: cubic meter (m^3)*

Chapter 32

Appendix H: Periodic Table of Elements



Two systems for numbering periodic groups are shown: 1–18 is the system currently recommended by the Inernational Union of Pure and Applied Chemistry (IUPAC); an older U.S. system, in which letters designate main group elements (A) and transition elements (B), is given parentheses.

An atomic mass in brackets indicates the mass of the longest-lived isotope of an element having no stable isotopes. Elements with atomic numbers 114 (ununquadium, 289 amu) and 116 (ununhexium, 293 amu) have been recognized by the International Union of Pure and Applied Chemistry (IUPAC). The collaborating scientists from the Joint Institute for Nuclear Research in Dubna, Russia, and Lawrence Livermore National Laboratory in California have been invited to propose names for the new elements. See http://iupac.org/publications/pac/asap/PAC-REP-10-05-01

List of Elements			
Name	**Symbol**	**Atomic Number**	**Atomic Mass**
Actinium	Ac	89	[227]*
Aluminum	Al	13	26.9815386(8)

List of Elements			
Name	Symbol	Atomic Number	Atomic Mass
Americium	Am	95	[243]*
Antimony	Sb	51	121.760(1)
Argon	Ar	18	39.948(1)
Arsenic	As	33	74.92160(2)
Astatine	At	85	[210]*
Barium	Ba	56	137.327(7)
Berkelium	Bk	97	[247]*
Beryllium	Be	4	9.012182(3)
Bismuth	Bi	83	208.98040(1)
Bohrium	Bh	107	[267]*
Boron	B	5	10.811(7)
Bromine	Br	35	79.904(1)
Cadmium	Cd	48	112.411(8)
Calcium	Ca	20	40.078(4)
Californium	Cf	98	[251]*
Carbon	C	6	12.0107(8)
Cerium	Ce	58	140.116(1)
Cesium	Cs	55	132.9054519(2)
Chlorine	Cl	17	35.453(2)
Chromium	Cr	24	51.9961(6)
Cobalt	Co	27	58.933195(5)
Copernicium†	Cn	112	[285]*
Copper	Cu	29	63.546(3)
Curium	Cm	96	[247]*
Darmstadtium	Ds	110	[281]*
Dubnium	Db	105	[268]*
Dysprosium	Dy	66	162.500(1)
Einsteinium	Es	99	[252]*
Erbium	Er	68	167.259(3)

List of Elements			
Name	Symbol	Atomic Number	Atomic Mass
Europium	Eu	63	151.964(1)
Fermium	Fm	100	[257]*
Fluorine	F	9	18.9984032(5)
Francium	Fr	87	[223]*
Gadolinium	Gd	64	157.25(3)
Gallium	Ga	31	69.723(1)
Germanium	Ge	32	72.64(1)
Gold	Au	79	196.966569(4)
Hafnium	Hf	72	178.49(2)
Hassium	Hs	108	[269]*
Helium	He	2	4.002602(2)
Holmium	Ho	67	164.93032(2)
Hydrogen	H	1	1.00794(7)
Indium	In	49	114.818(3)
Iodine	I	53	126.90447(3)
Iridium	Ir	77	192.217(3)
Iron	Fe	26	55.845(2)
Krypton	Kr	36	83.798(2)
Lanthanum	La	57	138.90547(7)
Lawrencium	Lr	103	[262]*
Lead	Pb	82	207.2(1)
Lithium	Li	3	6.941(2)
Lutetium	Lu	71	174.967(1)
Magnesium	Mg	12	24.3050(6)
Manganese	Mn	25	54.938045(5)
Meitnerium	Mt	109	[276]*
Mendelevium	Md	101	[258]*
Mercury	Hg	80	200.59(2)
Molybdenum	Mo	42	95.94(2)

