# THE MAJOR CLASSES OF CHEMICAL REACTIONS

**Figure: Precipitation up close.** Where aqueous sodium fluoride solution from the cylinder meets aqueous calcium chloride solution, $Ca^{2+}$ *(blue)* and $F^-$ *(yellow)* ions attract each other into particles of solid calcium fluoride. In this chapter, you'll see that precipitation is one of a remarkably small number of reaction classes that describes the great majority of chemical reactions.

The amazing variety that we see in nature is largely a consequence of the amazing variety of chemical reactions. Rapid chemical changes occur among gas molecules as sunlight bathes the atmosphere or lightning rips through a stormy sky. Oceans are gigantic containers in which aqueous reaction chemistry goes on unceasingly. In every cell of your body, thousands of reactions are taking place right now.

Of the millions of chemical reactions occurring in and around you, we have examined only a tiny fraction so far, and it would be impossible to examine them all. Fortunately, it isn't necessary to catalog every reaction, because when we survey even a small percentage of them, a few major reaction patterns emerge.

In this chapter, we examine the underlying nature of the three most common reaction processes. Since one of our main themes is aqueous reaction chemistry, we first investigate the crucial role water plays as a solvent for many reactions. With that as background, we focus on two of the major reaction processes—precipitation and acid-base—examining why they occur and describing the use of ionic equations to depict them. Next, we discuss the nature of the third process—oxidation-reduction—perhaps the most important of all. We classify several important types of oxidation-reduction reactions that include elemental substances as reactants or products. The chapter ends with an introductory look at the reversible nature of all chemical reactions.

## 4.1 THE ROLE OF WATER AS A SOLVENT

Many reactions take place in an aqueous environment, so our first step toward comprehending them is to understand how water acts as a solvent. The role a solvent plays in a reaction depends on its chemical nature. Some solvents play a passive role. They disperse the substances dissolved in them into individual molecules but do not interact with them in other ways. Water plays a much more active role. It interacts strongly with the reactants and, in some cases, even affects their bonds. Water is crucial to so many chemical and physical processes that we will discuss its properties frequently.
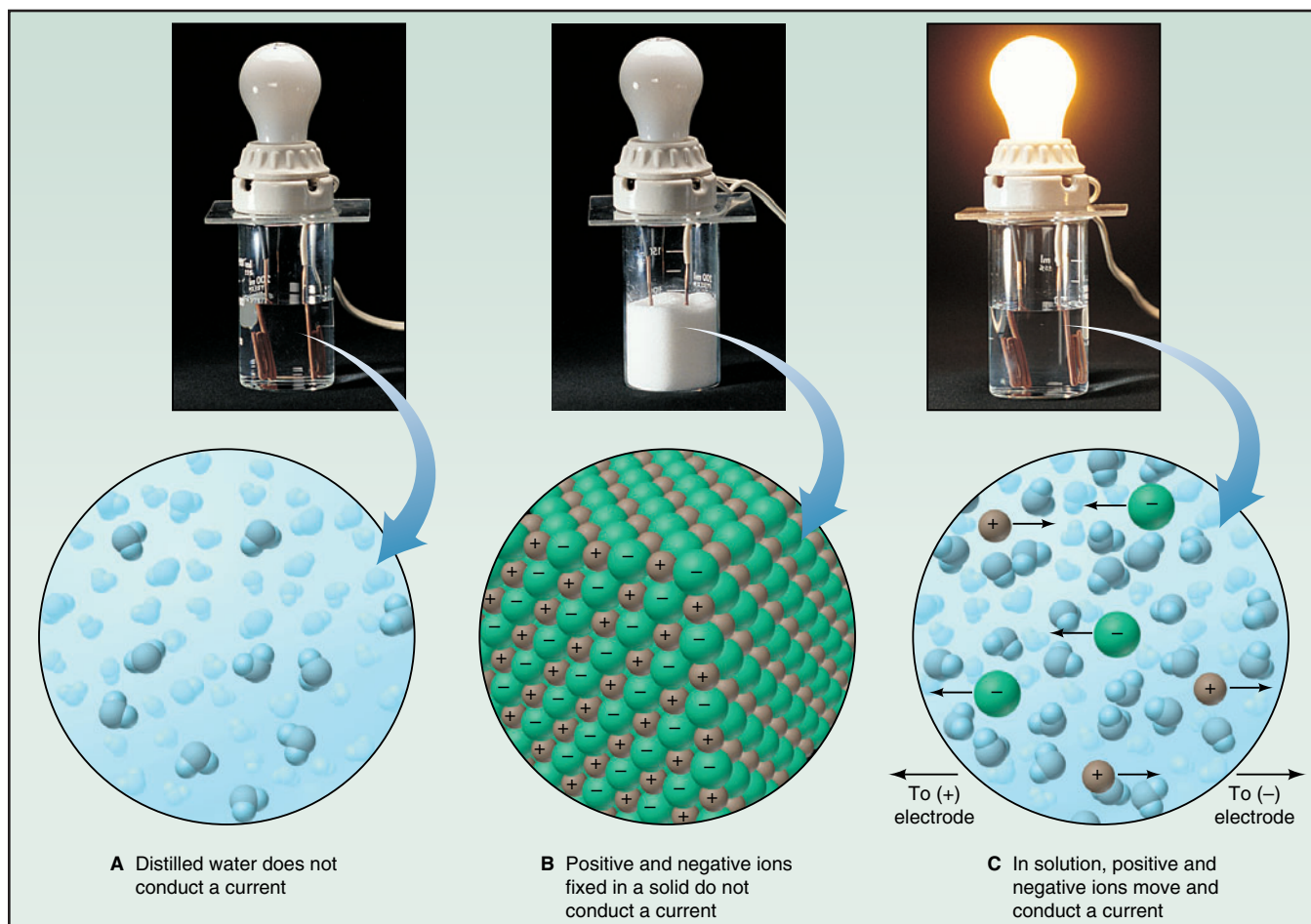
### The Solubility of Ionic Compounds

When water dissolves an ionic solid, such as potassium bromide (KBr), an important change occurs. Figure 4.1 shows this change with a simple apparatus that measures *electrical conductivity,* the flow of electric current. When the electrodes are immersed in pure water or pushed into solid KBr, no current flows. In the aqueous KBr solution, however, a significant current flows, as shown by the brightly lit bulb. The current flow in the solution implies the *movement of charged particles:* when KBr dissolves in water, the $K^+$ and $Br^-$ ions in the solid separate from each other (dissociate) and move toward the electrode whose charge is opposite the ion's charge. A substance that conducts a current when dissolved in water is an **electrolyte.** Soluble ionic compounds dissociate completely into ions and create a large current, so they are called *strong* electrolytes.

As the KBr dissolves, each ion becomes **solvated,** surrounded by solvent molecules. We express this dissociation into solvated ions in water as follows:

$$KBr(s) \xrightarrow{\text{H}_2\text{O}} K^+(aq) + Br^-(aq)$$

The "$H_2O$" above the arrow indicates that water is required but is not a reactant in the usual sense. When any water-soluble ionic compound dissolves, *the oppositely charged ions separate from each other, become surrounded by water molecules, and spread randomly throughout the solution*.

The formula of the compound tells us the number of moles of different ions that result when the compound dissolves. Thus, 1 mol of KBr dissociates into 2 mol of ions—1 mol of $K^+$ and 1 mol of $Br^-$.

**A** Distilled water does not conduct a current

**B** Positive and negative ions fixed in a solid do not conduct a current

**C** In solution, positive and negative ions move and conduct a current

**Figure 4.1** **The electrical conductivity of ionic solutions. A,** When electrodes connected to a power source are placed in distilled water, no current flows and the bulb is unlit. **B,** A solid ionic compound, such as KBr, conducts no current because the ions are bound tightly together. **C,** When KBr dissolves in $H_2O$, the ions separate and move through the solution toward the oppositely charged electrodes, thereby conducting a current.

**SAMPLE PROBLEM 4.1** Determining Moles of Ions in Aqueous Ionic Solutions

**Problem** How many moles of each ion are in the following solutions?
**(a)** 5.0 mol of ammonium sulfate dissolved in water
**(b)** 78.5 g of cesium bromide dissolved in water
**(c)** $7.42 \times 10^{22}$ formula units of copper(II) nitrate dissolved in water
**(d)** 35 mL of 0.84 $M$ zinc chloride
**Plan** We write an equation that shows the numbers of moles of ions released when 1 mol of compound dissolves. In **(a),** we multiply the moles of ions released by 5.0. In **(b),** we first convert grams to moles. In **(c),** we first convert formula units to moles. In **(d),** we first convert molarity and volume to moles.
**Solution (a)** $(NH_4)_2SO_4(s) \xrightarrow{H_2O} 2NH_4^+(aq) + SO_4^{2-}(aq)$
Remember that, in general, *polyatomic ions remain as intact units in solution.*
Calculating moles of $NH_4^+$ ions:

$$\text{Moles of } NH_4^+ = 5.0 \text{ mol } (NH_4)_2SO_4 \times \frac{2 \text{ mol } NH_4^+}{1 \text{ mol } (NH_4)_2SO_4} = \boxed{10. \text{ mol } NH_4^+}$$

$\boxed{5.0 \text{ mol of } SO_4^{2-}}$ is also present.

**(b)** $CsBr(s) \xrightarrow{H_2O} Cs^+(aq) + Br^-(aq)$
Converting from grams to moles:

$$\text{Moles of } CsBr = 78.5 \text{ g } CsBr \times \frac{1 \text{ mol } CsBr}{212.8 \text{ g } CsBr} = 0.369 \text{ mol } CsBr$$

Thus, $\boxed{0.369 \text{ mol of } Cs^+ \text{ and } 0.369 \text{ mol of } Br^-}$ are present.
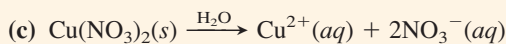
**(c)** $Cu(NO_3)_2(s) \xrightarrow{H_2O} Cu^{2+}(aq) + 2NO_3^-(aq)$
Converting from formula units to moles:

$$\text{Moles of } Cu(NO_3)_2 = 7.42 \times 10^{22} \text{ formula units } Cu(NO_3)_2$$

$$\times \frac{1 \text{ mol } Cu(NO_3)_2}{6.022 \times 10^{23} \text{ formula units } Cu(NO_3)_2}$$

$$= 0.123 \text{ mol } Cu(NO_3)_2$$

$$\text{Moles of } NO_3^- = 0.123 \text{ mol } Cu(NO_3)_2 \times \frac{2 \text{ mol } NO_3^-}{1 \text{ mol } Cu(NO_3)_2} = \boxed{0.246 \text{ mol } NO_3^-}$$

$\boxed{0.123 \text{ mol of } Cu^{2+}}$ is also present.
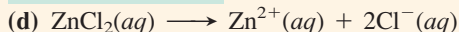
**(d)** $ZnCl_2(aq) \longrightarrow Zn^{2+}(aq) + 2Cl^-(aq)$
Converting from liters to moles:

$$\text{Moles of } ZnCl_2 = 35 \text{ mL} \times \frac{1 \text{ L}}{10^3 \text{ mL}} \times \frac{0.84 \text{ mol } ZnCl_2}{1 \text{ L}} = 2.9 \times 10^{-2} \text{ mol } ZnCl_2$$
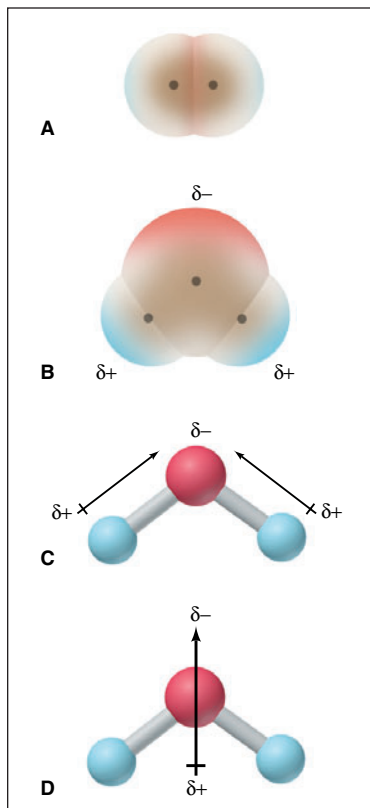
$$\text{Moles of } Cl^- = 2.9 \times 10^{-2} \text{ mol } ZnCl_2 \times \frac{2 \text{ mol } Cl^-}{1 \text{ mol } ZnCl_2} = \boxed{5.8 \times 10^{-2} \text{ mol } Cl^-}$$

$\boxed{2.9 \times 10^{-2} \text{ mol of } Zn^{2+}}$ is also present.