List of Elements			
Name	**Symbol**	**Atomic Number**	**Atomic Mass**
Neodymium	Nd	60	144.242(3)
Neon	Ne	10	20.1797(6)
Neptunium	Np	93	[237]*
Nickel	Ni	28	58.6934(2)
Niobium	Nb	41	92.90638(2)
Nitrogen	N	7	14.0067(2)
Nobelium	No	102	[259]*
Osmium	Os	76	190.23(3)
Oxygen	O	8	15.9994(3)
Palladium	Pd	46	106.42(1)
Phosphorus	P	15	30.973762(2)
Platinum	Pt	78	195.084(9)
Plutonium	Pu	94	[244]*
Polonium	Po	84	[209]*
Potassium	K	19	39.0983(1)
Praseodymium	Pr	59	140.90765(2)
Promethium	Pm	61	[145]*
Protactinium	Pa	91	231.03588(2)*
Radium	Ra	88	[226]*
Radon	Rn	86	[222]*
Rhenium	Re	75	186.207(1)
Rhodium	Rh	45	102.90550(2)
Roentgenium	Rg	111	[280]*
Rubidium	Rb	37	85.4678(3)
Ruthenium	Ru	44	101.07(2)
Rutherfordium	Rf	104	[267]*
Samarium	Sm	62	150.36(2)
Scandium	Sc	21	44.955912(6)
Seaborgium	Sg	106	[271]*

List of Elements			
Name	**Symbol**	**Atomic Number**	**Atomic Mass**
Selenium	Se	34	78.96(3)
Silicon	Si	14	28.0855(3)
Silver	Ag	47	107.8682(2)
Sodium	Na	11	22.98976928(2)
Strontium	Sr	38	87.62(1)
Sulfur	S	16	32.065(5)
Tantalum	Ta	73	180.94788(2)
Technetium	Tc	43	[98]*
Tellurium	Te	52	127.60(3)
Terbium	Tb	65	158.92535(2)
Thallium	Tl	81	204.3833(2)
Thorium	Th	90	232.03806(2)*
Thulium	Tm	69	168.93421(2)
Tin	Sn	50	118.710(7)
Titanium	Ti	22	47.867(1)
Tungsten	W	74	183.84(1)
Ununhexium	Uuh	116	[293]*
Ununpentium	Uup	115	[288]*
Ununquadium	Uuq	114	[289]*
Ununtrium	Uut	113	[284]*
Uranium	U	92	238.02891(3)*
Vanadium	V	23	50.9415(1)
Xenon	Xe	54	131.293(6)
Ytterbium	Yb	70	173.04(3)
Yttrium	Y	39	88.90585(2)
Zinc	Zn	30	65.409(4)
Zirconium	Zr	40	91.224(2)

***Element has no stable isotope. A value enclosed in brackets, e.g. [209], indicates the mass number of the longest-lived isotope of the element. Three such elements (Th, Pa, and U), however, do have a characteristic terrestrial isotopic composition, and an atomic mass is given**

List of Elements			
Name	**Symbol**	**Atomic Number**	**Atomic Mass**
for them. An uncertainty in the last digit in the Atomic Mass column is shown by the number in parentheses; e.g., 1.00794(7) indicates ±0.00007.			
†Element 112 named shortly before the release of this text. Other periodic tables in this version of the text may refer to it as Ununbium (Uub).			

Source of data: Atomic weights of the elements 2001 (IUPAC Technical Report) as supplemented by the Table of Standard Atomic Weights 2005 (to be published in Pure and Applied Chemistry) on the IUPAC web site, and "Nuclear Data Sheets for A-266-294" (to be published in Nuclear Data Sheets) at http://www.nndc.bnl.gov/superheavy.pdf.

Chapter 33

Appendix I: Experimentally Measured Masses of Selected Isotopes

Isotope	Mass (amu)	Isotope	Mass (amu)	Isotope	Mass (amu)
^{1}H	1.007825	^{14}N	14.003074	^{208}Po	207.981246
^{2}H	2.014102	^{16}O	15.994915	^{210}Po	209.982874
^{3}H	3.016049	^{52}Cr	51.940508	^{222}Rn	222.017578
^{3}He	3.016029	^{56}Fe	55.934938	^{226}Ra	226.025410
^{4}He	4.002603	^{59}Co	58.933195	^{230}Th	230.033134
^{6}Li	6.015123	^{58}Ni	57.935343	^{234}Th	234.043601
^{7}Li	7.016005	^{60}Ni	59.930786	^{234}Pa	234.043308
^{9}Be	9.012182	^{90}Rb	89.914802	^{233}U	233.039635
^{10}B	10.012937	^{144}Cs	143.932077	^{234}U	234.040952
^{11}B	11.009305	^{206}Pb	205.974465	^{235}U	235.043930
^{12}C	12	^{207}Pb	206.975897	^{238}U	238.050788
^{13}C	13.003355	^{208}Pb	207.976652	^{239}Pu	239.052163
^{14}C	14.003242				

Data source: G. Audi, A. H. Wapstra, and C. Thibault, *The AME2003 atomic mass evaluation*.