**Check** After you round off to check the math, see if the relative moles of ions are consistent with the formula. For instance, in (a), 10 mol $NH_4^+$/5.0 mol $SO_4^{2-}$ = 2 $NH_4^+$/1 $SO_4^{2-}$, or $(NH_4)_2SO_4$. In (d), 0.029 mol $Zn^{2+}$/0.058 mol $Cl^-$ = 1 $Zn^{2+}$/2 $Cl^-$, or $ZnCl_2$.

**FOLLOW-UP PROBLEM 4.1** How many moles of each ion are in each solution?
**(a)** 2 mol of potassium perchlorate dissolved in water
**(b)** 354 g of magnesium acetate dissolved in water
**(c)** $1.88 \times 10^{24}$ formula units of ammonium chromate dissolved in water
**(d)** 1.32 L of 0.55 *M* sodium bisulfate

## The Polar Nature of Water

Water separates ions in a process that greatly reduces the *electrostatic force* of attraction between them. To see how it does this, let's examine the water molecule closely. Water's power as an ionizing solvent results from two features of the water molecule: *the distribution of its bonding electrons* and *its overall shape*.

Recall from Section 2.7 that the electrons in a covalent bond are shared between the bonded atoms. In a covalent bond that exists between identical atoms (as in $H_2$, $Cl_2$, $O_2$, etc.), the sharing is equal. As Figure 4.2A shows, the shared electrons in $H_2$ are distributed equally, so no imbalance of charge appears. On the other hand, in covalent bonds between nonidentical atoms, the sharing is unequal: one atom attracts the electron pair more strongly than the other. For reasons discussed in Chapter 9, an O atom attracts electrons more strongly than an H atom. Therefore, in each of the O—H bonds of water, the electrons spend more time closer to the O (Figure 4.2B). This unequal distribution of the electron pair's negative charge creates partially charged "poles" at the ends of each O—H bond. The O end acts as a slightly negative pole (represented by the red shading and the $\delta-$), and the H end acts as a slightly positive pole (represented by the blue shading and the $\delta+$). In Figure 4.2C, the bond's polarity is also indicated by a *polar arrow* (the arrowhead points to the negative pole and the tail is crossed to make a "plus"). Partial charges, like the ones on the O and H atoms in water, are much less than full ionic charges. For instance, in an ionic compound like KBr, the electron has been *transferred* from the K atom to the Br atom and two ions exist. In a covalent compound like water, no ions exist; in each polar O—H bond, the electrons have just *shifted* their average position nearer to the O atom.

The water molecule also has a bent shape: the atoms in H—O—H form an angle, not a straight line. The combined effects of its bent shape and its polar bonds make water a **polar molecule.** As you can see in Figure 4.2D, the O portion of the molecule is the partially negative pole, and the region midway between the H atoms is the partially positive pole.



**Figure 4.2** **Electron distribution in molecules of H₂ and H₂O. A,** In H₂, the nuclei are identical, so they attract the electrons equally. Note how the central region of higher electron density (red) is balanced by the two outer regions of lower electron density (blue). **B,** In H₂O, the O nucleus attracts the shared electrons more strongly than the H nucleus, creating an uneven charge distribution in each bond. The partially negative O end is designated δ− and the partially positive H end is designated δ+. **C,** In this ball-and-stick model of H₂O, a polar arrow points to the negative end of each O—H bond. **D,** The two polar O—H bonds and the bent molecular shape give rise to the polar H₂O molecule, with the partially positive end located *between* the two H atoms.
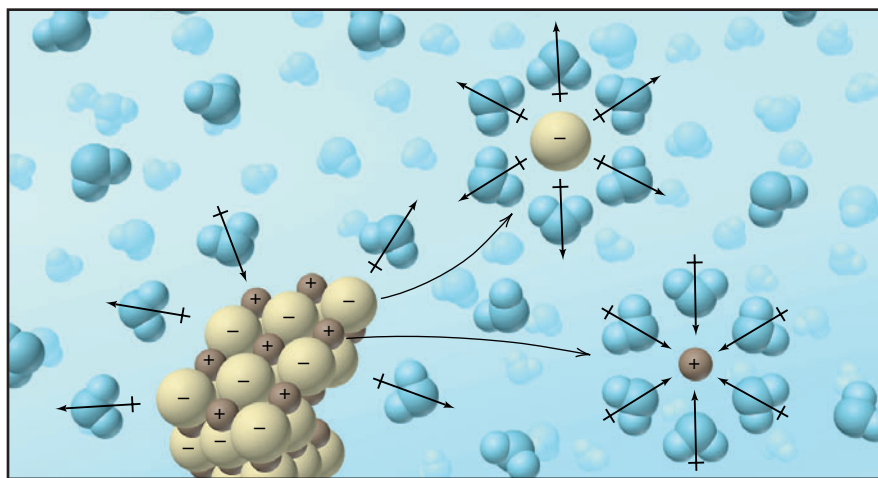
**Ionic Compounds in Water** Now imagine a granule of an ionic compound surrounded by bent, polar water molecules. They congregate near the orderly array of ions at the granule's surface; the negative ends of some water molecules are attracted to the cations, and the positive ends of others are attracted to the anions (Figure 4.3). An electrostatic "tug of war" occurs as the ions become partially solvated. The attraction between each ion and the water molecules gradually outweighs the attraction of the oppositely charged ions for each other. The ions become solvated as they separate from each other and move randomly throughout the solution. A similar scene occurs whenever an ionic compound dissolves in water. ●

Although many ionic compounds dissolve in water, many others do not. In such cases, the electrostatic attraction among ions in the compound is greater than the attraction between ions and water molecules, so the substance remains intact. Actually, these so-called insoluble substances *do* dissolve to a very small extent, usually several orders of magnitude less than so-called soluble substances. Compare, for example, the solubilities of NaCl (a "soluble" compound) and AgCl (an "insoluble" compound):

$$\text{Solubility of NaCl in H}_2\text{O at 20°C} = 365 \text{ g/L}$$
$$\text{Solubility of AgCl in H}_2\text{O at 20°C} = \phantom{0}0.009 \text{ g/L}$$
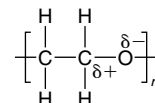
Actually, the process of dissolving is more complex than just a contest between the relative energies of attraction of the particles for each other or of the particles for the solvent. In Chapter 13, we'll see that it also involves the natural tendency of the particles to disperse randomly through the solution.

● **Solid Solvents for Ions** Because of its partial charges, water is an excellent liquid solvent for ionic species, but some solids behave in a similar way. For example, poly(ethylene oxide) is a polymer with a repeating structure written as

$$\left[\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{C}-\text{C}-\overset{\delta-}{\text{O}} \\ | \quad |_{\delta+} \\ \text{H} \quad \text{H} \end{array}\right]_n$$

where the *n* indicates many identical groups linked together covalently. The partial negative charges on the oxygen atoms can surround metal cations, such as $Li^+$, and solvate them while remaining in the solid state. Poly(ethylene oxide) and related polymers are parts of some lithium-ion batteries used in laptop computers and other portable electronic devices.



**Figure 4.3** **The dissolution of an ionic compound.** When an ionic compound dissolves in water, $H_2O$ molecules separate, surround, and disperse the ions into the liquid. Note that the negative ends of the $H_2O$ molecules face the positive ions and the positive ends face the negative ions.

**Covalent Compounds in Water** Water dissolves many covalent compounds also. Table sugar (sucrose, $C_{12}H_{22}O_{11}$), beverage (grain) alcohol (ethanol, $C_2H_6O$), and automobile antifreeze (ethylene glycol, $C_2H_6O_2$) are some familiar examples. All contain their own polar O—H bonds, which interact with those of water. However, even though these substances dissolve, they do not dissociate into ions but remain as intact molecules. Since their aqueous solutions do not conduct an electric current, these substances are called **nonelectrolytes.** Many other covalent substances, such as benzene ($C_6H_6$) and octane ($C_8H_{18}$), do not contain polar bonds, and these substances do not dissolve appreciably in water.

A small, but very important, group of H-containing covalent compounds interacts so strongly with water that their molecules *do* dissociate into ions.

DISSOLUTION OF AN IONIC COMPOUND AND A COVALENT COMPOUND ●

In aqueous solution, these substances are all *acids,* as you'll see shortly. The molecules contain polar bonds to hydrogen, in which the atom bonded to H pulls more strongly on the shared electron pair. A good example is hydrogen chloride gas. The Cl end of the HCl molecule is partially negative, and the H end is partially positive. When HCl dissolves in water, the partially charged poles of $H_2O$ molecules are attracted to the oppositely charged poles of HCl. The H—Cl bond breaks, with the H becoming the solvated cation $H^+(aq)$ (but see the discussion following the sample problem) and the Cl becoming the solvated anion $Cl^-(aq)$. Hydrogen bromide behaves similarly when it dissolves in water:

$$HBr(g) \xrightarrow{H_2O} H^+(aq) + Br^-(aq)$$

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**SAMPLE PROBLEM 4.2** Determining the Molarity of $H^+$ Ions in Aqueous Solutions of Acids

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**Problem** Nitric acid is a major chemical in the fertilizer and explosives industries. In aqueous solution, each molecule dissociates and the H becomes a solvated $H^+$ ion. What is the molarity of $H^+(aq)$ in 1.4 *M* nitric acid?
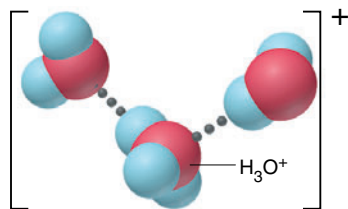
**Plan** We know the molarity of acid (1.4 *M*), so we just need the formula to find the number of moles of $H^+(aq)$ present in 1 L of solution.

**Solution** Nitrate ion is $NO_3^-$, so nitric acid is $HNO_3$. Thus, 1 mol of $H^+(aq)$ is released per mole of acid:
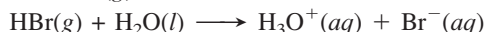
$$HNO_3(l) \xrightarrow{H_2O} H^+(aq) + NO_3^-(aq)$$
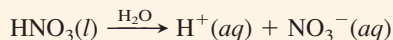
Therefore, 1.4 *M* $HNO_3$ contains 1.4 mol of $H^+(aq)$/L and is  1.4 *M* $H^+(aq)$.

**FOLLOW-UP PROBLEM 4.2** How many moles of $H^+(aq)$ are present in 451 mL of 3.20 *M* hydrobromic acid?

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**The Nature of $H^+$ and Other Ions in Water** Water interacts strongly with many ions, but most strongly with the hydrogen cation, $H^+$, a very unusual species. The H atom is a proton surrounded by an electron, so the $H^+$ ion is just a proton. Because its full positive charge is concentrated in such a tiny volume, $H^+$ attracts the negative pole of surrounding water molecules so strongly that it actually forms a covalent bond to one of them. We usually show this interaction by writing the aqueous $H^+$ ion as $H_3O^+$ (hydronium ion). For instance, to show more accurately what takes place when HBr(g) dissolves, we write

$$HBr(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Br^-(aq)$$



**Figure 4.4 The hydrated proton.** The charge of the $H^+$ ion is highly concentrated because the ion is so small. In aqueous solution, it forms a covalent bond to a water molecule and exists as an $H_3O^+$ ion associated tightly with other $H_2O$ molecules. Here, the $H_7O_3^+$ ion is shown.

To make a point here about the interactions with water, let's write the hydronium ion as $(H_2O)H^+$. The hydronium ion associates with other water molecules in a mixture that includes $H_5O_2^+$ [or $(H_2O)_2H^+$], $H_7O_3^+$ [or $(H_2O)_3H^+$], $H_9O_4^+$ [or $(H_2O)_4H^+$], and still larger aggregates; $H_7O_3^+$ is shown in Figure 4.4. These various species exist together, but we use $H^+(aq)$ as a general, simplified notation. Later in this chapter and much of the rest of the text, we show the solvated proton as $H_3O^+(aq)$ to emphasize water's role. Water interacts covalently with many metal ions as well. For example, $Fe^{3+}$ exists in water as $Fe(H_2O)_6^{3+}$, an $Fe^{3+}$ ion bound to six $H_2O$ molecules. We discuss these species fully in later chapters.

**SECTION SUMMARY**

When an ionic compound dissolves in water, the ions dissociate from each other and become solvated by water molecules. Because the ions are free to move, their solutions conduct electricity. Water plays an active role in dissolving ionic compounds because it consists of polar molecules that are attracted to the ions. Water also dissolves many covalent substances, and it interacts with some H-containing molecules so strongly that it breaks their covalent bonds and dissociates them into $H^+(aq)$ ions and anions. In water, the $H^+$ ion is bound to an $H_2O$ and exists as $H_3O^+$.

# 4.2 WRITING EQUATIONS FOR AQUEOUS IONIC REACTIONS

Of the many thousands of reactions that occur in the environment and in organisms, the overwhelming majority take place in aqueous solution, and many of those involve ions. Chemists use three types of equations to represent aqueous ionic reactions: molecular, total ionic, and net ionic equations. In the two types of ionic equations, atoms and charges must balance; as you'll see, by balancing the atoms, we balance the charges also.

Let's examine a reaction to see what each of these equations shows. When solutions of silver nitrate and sodium chromate are mixed, the brick-red solid silver chromate ($Ag_2CrO_4$) forms. Figure 4.5 depicts three views of this reaction: the change you would see if you mixed these solutions in the lab, how you might imagine the change at the atomic level among the ions, and how you can symbolize the change with the three types of equations.

The **molecular equation** (*top*) reveals the least about the species in solution, and is actually somewhat misleading, because *it shows all the reactants and products as if they were intact, undissociated compounds*:

$$2AgNO_3(aq) + Na_2CrO_4(aq) \longrightarrow Ag_2CrO_4(s) + 2NaNO_3(aq)$$
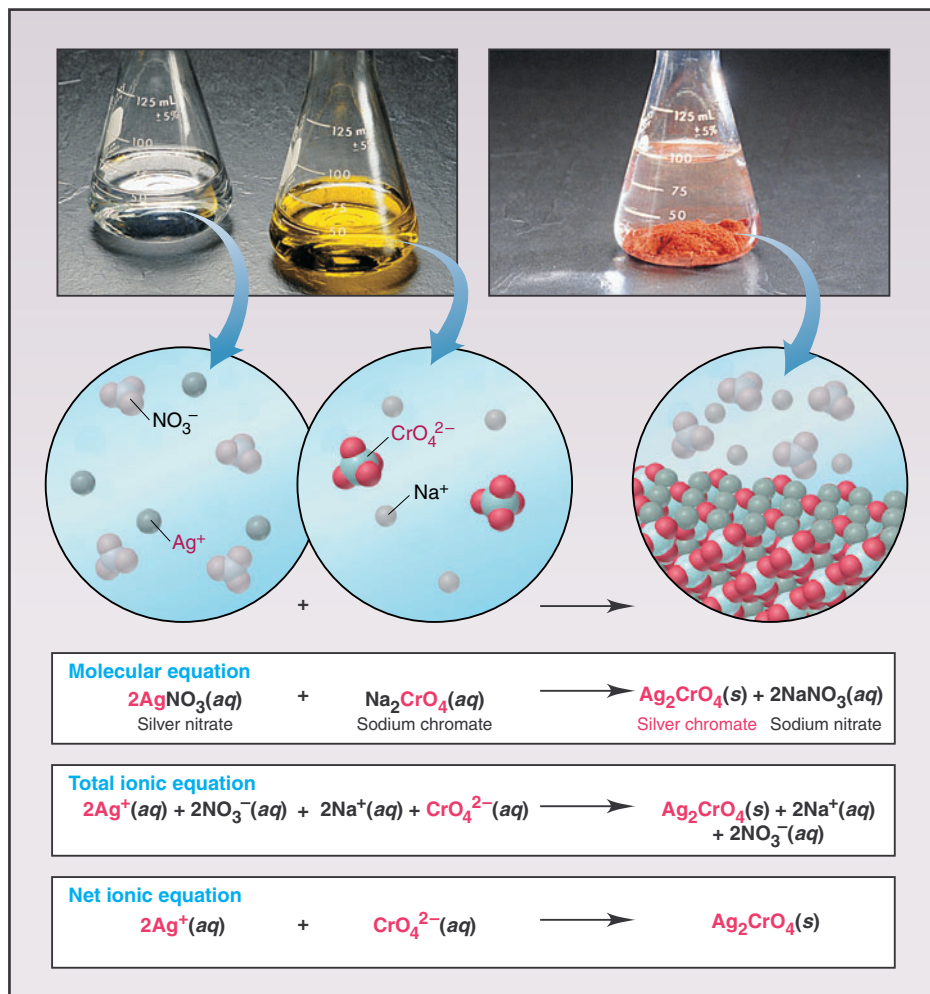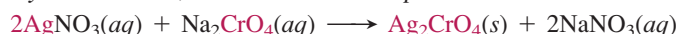


**Figure 4.5** **A precipitation reaction and its equations.** When silver nitrate and sodium chromate solutions are mixed, a reaction occurs that forms solid silver chromate and a solution of sodium nitrate. The photos present the macroscopic view of the reaction, the view the chemist sees in the lab. The blow-up arrows lead to an atomic-scale view, a representation of the chemist's mental picture of the reactants and products. (The pale ions are spectator ions, present for electrical neutrality, but not involved in the reaction.) Three equations represent the reaction in symbols. The molecular equation shows all substances intact. The total ionic equation shows all *soluble* substances as separate, solvated ions. The net ionic equation eliminates the spectator ions to show only the reacting species.

**Molecular equation**

$2AgNO_3(aq)$ + $Na_2CrO_4(aq)$ $\longrightarrow$ $Ag_2CrO_4(s) + 2NaNO_3(aq)$
Silver nitrate      Sodium chromate              Silver chromate   Sodium nitrate

**Total ionic equation**

$2Ag^+(aq) + 2NO_3^-(aq) + 2Na^+(aq) + CrO_4^{2-}(aq) \longrightarrow Ag_2CrO_4(s) + 2Na^+(aq) + 2NO_3^-(aq)$

**Net ionic equation**

$2Ag^+(aq)$ + $CrO_4^{2-}(aq)$ $\longrightarrow$ $Ag_2CrO_4(s)$

The **total ionic equation** *(middle)* is a much more accurate representation of the reaction because *it shows all the soluble ionic substances dissociated into ions.* Now the $Ag_2CrO_4(s)$ stands out as the only undissociated substance:

$$2Ag^+(aq) + 2NO_3^-(aq) + 2Na^+(aq) + CrO_4^{2-}(aq) \longrightarrow$$
$$Ag_2CrO_4(s) + 2Na^+(aq) + 2NO_3^-(aq)$$

Notice that the $Na^+(aq)$ and $NO_3^-(aq)$ ions appear in the same form on both sides of the equation. They are called **spectator ions** because they are not involved in the actual chemical change. These ions are present as part of the reactants to balance the charge. That is, we can't add $Ag^+$ ions without also adding an anion, in this case, $NO_3^-$ ion. Also notice that charges balance: there are four positive and four negative charges on the left for a net zero charge, and there are two positive and two negative charges on the right for a net zero charge.

The **net ionic equation** *(bottom)* is the most useful because *it eliminates the spectator ions and shows the actual chemical change taking place*:

$$2Ag^+(aq) + CrO_4^{2-}(aq) \longrightarrow Ag_2CrO_4(s)$$
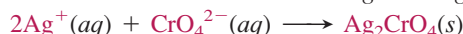
The formation of solid silver chromate from silver ions and chromate ions *is* the only change. In fact, if we had originally mixed solutions of potassium chromate, $K_2CrO_4(aq)$, and silver acetate, $AgC_2H_3O_2(aq)$, instead of sodium chromate and silver nitrate, the same change would have occurred. Only the spectator ions would differ—$K^+(aq)$ and $C_2H_3O_2^-(aq)$ instead of $Na^+(aq)$ and $NO_3^-(aq)$. Thus, writing the net ionic equation is an excellent way to isolate the key chemical event.

Now, let's discuss the three most important types of chemical reaction processes—precipitation, acid-base, and oxidation-reduction—and apply these ways of writing equations.

### SECTION SUMMARY

A molecular equation for an aqueous ionic reaction shows undissociated substances. A total ionic equation shows all soluble ionic compounds as separate, solvated ions. Spectator ions appear unchanged on both sides of the equation. By eliminating them, you see the actual chemical change in a net ionic equation.

## 4.3 PRECIPITATION REACTIONS

Precipitation reactions are common in both nature and industry. Many geological formations, including coral reefs, some gems and minerals, and deep-sea structures form, in part, through this type of chemical process. And, as you'll see, the chemical industry employs precipitation methods to produce several key inorganic compounds.

In **precipitation reactions,** two soluble ionic compounds react to form an insoluble product, a **precipitate.** The reaction you just saw between silver nitrate and sodium chromate is an example. Precipitates form for the same reason that some ionic compounds do not dissolve: the electrostatic attraction between the ions outweighs the tendency of the ions to become solvated and move randomly throughout the solution. When solutions of such ions are mixed, the ions collide and stay together, and the resulting substance "comes out of solution" as a solid.

### The Driving Force for a Precipitation Reaction

Because these reactions are so common, it may seem that a precipitate forms whenever aqueous solutions of two ionic compounds are mixed, but that is not the case. In many aqueous ionic reactions, especially in precipitation and acid-base reactions, the "driving force" for the reaction, the event that causes the reaction to occur, is the *net removal of ions from solution to form the product*. Consider this example. When solid sodium iodide and potassium nitrate are each

dissolved in water, each solution consists of separated ions dispersed throughout the solution:

$$NaI(s) \xrightarrow{H_2O} Na^+(aq) + I^-(aq)$$

$$KNO_3(s) \xrightarrow{H_2O} K^+(aq) + NO_3^-(aq)$$
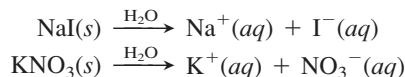
Does a reaction occur if you mix these solutions? To answer this, *you must examine the possible ion combinations to see whether some of the ions are removed from solution*; that is, whether any of the possible products are insoluble. The reactant ions are

$$Na^+(aq) + I^-(aq) + K^+(aq) + NO_3^-(aq) \longrightarrow ?$$
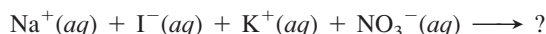
In addition to the two original reactants, NaI and $KNO_3$, which you know are soluble, the other possible cation-anion combinations are $NaNO_3$ and KI. A reaction does *not* occur when you mix these starting solutions because $NaNO_3$ and KI are also soluble ionic compounds. Therefore, all the ions just remain in solution. (You'll see shortly how to tell if a product is soluble or not.)

Now substitute a solution of lead(II) nitrate, $Pb(NO_3)_2$, for the $KNO_3$; when you mix $Pb(NO_3)_2$ solution with NaI solution, a yellow solid forms (Figure 4.6). In addition to the two soluble reactants, the other two possible ion combinations are $NaNO_3$ and $PbI_2$, so the solid must be lead(II) iodide. Therefore, in this case, a reaction *does* occur because ions are removed from the solution to form $PbI_2$:

$$2Na^+(aq) + 2I^-(aq) + Pb^{2+}(aq) + 2NO_3^-(aq) \longrightarrow$$
$$2Na^+(aq) + 2NO_3^-(aq) + PbI_2(s)$$
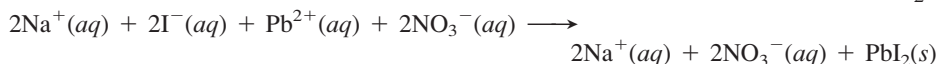
If we use color and look closely at the molecular equation for this reaction, we see that *the ions are exchanging partners*:

$$2NaI(aq) + Pb(NO_3)_2(aq) \longrightarrow PbI_2(s) + 2NaNO_3(aq)$$
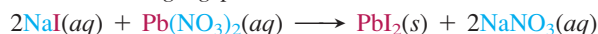
Such reactions are called double-displacement, or **metathesis** (pronounced *meh-TA-thuh-sis*) **reactions**. Several are important in industry, such as the preparation of silver bromide for the manufacture of black-and-white film:

$$AgNO_3(aq) + KBr(aq) \longrightarrow AgBr(s) + KNO_3(aq)$$

## Predicting Whether a Precipitation Reaction Will Occur

As you just saw, three steps allow you to predict whether a precipitate will form:

1. Note the ions present in the reactants.
2. Consider the possible cation-anion combinations.
3. Decide whether any of the combinations is insoluble.

A difficulty arises with the last step because there is no simple way to decide whether a given combination is insoluble. Rather, you must memorize a short list of solubility rules (Table 4.1). These rules don't cover every possibility, but learning them allows you to predict the outcome of many precipitation reactions.



**Figure 4.6** **The reaction of $Pb(NO_3)_2$ and NaI.** When aqueous solutions of these ionic compounds are mixed, the yellow solid $PbI_2$ forms.