This table is provided as a reference.

Isotope	Mass (amu)	Isotope	Mass (amu)
^{8}B	8.024607	^{209}Fr	208.99592
^{40}K	39.963998	^{210}Po	209.982874
^{52}Cr	51.940508	^{212}At	211.990745
^{58}Ni	57.935343	^{214}Pb	213.999797
^{59}Co	58.933195	^{214}Bi	213.998712
^{60}Co	59.933817	^{216}Fr	216.003198
^{60}Ni	59.930786	^{199}Pb	198.972917
^{90}Sr	89.907738	^{222}Rn	222.017578
^{92}Kr	91.926156	^{226}Ra	226.025410
^{141}Ba	140.914411	^{227}Ra	227.029178
^{143}Xe	142.935110	^{228}Ac	228.031021
^{167}Os	166.971550	^{230}Th	230.033134

Isotope	Mass (amu)	Isotope	Mass (amu)
^{171}Pt	170.981240	^{233}U	233.039635
^{194}Hg	193.965439	^{234}Th	234.043601
^{194}Tl	193.971200	^{234}Pa	234.043308
^{199}Pb	198.972917	^{233}U	233.039635
^{199}Bi	198.977672	^{234}U	234.040952
^{206}Pb	205.974465	^{235}U	235.043930
^{207}Pb	206.975897	^{238}Pa	238.054500
^{208}Pb	207.976652	^{238}U	238.050788
^{208}Bi	207.979742	^{239}Pu	239.052163
^{208}Po	207.981246	^{245}Pu	245.067747

Chapter 34
Art Credits

34.1 Molecular Models

We wish to thank the Cambridge Crystallographic Data Centre (CCDC) and the Fachinformationszentrum Karlsruhe (FIZ Karlsruhe) for allowing Imagineering Media Services (IMS) to access their databases of atomic coordinates for experimentally determined three-dimensional structures. CCDC's **Cambridge Structural Database (CSD)** is the world repository of small molecule crystal structures (distributed as part of the CSD System), and in FIZ Karlsruhe's **Inorganic Crystal Structure Database (ICSD)** is the world's largest inorganic crystal structure database. The coordinates of organic and organometallic compounds in CSD and inorganic and intermetallic compounds in ICSD were invaluable in ensuring the accuracy of the molecular models produced by IMS for this textbook. The authors, the publisher, and IMS gratefully acknowledge the assistance of both organizations. Any errors in the molecular models in this text are entirely the responsibility of the authors, the publisher, and IMS.

The CSD System: The Cambridge Structural Database: a quarter of a million crystal structures and rising. Allen, F.H., *Acta Cryst*. (2002), **B58,** 380–388. *ConQuest:* New Software for searching the Cambridge Structural Database and visualizing crystal structures. Bruno, I.J., Cole, J.C., Edgington, P.R., Kessler, M., Macrae, C.F., McCabe, P., Pearson, J., Taylor, R., *Acta Cryst*. (2002), **B58,** 389–397. *IsoStar:* IsoStar: A Library of Information about Nonbonded Interactions. Bruno, I.J., Cole, J.C., Lommerse, J.P.M., Rowland, R.S., Taylor, R., Verdonk, M., *Journal of Computer-Aided Molecular Design* (1997), **11-6,** 525–537.

The Inorganic Crystal Structure Database (ICSD) is produced and owned by Fachinformationszentrum Karlsruhe (FIZ Karlsruhe) and National Institute of Standards and Technology, an agency of the U.S. Commerce Department's Technology Administration (NIST).

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the world repository of small molecule crystal structures (distributed as part of the CSD System), and in FIZ Karlsruhe's **Inorganic Crystal Structure Database (ICSD)** is the world's largest inorganic crystal structure database. The coordinates of organic and organometallic compounds in CSD and inorganic and intermetallic compounds in ICSD were invaluable in ensuring the accuracy of the molecular models produced by IMS for this textbook. The authors, the publisher, and IMS gratefully acknowledge the assistance of both organizations. Any errors in the molecular models in this text are entirely the responsibility of the authors, the publisher, and IMS.

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