PRECIPITATION REACTIONS

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**Table 4.1** **Solubility Rules for Ionic Compounds in Water**
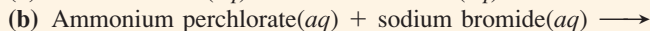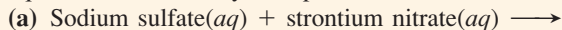
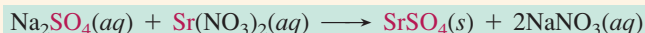| Soluble Ionic Compounds | Insoluble Ionic Compounds |
| --- | --- |
| 1. All common compounds of Group 1A(1) ions ($Li^+$, $Na^+$, $K^+$, etc.) and ammonium ion ($NH_4^+$) are soluble. | 1. All common metal hydroxides are insoluble, *except* those of Group 1A(1) and the larger members of Group 2A(2) (beginning with $Ca^{2+}$). |
| 2. All common nitrates ($NO_3^-$), acetates ($CH_3COO^-$ or $C_2H_3O_2^-$), and most perchlorates ($ClO_4^-$) are soluble. | 2. All common carbonates ($CO_3^{2-}$) and phosphates ($PO_4^{3-}$) are insoluble, *except* those of Group 1A(1) and $NH_4^+$. |
| 3. All common chlorides ($Cl^-$), bromides ($Br^-$), and iodides ($I^-$) are soluble, *except* those of $Ag^+$, $Pb^{2+}$, $Cu^+$, and $Hg_2^{2+}$. | 3. All common sulfides are insoluble *except* those of Group 1A(1), Group 2A(2), and $NH_4^+$. |
| 4. All common sulfates ($SO_4^{2-}$) are soluble, *except* those of $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$, and $Pb^{2+}$. | |

**SAMPLE PROBLEM 4.3** Predicting Whether a Precipitation Reaction Occurs; Writing Ionic Equations

**Problem** Predict whether a reaction occurs when each of the following pairs of solutions are mixed. If a reaction does occur, write balanced molecular, total ionic, and net ionic equations, and identify the spectator ions.
**(a)** Sodium sulfate(*aq*) + strontium nitrate(*aq*) ⟶
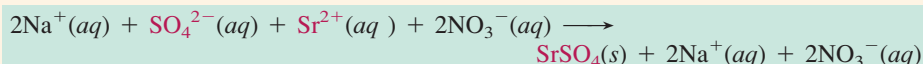**(b)** Ammonium perchlorate(*aq*) + sodium bromide(*aq*) ⟶
**Plan** For each pair of solutions, we note the ions present in the reactants, write the cation-anion combinations, and refer to Table 4.1 to see if any are insoluble. For the molecular equation, we predict the products. For the total ionic equation, we write the soluble compounds as separate ions. For the net ionic equation, we eliminate the spectator ions.
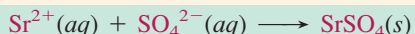**Solution (a)** In addition to the reactants, the two other ion combinations are strontium sulfate and sodium nitrate. Table 4.1 shows that strontium sulfate is insoluble, so a reaction *does* occur. Writing the molecular equation:

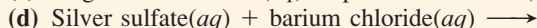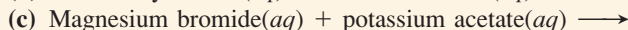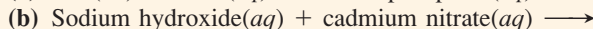$$Na_2SO_4(aq) + Sr(NO_3)_2(aq) \longrightarrow SrSO_4(s) + 2NaNO_3(aq)$$

Writing the total ionic equation:

$$2Na^+(aq) + SO_4^{2-}(aq) + Sr^{2+}(aq) + 2NO_3^-(aq) \longrightarrow$$
$$SrSO_4(s) + 2Na^+(aq) + 2NO_3^-(aq)$$

Writing the net ionic equation:

$$Sr^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow SrSO_4(s)$$

The spectator ions are $Na^+$ and $NO_3^-$.
**(b)** The other ion combinations are ammonium bromide and sodium perchlorate. Table 4.1 shows that all ammonium, sodium, and most perchlorate compounds are soluble, and all bromides are soluble except those of $Ag^+$, $Pb^{2+}$, $Cu^+$, and $Hg_2^{2+}$. Therefore, *no* reaction occurs. The compounds remain dissociated in solution as solvated ions.

**FOLLOW-UP PROBLEM 4.3** Predict whether a reaction occurs, and write balanced total and net ionic equations:

**(a)** Iron(III) chloride(*aq*) + cesium phosphate(*aq*) ⟶
**(b)** Sodium hydroxide(*aq*) + cadmium nitrate(*aq*) ⟶
**(c)** Magnesium bromide(*aq*) + potassium acetate(*aq*) ⟶
**(d)** Silver sulfate(*aq*) + barium chloride(*aq*) ⟶
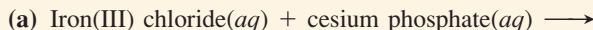
**SECTION SUMMARY**

Precipitation reactions involve the formation of an insoluble ionic compound from two soluble ones. They occur because electrostatic attractions among certain pairs of solvated ions are strong enough to cause their removal from solution. Such reactions can be predicted by noting whether any possible ion combinations are insoluble, based on a set of solubility rules.

## 4.4 ACID-BASE REACTIONS

Aqueous acid-base reactions involve water not only as solvent but also in the more active roles of reactant and product. These reactions are the essential chemical events in processes as diverse as the biochemical synthesis of proteins, the industrial production of several fertilizers, and some of the proposed methods for revitalizing lakes damaged by acid rain.

Obviously, an **acid-base reaction** (also called a **neutralization reaction**) occurs when an acid reacts with a base, but the definitions of these terms and the scope of this reaction process have changed considerably over the years. For our

purposes at this point, we'll use definitions that apply to the chemicals you'll commonly encounter in the lab:

- An **acid** is a substance that produces $H^+$ ions when dissolved in water.

$$HX \xrightarrow{H_2O} H^+(aq) + X^-(aq)$$
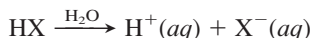
- A **base** is a substance that produces $OH^-$ ions when dissolved in water.

$$MOH \xrightarrow{H_2O} M^+(aq) + OH^-(aq)$$

(Other definitions of acid and base are presented later in this section and again in Chapter 18, along with a fuller meaning of neutralization.) Acids and bases are the active ingredients in many everyday products: most drain, window, and oven cleaners contain bases; vinegar and lemon juice contain acids.

Acids and bases are electrolytes and are often categorized in terms of "strength," which refers to their degree of dissociation into ions in aqueous solution. *Strong acids and strong bases dissociate completely* into i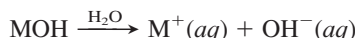ons when they dissolve in water. Therefore, like soluble ionic compounds, they are *strong* electrolytes and conduct a current well (see left photo). In contrast, *weak acids and weak bases dissociate so little that most of their molecules remain intact*. As a result, they conduct only a small current (see right photo), and are *weak* electrolytes. Table 4.2 lists some acids and bases in terms of their strength.

Both strong and weak acids have one or more H atoms as part of their structure. Strong bases have either the $OH^-$ or the $O^{2-}$ ion as part of their structure. Soluble ionic oxides, such as $K_2O$, act as strong bases because the oxide ion is not stable in water and reacts immediately to form hydroxide ion:

$$K_2O(s) + H_2O(l) \longrightarrow 2K^+(aq) + 2OH^-(aq)$$
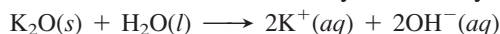
Weak bases, such as ammonia, do not contain $OH^-$ ions, but they produce them in a reaction with water that occurs to a small extent:

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

(Note the reaction arrow in the preceding equation. This type of arrow indicates that the reaction proceeds in both directions; we'll discuss this important idea further in Section 4.7.)

## The Driving Force and Net Change: Formation of $H_2O$ from $H^+$ and $OH^-$

Let's use ionic equations to see why acid-base reactions occur. We begin with the molecular equation for the reaction between the strong acid HCl and the strong base $Ba(OH)_2$:

$$2HCl(aq) + Ba(OH)_2(aq) \longrightarrow BaCl_2(aq) + 2H_2O(l)$$
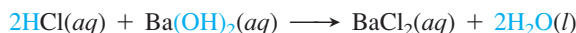
Since HCl and $Ba(OH)_2$ dissociate completely and $H_2O$ remains undissociated, the total ionic equation is

$$2H^+(aq) + 2Cl^-(aq) + Ba^{2+}(aq) + 2OH^-(aq) \longrightarrow Ba^{2+}(aq) + 2Cl^-(aq) + 2H_2O(l)$$

In the net ionic equation, we eliminate the spectator ions $Ba^{2+}(aq)$ and $Cl^-(aq)$ and see the actual reaction:

$$2H^+(aq) + 2OH^-(aq) \longrightarrow 2H_2O(l) \quad \text{or} \quad H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

Thus, *the essential change in all aqueous reactions between strong acids and strong bases is that an $H^+$ ion from the acid and an $OH^-$ ion from the base form a water molecule;* only the spectator ions differ from one reaction to another.

Now it's easy to understand the driving force for these reactions: like precipitation reactions, acid-base reactions are driven by *the electrostatic attraction of ions and their removal from solution* in the formation of the product. In this case, the ions are $H^+$ and $OH^-$ and the product is $H_2O$, which consists almost entirely of undissociated molecules. (Actually, water molecules dissociate *very*
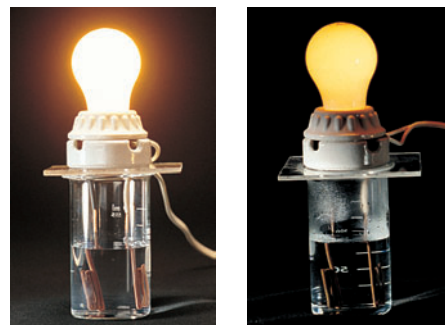


Strong electrolyte      Weak electrolyte

**Table 4.2 Selected Acids and Bases**

**Acids**

**Strong**

Hydrochloric acid, HCl
Hydrobromic acid, HBr
Hydriodic acid, HI
Nitric acid, $HNO_3$
Sulfuric acid, $H_2SO_4$
Perchloric acid, $HClO_4$

**Weak**

Hydrofluoric acid, HF
Phosphoric acid, $H_3PO_4$
Acetic acid, $CH_3COOH$
  (or $HC_2H_3O_2$)

**Bases**

**Strong**

Sodium hydroxide, NaOH
Potassium hydroxide, KOH
Calcium hydroxide, $Ca(OH)_2$
Strontium hydroxide, $Sr(OH)_2$
Barium hydroxide, $Ba(OH)_2$

**Weak**

Ammonia, $NH_3$

Amino acid units

Protein molecule

$H_2O$    $H_2O$

Synthesis of organism's proteins

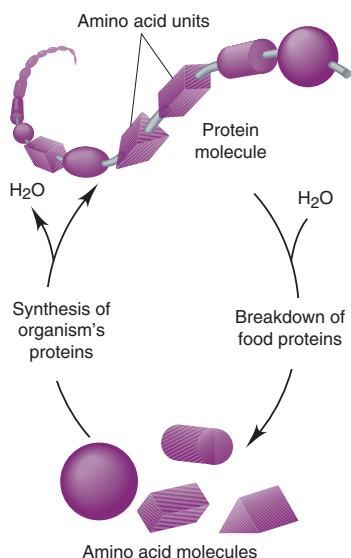Breakdown of food proteins

Amino acid molecules

**Displacement Reactions Inside You** The digestion of food proteins and the formation of an organism's own proteins form a continuous cycle of displacement reactions. A protein consists of hundreds or thousands of smaller molecules, called *amino acids,* linked in a long chain. When you eat proteins, your digestive processes use $H_2O$ to displace one amino acid at a time. These are transported by the blood to your cells, where other metabolic processes link them together, displacing $H_2O$, to make your own proteins.

slightly, as you'll see in Chapter 18, but the formation of water in a neutralization reaction represents an enormous net removal of $H^+$ and $OH^-$ ions.)

If we evaporate the water from the above reaction mixture, the ionic solid barium chloride remains. An ionic compound that results from the reaction of an acid and a base is called a **salt.** Thus, in a typical aqueous neutralization reaction, *the reactants are an acid and a base, and the products are a salt solution and water:*

$$HX(aq) + MOH(aq) \longrightarrow MX(aq) + H_2O(l)$$
$$\text{acid} \qquad \text{base} \qquad \qquad \text{salt} \qquad \text{water}$$
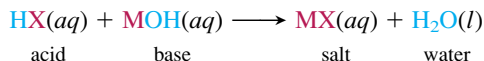
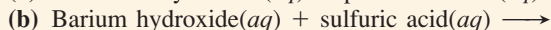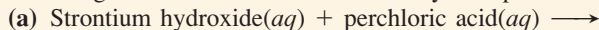The color shows that *the cation of the salt comes from the base and the anion comes from the acid.*

As this general equation indicates, acid-base reactions, like precipitation reactions, are metathesis (double-displacement) reactions. The molecular equation for the reaction of aluminum hydroxide, the active ingredient in some antacid tablets, with HCl, the major component of stomach acid, shows this clearly:

$$3HCl(aq) + Al(OH)_3(s) \longrightarrow AlCl_3(aq) + 3H_2O(l)$$
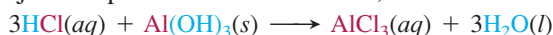
Acid-base reactions occur frequently in the synthesis and breakdown of biological macromolecules.

---

**SAMPLE PROBLEM 4.4** Writing Ionic Equations for Acid-Base Reactions

---

**Problem** Write balanced molecular, total ionic, and net ionic equations for each of the following acid-base reactions and identify the spectator ions:
**(a)** Strontium hydroxide(*aq*) + perchloric acid(*aq*) $\longrightarrow$
**(b)** Barium hydroxide(*aq*) + sulfuric acid(*aq*) $\longrightarrow$
**Plan** All are strong acids and bases (see Table 4.2), so the essential reaction is between $H^+$ and $OH^-$. The products are $H_2O$ and a salt solution consisting of the spectator ions. Note that in **(b),** the salt ($BaSO_4$) is insoluble (see Table 4.1), so virtually all ions are removed from solution.
**Solution (a)** Writing the molecular equation:

$$Sr(OH)_2(aq) + 2HClO_4(aq) \longrightarrow Sr(ClO_4)_2(aq) + 2H_2O(l)$$

Writing the total ionic equation:

$$Sr^{2+}(aq) + 2OH^-(aq) + 2H^+(aq) + 2ClO_4^-(aq) \longrightarrow$$
$$Sr^{2+}(aq) + 2ClO_4^-(aq) + 2H_2O(l)$$

Writing the net ionic equation:

$$2OH^-(aq) + 2H^+(aq) \longrightarrow 2H_2O(l) \quad \text{or} \quad OH^-(aq) + H^+(aq) \longrightarrow H_2O(l)$$
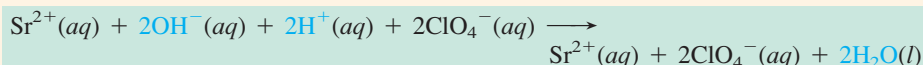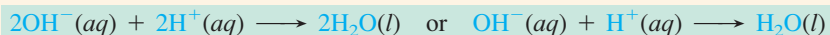
$Sr^{2+}(aq)$ and $ClO_4^-(aq)$ are the spectator ions.
**(b)** Writing the molecular equation:

$$Ba(OH)_2(aq) + H_2SO_4(aq) \longrightarrow BaSO_4(s) + 2H_2O(l)$$

Writing the total ionic equation:

$$Ba^{2+}(aq) + 2OH^-(aq) + 2H^+(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s) + 2H_2O(l)$$
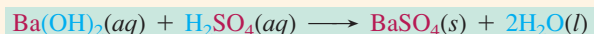
The net ionic equation is the same as the total ionic equation. This is a precipitation *and* a neutralization reaction. There are no spectator ions because all the ions are used to form the two products.

**FOLLOW-UP PROBLEM 4.4** Write balanced molecular, total ionic, and net ionic equations for the reaction between aqueous solutions of calcium hydroxide and nitric acid.

## Acid-Base Titrations

Chemists study acid-base reactions quantitatively through titrations. In any **titration,** *one solution of known concentration is used to determine the concentration of another solution through a monitored reaction.* In a typical acid-base titration, a *standardized* solution of base, one whose concentration is *known,* is added slowly to an acid solution of *unknown* concentration.

The laboratory procedure is straightforward but requires careful technique (Figure 4.7). A known volume of the acid solution is placed in a flask, and a few drops of indicator solution are added. An *acid-base indicator* is a substance whose color is different in acid than in base. (We examine indicators in Chapters 18 and 19.) The standardized solution of base is added slowly to the flask from a buret. As the titration nears its end, indicator molecules change color near a drop of added base due to the temporary excess of $OH^-$ ions there. As soon as the solution is swirled, however, the indicator's acidic color returns. The **equivalence point** in the titration occurs when *all the moles of $H^+$ ions present in the original volume of acid solution have reacted with an equivalent number of moles of $OH^-$ ions added from the buret:*

Moles of $H^+$ (originally in flask) = moles of $OH^-$ (added from buret)

The **end point** of the titration occurs when a tiny excess of $OH^-$ ions changes the indicator permanently to its color in base. In calculations, we assume this tiny excess is insignificant, and therefore *the amount of base needed to reach the end point is the same as the amount needed to reach the equivalence point.*



$$H^+(aq) + X^-(aq) + M^+(aq) + OH^-(aq) \longrightarrow H_2O(l) + M^+(aq) + X^-(aq)$$
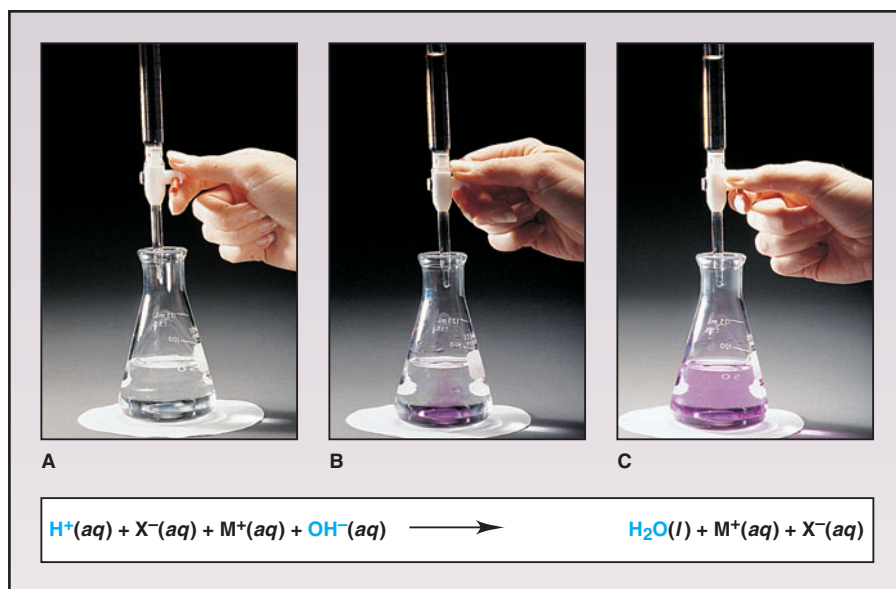
**Figure 4.7** **An acid-base titration. A,** In this procedure, a measured volume of the unknown acid solution is placed in a flask beneath a buret containing the known (standardized) base solution. A few drops of indicator are added to the flask; the indicator used here is phenolphthalein, which is colorless in acid and pink in base. After an initial buret reading, base ($OH^-$ ions) is added slowly to the acid ($H^+$ ions). **B,** Near the end of the titration, the indicator momentarily changes to its base color but reverts to its acid color with swirling. **C,** When the end point is reached, a tiny excess of $OH^-$ is present, shown by the permanent change in color of the indicator. The difference between the final buret reading and the initial buret reading gives the volume of base used.

**SAMPLE PROBLEM 4.5** Finding the Concentration of Acid from an Acid-Base Titration

**Problem** You perform an acid-base titration to standardize an HCl solution by placing 50.00 mL of HCl in a flask with a few drops of indicator solution. You put 0.1524 *M* NaOH into the buret, and the initial reading is 0.55 mL. At the end point, the buret reading is 33.87 mL. What is the concentration of the HCl solution?

**Plan** We must find the molarity of acid from the volume of acid (50.00 mL), the initial (0.55 mL) and final (33.87 mL) volumes of base, and the molarity of base (0.1524 *M*). First, we balance the equation. We find the volume of base added from the difference in buret readings and use the base's molarity to calculate the amount (mol) of base added. Then, we use the molar ratio from the balanced equation to find the amount (mol) of acid originally present and divide by the acid's original volume to find the molarity.

**Solution** Writing the balanced equation:

$$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$$
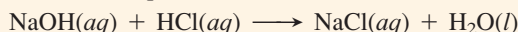
Finding volume (L) of NaOH solution added:

$$\text{Volume (L) of solution} = (33.87 \text{ mL soln} - 0.55 \text{ mL soln}) \times \frac{1 \text{ L}}{1000 \text{ mL}}$$
$$= 0.03332 \text{ L soln}$$

Finding amount (mol) of NaOH added:

$$\text{Moles of NaOH} = 0.03332 \text{ L soln} \times \frac{0.1524 \text{ mol NaOH}}{1 \text{ L soln}}$$
$$= 5.078 \times 10^{-3} \text{ mol NaOH}$$

Finding amount (mol) of HCl originally present: Since the molar ratio is 1:1,

$$\text{Moles of HCl} = 5.078 \times 10^{-3} \text{ mol NaOH} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} = 5.078 \times 10^{-3} \text{ mol HCl}$$

Calculating molarity of HCl:

$$\text{Molarity of HCl} = \frac{5.078 \times 10^{-3} \text{ mol HCl}}{50.00 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = \boxed{0.1016 \ M \text{ HCl}}$$

**Check** The answer makes sense: a larger volume of less concentrated acid neutralized a smaller volume of more concentrated base. Rounding shows that the moles of $H^+$ and $OH^-$ are about equal: 50 mL $\times$ 0.1 *M* $H^+$ = 0.005 mol = 33 mL $\times$ 0.15 *M* $OH^-$.

**FOLLOW-UP PROBLEM 4.5** What volume of 0.1292 *M* $Ba(OH)_2$ would neutralize 50.00 mL of the HCl solution standardized in the sample problem above?

Volume (L) of base
(difference in buret readings)

multiply by *M* (mol/L) of base

Amount (mol) of base

molar ratio

Amount (mol) of acid

divide by volume (L) of acid

*M* (mol/L) of acid

## Acid-Base Reactions as Proton-Transfer Processes

We gain deeper insight into acid-base reactions if we look more closely at the actual species present in solution. Let's see what takes place when HCl gas dissolves in water. As we discussed earlier, the polar water molecules pull apart the HCl molecule and the $H^+$ ion bonds to a water molecule. In essence, we can say that HCl *transfers its proton* to $H_2O$:

$$\overset{\frown}{\text{H}}Cl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$
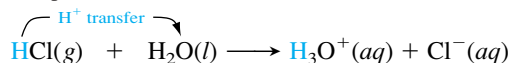
Thus, hydrochloric acid (an aqueous solution of HCl gas) actually consists of solvated $H_3O^+$ and solvated $Cl^-$ ions.

When sodium hydroxide solution is added, the $H_3O^+$ ion transfers a proton to the $OH^-$ ion of the base (with the product water shown here as HOH):

$$[H_3O^+(aq) + Cl^-(aq)] + [Na^+(aq) + OH^-(aq)] \longrightarrow$$
$$H_2O(l) + Na^+(aq) + Cl^-(aq) + HOH(l)$$
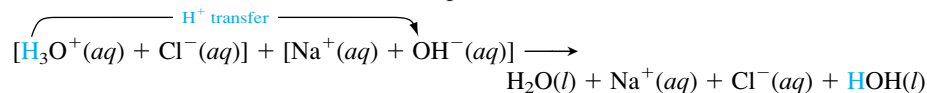
Without the spectator ions, the transfer of a proton from $H_3O^+$ to $OH^-$ is obvious:

$$H_3O^+(aq) + OH^-(aq) \longrightarrow H_2O(l) + HOH(l) \quad [\text{or } 2H_2O(l)]$$
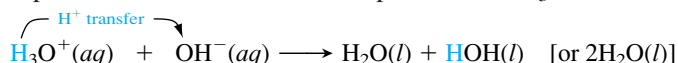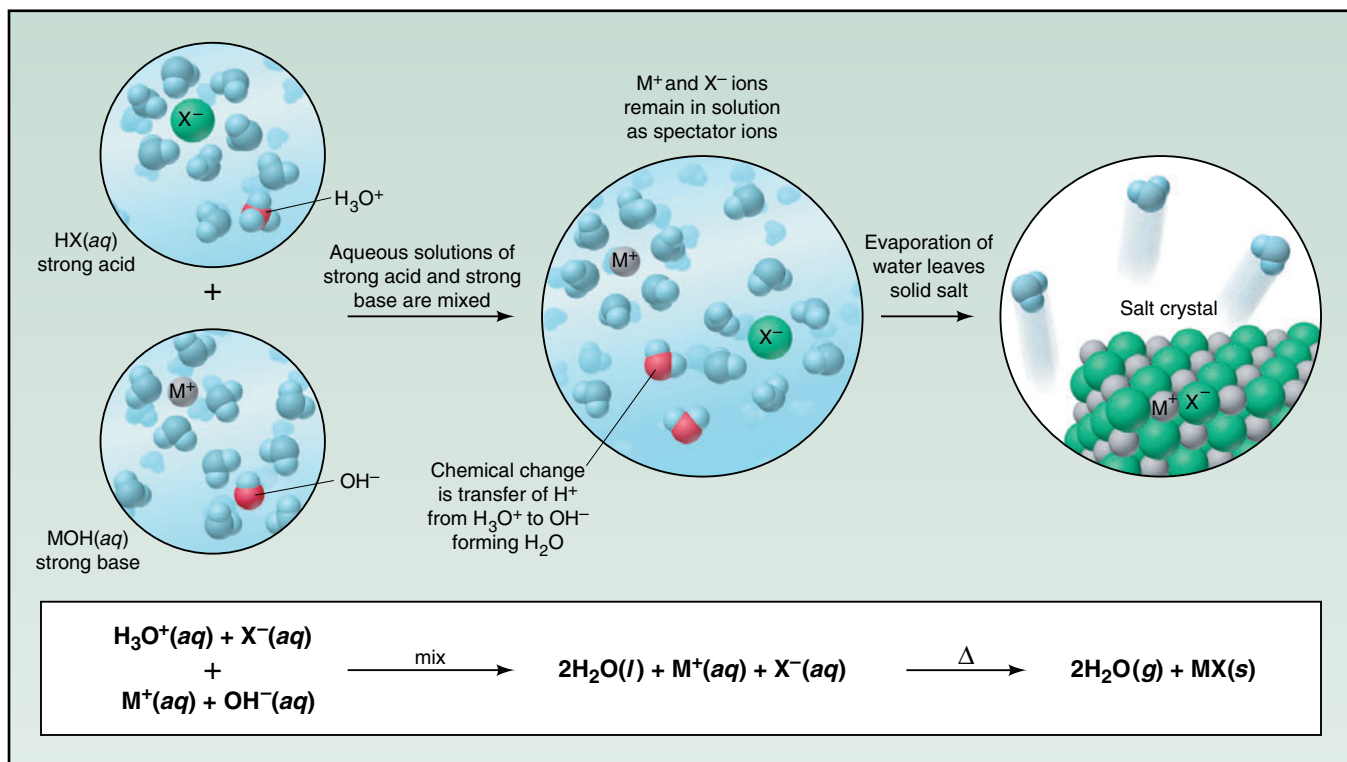
**Figure 4.8** **An aqueous strong acid–strong base reaction on the atomic scale.** When solutions of a strong acid (HX) and a strong base (MOH) are mixed, the $H_3O^+$ from the acid transfers a proton to the $OH^-$ from the base to form an $H_2O$ molecule. Evaporation of the water leaves the spectator ions, $X^-$ and $M^+$, as a solid ionic compound called a *salt.*

Compare this net ionic reaction with the one we saw earlier (see p. 141):

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$
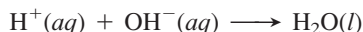
and you'll see they are identical, with the additional $H_2O$ molecule coming from the $H_3O^+$. Clearly, *an acid-base reaction is a proton-transfer process.* The $Na^+$ and $Cl^-$ ions remain in solution, and if the water is evaporated, they crystallize as the salt NaCl. Figure 4.8 shows this process on the atomic level.

In the early 20th century, the chemists Johannes Brønsted and Thomas Lowry realized the proton-transfer nature of acid-base reactions. They defined *an acid as a molecule (or ion) that donates a proton, and a base as a molecule (or ion) that accepts a proton.* Therefore, in the aqueous reaction between strong acid and strong base, *$H_3O^+$ ion acts as the acid and $OH^-$ ion acts as the base.* Because they ionize completely, a given amount of strong acid (or strong base) creates an equivalent amount of $H_3O^+$ (or $OH^-$) when it dissolves in water. (We discuss the Brønsted-Lowry concept thoroughly in Chapter 18.)

Thinking of acid-base reactions as proton-transfer processes helps us understand another common type of aqueous ionic reaction, those that form a gaseous product. For example, when an ionic carbonate, such as $K_2CO_3$, is treated with an acid, such as HCl, one of the products is carbon dioxide. *The driving force for this and similar reactions is formation of a gas **and** water because both products remove reactant ions from solution:*

$$2HCl(aq) + K_2CO_3(aq) \longrightarrow 2KCl(aq) + [H_2CO_3(aq)]$$
$$[H_2CO_3(aq)] \longrightarrow H_2O(l) + CO_2(g)$$

The product $H_2CO_3$ is shown in brackets to indicate that it is very unstable. It decomposes immediately into water and carbon dioxide. Combining these two equations gives the overall equation:

$$2HCl(aq) + K_2CO_3(aq) \longrightarrow 2KCl(aq) + H_2O(l) + CO_2(g)$$
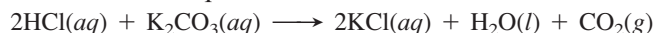
When we show $H_3O^+$ ions from the HCl as the actual species in solution and write the net ionic equation, $Cl^-$ and $K^+$ ions are eliminated. Note that each of the two $H_3O^+$ ions transfers a proton to the carbonate ion:

$$\overset{\overparen{\text{2H}^+ \text{ transfer}}}{2H_3O^+(aq)\ +\ CO_3^{2-}(aq) \longrightarrow 2H_2O(l) + [H_2CO_3(aq)] \longrightarrow 3H_2O(l) + CO_2(g)}$$
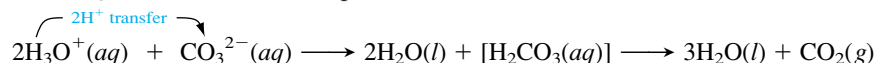
In essence, then, this is an acid-base reaction, with carbonate ion accepting the protons and, therefore, acting as the base.

Several other polyatomic ions act similarly when reacting with an acid, as in the formation of $SO_2$ from ionic sulfites. For the reaction of a strong acid with an ionic sulfite, the net ionic equation is

$$\overset{\overparen{\text{2H}^+ \text{ transfer}}}{2H_3O^+(aq)\ +\ SO_3^{2-}(aq) \longrightarrow 3H_2O(l) + SO_2(g)}$$

Ionic equations are written differently for the reactions of weak acids. Figure 4.9 shows a household example of the gas-forming reaction between vinegar (an aqueous 5% solution of acetic acid) and baking soda (sodium hydrogen carbonate) solution. Look closely at the equations. Since acetic acid is a weak acid (see Table 4.2), it dissoci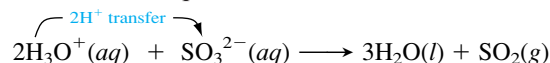ates very little. To show this, *weak acids appear undissociated in the net ionic equation;* note that $H_3O^+$ does not appear. Therefore, only $Na^+(aq)$ is a spectator ion; $CH_3COO^-(aq)$ is not.



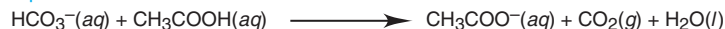**Figure 4.9** **An acid-base reaction that forms a gaseous product.** Carbonates and hydrogen carbonates react with acids to form gaseous $CO_2$ and $H_2O$. Here, dilute acetic acid solution (vinegar) is added to sodium hydrogen carbonate (baking soda) solution, and bubbles of $CO_2$ gas form. (Note that the net ionic equation includes acetic acid because it is a weak acid and does *not* dissociate into ions to an appreciable extent.)

Molecular equation
$$NaHCO_3(aq) + CH_3COOH(aq) \longrightarrow CH_3COONa(aq) + CO_2(g) + H_2O(l)$$

Total ionic equation
$$Na^+(aq) + HCO_3^-(aq) + CH_3COOH(aq) \longrightarrow CH_3COO^-(aq) + Na^+(aq) + CO_2(g) + H_2O(l)$$

Net ionic equation
$$HCO_3^-(aq) + CH_3COOH(aq) \longrightarrow CH_3COO^-(aq) + CO_2(g) + H_2O(l)$$

**SECTION SUMMARY**
Acid-base (neutralization) reactions occur when ions are removed as an acid (an $H^+$-yielding substance) and a base (an $OH^-$-yielding substance) form a water molecule. Strong acids and bases dissociate completely; weak acids and bases dissociate slightly. In a titration, a known concentration of one reactant is used to determine the concentration of the other. An acid-base reaction can also be viewed as the transfer of a proton from an acid to a base. An ionic gas-forming reaction is an acid-base reaction in which an acid transfers a proton to a polyatomic ion (carbonate or sulfite), forming a gas that leaves the reaction mixture.

## 4.5 OXIDATION-REDUCTION (REDOX) REACTIONS

Redox reactions are the third and, perhaps, most important type of chemical processes. They include the formation of a compound from its elements (and vice versa), all combustion reactions, the reactions that generate electricity in batteries, the reactions that produce cellular energy, and many others. In this section, we examine the redox process in detail and learn some essential terminology. We see one way to balance redox equations and one way to apply them quantitatively.

## The Driving Force for Redox Processes

In **oxidation-reduction** (or **redox**) **reactions,** the key chemical event is the *net movement of electrons* from one reactant to the other. The driving force for these reactions is that the movement of electrons occurs in a specific direction—*from the reactant (or atom in the reactant) with less attraction for electrons to the reactant with more attraction for electrons.*

Such movement of electron charge occurs in the formation of both ionic and covalent compounds. As an example, let's reconsider the flashbulb reaction (see Figure 3.7, p. 103), in which an ionic compound, MgO, forms from its elements:
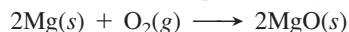
$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$

Figure 4.10A shows that during the reaction, each Mg atom loses two electrons and each O atom gains them; that is, two electrons move from each Mg atom to each O atom. This change represents a ***transfer*** *of electron charge* away from each Mg atom and toward each O atom, resulting in the formation of $Mg^{2+}$ and $O^{2-}$ ions. The ions aggregate and form an ionic solid.

During the formation of a covalent compound from its elements, there is again a net movement of electrons; but it is more of a "shift" in electron charge than a transfer and, thus, *not* enough to form ions. Consider the formation of HCl gas:

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$
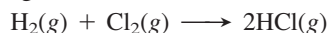
To see the electron movement here, compare the electron charge distributions in the reactant bonds and in the product bonds. As Figure 4.10B shows, $H_2$ and $Cl_2$ molecules are each held together by pure covalent bonds; that is, the electrons are shared equally between the bonded atoms. In the HCl molecule, the electrons are shared unequally because the Cl atom attracts them more strongly than the H atom does. Thus, in HCl, the H has less electron charge *(blue shading)* than it had in $H_2$, whereas the Cl has more charge *(red shading)* than it had in $Cl_2$. In other words, in the formation of HCl, there has been a relative ***shift*** *of electron charge* away from the H atom and toward the Cl atom. This electron *shift* is not nearly as extreme as the electron *transfer* during MgO formation. In fact, in some cases, the net movement of electrons may be very slight, but the reaction is still a redox process.



A **Formation of an ionic compound**

B **Formation of a covalent compound**
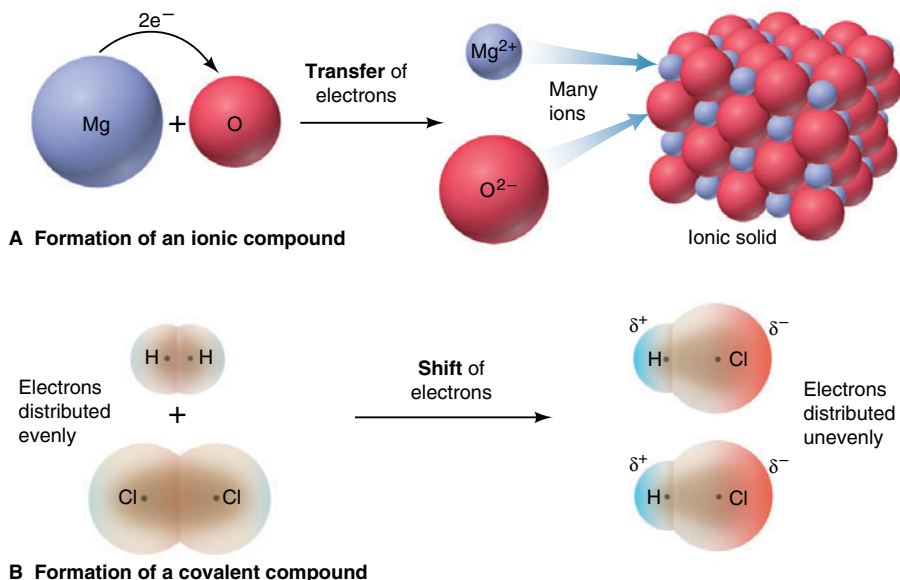
**Figure 4.10** The redox process in compound formation. **A,** In forming the ionic compound MgO, each Mg atom transfers two electrons to each O atom. (Note that atoms become smaller when they lose electrons and larger when they gain electrons.) The resulting $Mg^{2+}$ and $O^{2-}$ ions aggregate with many others to form an ionic solid. **B,** In the reactants $H_2$ and $Cl_2$, the electron pairs are shown centrally located to indicate that they are shared equally. In the covalent compound HCl, the Cl attracts the shared electrons more strongly than the H does. In effect, the H electron shifts toward Cl. Note the polar nature of the HCl molecule, as shown by higher electron density *(red)* near the Cl end and lower electron density *(blue)* near the H end.

## Some Essential Redox Terminology

Chemists use some important terminology to describe the movement of electrons that occurs in oxidation-reduction reactions. **Oxidation** is the *loss* of electrons, and **reduction** is the *gain* of electrons. (The original meaning of *reduction* comes from the process of reducing large amounts of metal ore to smaller amounts of metal, but you'll see shortly why we use the term for the act of gaining.) For example, during the formation of magnesium oxide, Mg undergoes oxidation (electron loss) and $O_2$ undergoes reduction (electron gain). The loss and gain are simultaneous, but we can imagine them occurring in separate steps:

Oxidation (electron loss by Mg):     $Mg \longrightarrow Mg^{2+} + 2e^-$
Reduction (electron gain by $O_2$):    $\frac{1}{2}O_2 + 2e^- \longrightarrow O^{2-}$
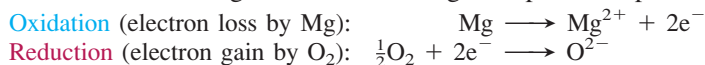
Since $O_2$ gained the electrons that Mg lost when it was oxidized, we say that *$O_2$ oxidized Mg*. Thus, $O_2$ is the **oxidizing agent,** the species doing the oxidizing. Similarly, since Mg gave up the electrons that $O_2$ gained when it was reduced, we say that *Mg reduced $O_2$*. Thus, Mg is the **reducing agent,** the species doing the reducing.

Once this relationship is clear, you will realize that *the oxidizing agent becomes reduced* because it removes the electrons (and thus gains them), whereas *the reducing agent becomes oxidized* because it gives up the electrons (and thus loses them). In the formation of HCl, $Cl_2$ oxidizes $H_2$ (H loses some electron charge and Cl gains it), which is the same as saying that $H_2$ reduces $Cl_2$. The reducing agent, $H_2$, is oxidized and the oxidizing agent, $Cl_2$, is reduced.

## Using Oxidation Numbers to Monitor the Movement of Electron Charge

Chemists have devised a useful "bookkeeping" system to monitor which atom loses electron charge and which atom gains it. Each atom in a molecule (or ionic compound) is assigned an **oxidation number (O.N.),** or *oxidation state,* the charge the atom would have **if** electrons were not shared but were transferred completely. Oxidation numbers are determined by the set of rules in Table 4.3. [Note that an oxidation number has the sign *before* the number (+2), whereas an ionic charge has the sign *after* the number (2+).]

---

**Table 4.3** **Rules for Assigning an Oxidation Number (O.N.)**

**General rules**

1.  For an atom in its elemental form (Na, $O_2$, $Cl_2$, etc.):   O.N. = 0
2.  For a monatomic ion:   O.N. = ion charge
3.  The sum of O.N. values for the atoms in a compound equals zero. The sum of O.N. values for the atoms in a polyatomic ion equals the ion's charge.

**Rules for specific atoms or periodic table groups**

1.  For Group 1A(1):    O.N. = +1 in all compounds
2.  For Group 2A(2):    O.N. = +2 in all compounds
3.  For hydrogen:       O.N. = +1 in combination with nonmetals
                        O.N. = −1 in combination with metals and boron
4.  For fluorine:       O.N. = −1 in all compounds
5.  For oxygen:         O.N. = −1 in peroxides
                        O.N. = −2 in all other compounds (except with F)
6.  For Group 7A(17):   O.N. = −1 in combination with metals, nonmetals (except O),
                          and other halogens lower in the group

## SAMPLE PROBLEM 4.6 Determining the Oxidation Number of an Element

**Problem** Determine the oxidation number (O.N.) of each element in these compounds:
(a) Zinc chloride  (b) Sulfur trioxide  (c) Nitric acid

**Plan** We apply Table 4.3, noting the general rules that the O.N. values in a compound add up to zero, and the O.N. values in a polyatomic ion add up to the ion's charge.

**Solution** (a) $ZnCl_2$. The sum of O.N.s for the monatomic ions in the compound must equal zero. The O.N. of the $Zn^{2+}$ ion is $+2$. The O.N. of each $Cl^-$ ion is $-1$, for a total of $-2$. The sum of O.N.s is $+2 + (-2)$, or 0.

(b) $SO_3$. The O.N. of each oxygen is $-2$, for a total of $-6$. Since the O.N.s must add up to zero, the O.N. of S is $+6$.

(c) $HNO_3$. The O.N. of H is $+1$, so the O.N.s of the $NO_3$ group must add up to $-1$ to give zero for the compound. The O.N. of each O is $-2$ for a total of $-6$. Therefore, the O.N. of N is $+5$.

**FOLLOW-UP PROBLEM 4.6** Determine the O.N. of each element in the following:
(a) Scandium oxide ($Sc_2O_3$)   (b) Gallium chloride ($GaCl_3$)
(c) Hydrogen phosphate ion   (d) Iodine trifluoride

**Figure 4.11** **Highest and lowest oxidation numbers of reactive main-group elements.** The A-group number shows the highest possible oxidation number (O.N.) for a main-group element. (Two important exceptions are O, which never has an O.N. of $+6$, and F, which never has an O.N. of $+7$.) For nonmetals *(yellow)* and metalloids *(green),* the A-group number minus 8 gives the lowest possible oxidation number.

The periodic table is a great help in learning the highest and lowest oxidation numbers of most main-group elements, as Figure 4.11 shows:

- For most main-group elements, the A-group number (1A, 2A, and so on) is the *highest* oxidation number (always positive) of any element in the group. The exceptions are O and F (see Table 4.3).
- For main-group nonmetals and some metalloids, the A-group number minus 8 is the *lowest* oxidation number (always negative) of any element in the group.

For example, the highest oxidation number of S (Group 6A) is $+6$, as in $SF_6$, and the lowest is $(6 - 8)$, or $-2$, as in FeS and other metal sulfides.

As you can see, the oxidation number for an element in a binary *ionic* compound has a value based in reality, because it usually equals the ionic charge. On the other hand, the oxidation number has a very unrealistic value for an element in a *covalent* compound (or polyatomic ion) because whole charges don't exist on the atoms in those species.

Another way to define a redox reaction is one in which *the oxidation numbers of the species change,* and the most important use of oxidation numbers is to monitor these changes:

- If a given atom has a higher (more positive or less negative) oxidation number in the product than it had in the reactant, the reactant molecule or ion that contained the atom was oxidized (lost electrons). Thus, *oxidation is represented by an increase in oxidation number.*
- If an atom has a lower (more negative or less positive) oxidation number in the product than it had in the reactant, the reactant molecule or ion that contained the atom was reduced (gained electrons). Thus, *the gain of electrons is represented by a decrease (a "reduction") in oxidation number.* (*Reduction,* as mentioned earlier, refers to an ore being "reduced" to the metal. The reducing agents used provide electrons that convert the metal ion to its elemental form.)

Figure 4.12 summarizes redox terminology. Since oxidation numbers are assigned according to the relative attraction of an atom for electrons, they are ultimately based on atomic properties, as you'll see in Chapters 8 and 9. (For the remainder of this section and the next, blue oxidation numbers represent oxidation, and red oxidation numbers indicate reduction.)

**Figure 4.12** **A summary of terminology for oxidation-reduction (redox) reactions.**

## SAMPLE PROBLEM 4.7 Recognizing Oxidizing and Reducing Agents

**Problem** Identify the oxidizing agent and reducing agent in each of the following:
(a) $2Al(s) + 3H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 3H_2(g)$
(b) $PbO(s) + CO(g) \longrightarrow Pb(s) + CO_2(g)$
(c) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$
**Plan** We first assign an oxidation number (O.N.) to each atom (or ion) based on the rules in Table 4.3. The reactant is the reducing agent if it contains an atom that is oxidized (O.N. increased from left side to right side of the equation). The reactant is the oxidizing agent if it contains an atom that is reduced (O.N. decreased).
**Solution (a)** Assigning oxidation numbers:

$$\overset{0}{2Al}(s) + \overset{+1}{3H_2}\overset{+6}{S}\overset{-2}{O_4}(aq) \longrightarrow \overset{+3}{Al_2}(\overset{+6}{S}\overset{-2}{O_4})_3(aq) + \overset{0}{3H_2}(g)$$

The O.N. of Al increased from 0 to +3 (Al lost electrons), so Al was oxidized; Al is the reducing agent.
The O.N. of H decreased from +1 to 0 (H gained electrons), so $H^+$ was reduced; $H_2SO_4$ is the oxidizing agent.
**(b)** Assigning oxidation numbers:

$$\overset{+2}{Pb}\overset{-2}{O}(s) + \overset{+2}{C}\overset{-2}{O}(g) \longrightarrow \overset{0}{Pb}(s) + \overset{+4}{C}\overset{-2}{O_2}(g)$$

Pb decreased its O.N. from +2 to 0, so PbO was reduced; PbO is the oxidizing agent.

C increased its O.N. from +2 to +4, so CO was oxidized; CO is the reducing agent.
In general, when a substance (such as CO) bonds to more O atoms (as in $CO_2$), it is oxidized; and when a substance (such as PbO) bonds to fewer O atoms (as in Pb), it is reduced.
**(c)** Assigning oxidation numbers:

$$\overset{0}{2H_2}(g) + \overset{0}{O_2}(g) \longrightarrow \overset{+1}{2H_2}\overset{-2}{O}(g)$$

$O_2$ was reduced (O.N. of O decreased from 0 to −2); $O_2$ is the oxidizing agent.

$H_2$ was oxidized (O.N. of H increased from 0 to +1); $H_2$ is the reducing agent.
Oxygen is always the oxidizing agent in a combustion reaction.
**Comment 1.** Compare the O.N. values in (c) with those in another common reaction that forms water—the net ionic equation for an acid-base reaction:

$$\overset{+1}{H^+}(aq) + \overset{+1}{O}\overset{-2}{H^-}(aq) \longrightarrow \overset{+1}{H_2}\overset{-2}{O}(l)$$

Note that the O.N. values remain the same on both sides of the acid-base equation. Therefore, *an acid-base reaction is* **not** *a redox reaction.*
**2.** If a substance occurs in its elemental form on one side of an equation, it can't possibly be in its elemental form on the other side, so the reaction must be a redox process. Notice that elements appear in all three cases above.

**FOLLOW-UP PROBLEM 4.7** Identify each oxidizing agent and each reducing agent:
(a) $2Fe(s) + 3Cl_2(g) \longrightarrow 2FeCl_3(s)$
(b) $2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(g)$
(c) $5CO(g) + I_2O_5(s) \longrightarrow I_2(s) + 5CO_2(g)$

## Balancing Redox Equations

It is essential to realize that *the reducing agent loses electrons and the oxidizing agent gains them* **simultaneously.** A chemical change can be an "oxidation-reduction reaction" but *not* an "oxidation reaction" *or* a "reduction reaction." The transferred electrons are never free, which means that we can balance a redox

reaction by making sure that *the number of electrons lost by the reducing agent equals the number of electrons gained by the oxidizing agent*.

Two methods used to balance redox equations are the *oxidation number* method and the *half-reaction* method. This section describes the oxidation number method in detail; the half-reaction method is covered in Chapter 21. (If your professor chooses to cover that section here, it is completely transferable with no loss in continuity.)

The **oxidation number method** for balancing redox equations consists of five steps that use the changes in oxidation numbers to generate balancing coefficients. The first two steps are identical to those in Sample Problem 4.7:

*Step 1.* Assign oxidation numbers to all elements in the reaction.
*Step 2.* From the changes in oxidation numbers, identify the oxidized and reduced species.
*Step 3.* Compute the number of electrons lost in the oxidation and gained in the reduction from the oxidation number changes. (Draw tie-lines between these atoms to show the changes.)
*Step 4.* Multiply one or both of these numbers by appropriate factors to make the electrons lost equal the electrons gained, and use the factors as balancing coefficients.
*Step 5.* Complete the balancing by inspection, adding states of matter.

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**SAMPLE PROBLEM 4.8** Balancing Redox Equations by the Oxidation Number Method

**Problem** Use the oxidation number method to balance the following equations:
(a) $Cu(s) + HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + NO_2(g) + H_2O(l)$
(b) $PbS(s) + O_2(g) \longrightarrow PbO(s) + SO_2(g)$
**Solution (a)** *Step 1.* Assign oxidation numbers to all elements:
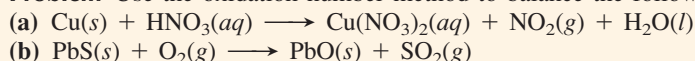
$$\overset{0}{Cu} + \overset{+1}{H}\overset{+5}{N}\overset{-2}{O_3} \longrightarrow \overset{+2}{Cu}(\overset{+5}{N}\overset{-2}{O_3})_2 + \overset{+4}{N}\overset{-2}{O_2} + \overset{+1}{H_2}\overset{-2}{O}$$
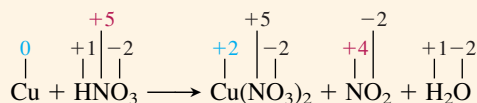
*Step 2.* Identify oxidized and reduced species. The O.N. of Cu increased from 0 (in Cu metal) to +2 (in $Cu^{2+}$); Cu was oxidized. The O.N. of N decreased from +5 (in $HNO_3$) to +4 (in $NO_2$); $HNO_3$ was reduced. Note that some $NO_3^-$ also acts as a spectator ion, appearing unchanged in the $Cu(NO_3)_2$; this is common in redox reactions.
*Step 3.* Compute $e^-$ lost and $e^-$ gained and draw tie-lines between the atoms. In the oxidation, $2e^-$ were lost from Cu. In the reduction, $1e^-$ was gained by N:


Copper in nitric acid

$$\overset{\text{loses } 2e^-}{Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O}$$
$$\underset{\text{gains } 1e^-}{}$$
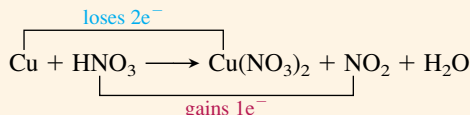
*Step 4.* Multiply by factors to make $e^-$ lost equal $e^-$ gained, and use the factors as coefficients. Cu lost $2e^-$, so the $1e^-$ gained by N should be multiplied by 2. We put the coefficient 2 before $NO_2$ and $HNO_3$:

$$Cu + 2HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + H_2O$$
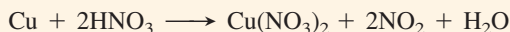
*Step 5.* Complete the balancing by inspection. Balancing N atoms requires a 4 in front of $HNO_3$ because two additional N atoms are in the $NO_3^-$ ions in $Cu(NO_3)_2$:

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + H_2O$$
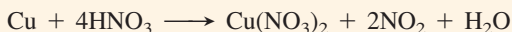
Then, balancing H atoms requires a 2 in front of $H_2O$, and we add states of matter:

$$Cu(s) + 4HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$
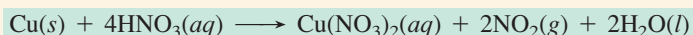
**Check**
Reactants (1 Cu, 4 H, 4 N, 12 O) $\longrightarrow$ products [1 Cu, 4 H, (2 + 2) N, (6 + 4 + 2) O]
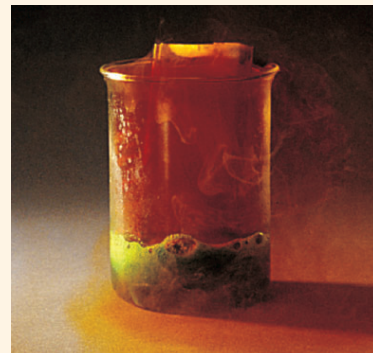
**(b)** *Step 1*. Assign oxidation numbers:

$$\overset{+2}{\underset{}{Pb}}\overset{-2}{S} + \overset{0}{O_2} \longrightarrow \overset{+2}{Pb}\overset{-2}{O} + \overset{+4}{S}\overset{-2}{O_2}$$
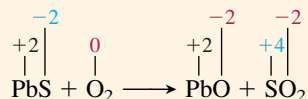
*Step 2*. Identify species that are oxidized and reduced. PbS was oxidized: the O.N. of S increased from $-2$ in PbS to $+4$ in $SO_2$. $O_2$ was reduced: the O.N. of O decreased from 0 in $O_2$ to $-2$ in PbO and in $SO_2$.

*Step 3*. Compute $e^-$ lost and $e^-$ gained and draw tie-lines. The S lost $6e^-$ and each O gained $2e^-$:

$$\overset{\text{loses } 6e^-}{PbS + O_2 \longrightarrow PbO + SO_2}$$
$$\underset{\text{gains } 4e^- \text{ (}2e^- \text{ per O)}}{}$$
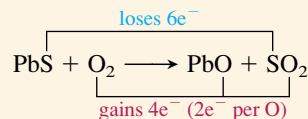
*Step 4*. Multiply by factors to make $e^-$ lost equal $e^-$ gained. The S atom loses $6e^-$, and each O in $O_2$ gains $2e^-$, for a total gain of $4e^-$. Thus, placing the coefficient $\frac{3}{2}$ before $O_2$ gives 3 O atoms that each gain $2e^-$, for a total gain of $6e^-$:

$$PbS + \tfrac{3}{2}O_2 \longrightarrow PbO + SO_2$$
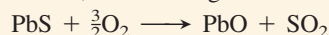
*Step 5*. Complete the balancing by inspection. The atoms are balanced, but all coefficients must be multiplied by 2 to obtain integers, and we add states of matter:

$$2PbS(s) + 3O_2(g) \longrightarrow 2PbO(s) + 2SO_2(g)$$

**Check** Reactants (2 Pb, 2 S, 6 O) $\longrightarrow$ products [2 Pb, 2 S, (2 + 4) O]

**FOLLOW-UP PROBLEM 4.8** Use the oxidation number method to balance the following: $K_2Cr_2O_7(aq) + HI(aq) \longrightarrow KI(aq) + CrI_3(aq) + I_2(s) + H_2O(l)$

## Redox Titrations

In an acid-base titration, a known concentration of base is used to find an unknown concentration of an acid (or vice versa). Similarly, in a redox titration, a known concentration of oxidizing agent is used to find an unknown concentration of reducing agent (or vice versa). This application of stoichiometry is used in a wide range of situations, including measuring the iron content in drinking water and the vitamin C content in fruits and vegetables.

The permanganate ion, $MnO_4^-$, is a common oxidizing agent in these titrations because it is strongly colored and, thus, also serves as an indicator. In Figure 4.13, $MnO_4^-$ is used to oxidize the oxalate ion, $C_2O_4^{2-}$, to determine its

**Figure 4.13 A redox titration.** The oxidizing agent in the buret, $KMnO_4$, is strongly colored, so it also serves as the indicator. When it reacts with the reducing agent $C_2O_4^{2-}$ in the flask, its color changes from deep purple to almost colorless *(left)*. When all the $C_2O_4^{2-}$ is oxidized, the next drop of $KMnO_4$ remains unreacted and turns the solution light purple *(right)*, signaling the end point of the titration.



Net ionic equation:

$$2\overset{+7}{Mn}O_4^-(aq) + 5\overset{+3}{C_2}O_4^{2-}(aq) + 16H^+(aq) \longrightarrow 2\overset{+2}{Mn}^{2+}(aq) + 10\overset{+4}{C}O_2(g) + 8H_2O(l)$$
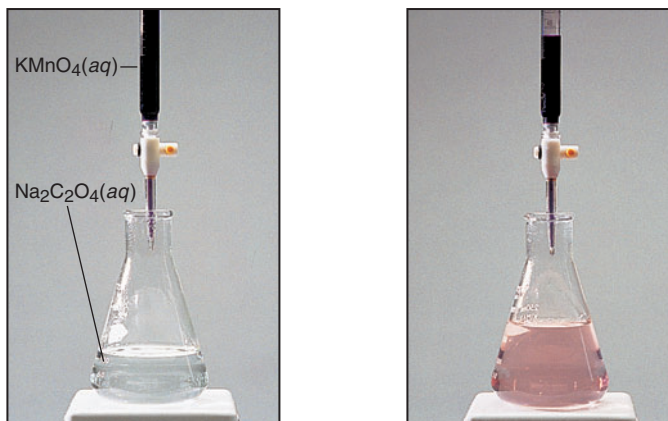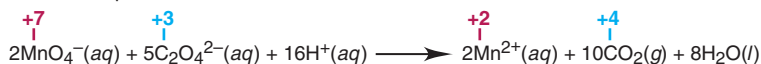
concentration. As long as any $C_2O_4^{2-}$ is present, it reduces the deep purple $MnO_4^-$ to the very faint pink (nearly colorless) $Mn^{2+}$ ion (Figure 4.13, *left*). As soon as all the available $C_2O_4^{2-}$ has been oxidized, the next drop of $MnO_4^-$ turns the solution light purple (Figure 4.13, *right*). This color change indicates the end point, the point at which the electrons lost by the oxidized species ($C_2O_4^{2-}$) equal the electrons gained by the reduced species ($MnO_4^-$). We then calculate the concentration of the $C_2O_4^{2-}$ solution from its known volume, the known volume and concentration of the $MnO_4^-$ solution, and the balanced equation.

Preparing a sample for a redox titration sometimes requires several laboratory steps. In Sample Problem 4.9, for instance, the $Ca^{2+}$ ion concentration of blood is determined. The $Ca^{2+}$ is first precipitated as calcium oxalate ($CaC_2O_4$), using excess sodium oxalate ($Na_2C_2O_4$). The precipitate is filtered and dilute $H_2SO_4$ dissolves it and releases the $C_2O_4^{2-}$ ion, which is then titrated with standardized $KMnO_4$ solution. After the $C_2O_4^{2-}$ concentration has been determined, it is used to find the original blood $Ca^{2+}$ concentration.

---

**SAMPLE PROBLEM 4.9** Finding an Unknown Concentration by a Redox Titration

**Problem** Calcium ion ($Ca^{2+}$) is required for blood to clot and for many other cell processes. An abnormal $Ca^{2+}$ concentration is indicative of disease. To measure the $Ca^{2+}$ concentration, 1.00 mL of human blood was treated with $Na_2C_2O_4$ solution. The resulting $CaC_2O_4$ precipitate was filtered and dissolved in dilute $H_2SO_4$. This solution required 2.05 mL of $4.88\times10^{-4}$ $M$ $KMnO_4$ to reach the end point. The unbalanced equation is

$KMnO_4(aq) + CaC_2O_4(s) + H_2SO_4(aq) \longrightarrow$
$$MnSO_4(aq) + K_2SO_4(aq) + CaSO_4(s) + CO_2(g) + H_2O(l)$$
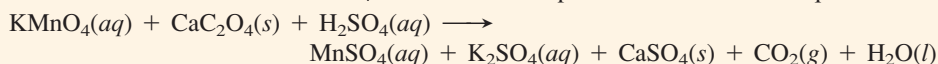
**(a)** Calculate the amount (mol) of $Ca^{2+}$.
**(b)** Calculate the $Ca^{2+}$ ion concentration expressed in units of mg $Ca^{2+}$/100 mL blood.

**(a) Calculating the moles of $Ca^{2+}$**

**Plan** As always, we first balance the equation. All the $Ca^{2+}$ ion in the 1.00-mL blood sample is precipitated and then dissolved in the $H_2SO_4$. We find the number of moles of $KMnO_4$ needed to reach the end point from the volume (2.05 mL) and molarity ($4.88\times10^{-4}$ $M$) and use the molar ratio to calculate the number of moles of $CaC_2O_4$ dissolved in the $H_2SO_4$. Then, from the chemical formula, we find moles of $Ca^{2+}$ ions.

**Solution** Balancing the equation:

$2KMnO_4(aq) + 5CaC_2O_4(s) + 8H_2SO_4(aq) \longrightarrow$
$$2MnSO_4(aq) + K_2SO_4(aq) + 5CaSO_4(s) + 10CO_2(g) + 8H_2O(l)$$
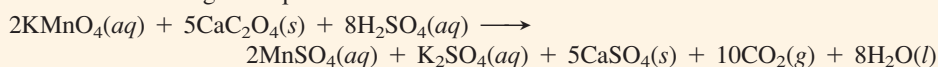
Converting from milliliters and molarity to moles of $KMnO_4$ to reach the end point:

$$\text{Moles of KMnO}_4 = 2.05 \text{ mL soln} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{4.88\times10^{-4} \text{ mol KMnO}_4}{1 \text{ L soln}}$$
$$= 1.00\times10^{-6} \text{ mol KMnO}_4$$

Converting from moles of $KMnO_4$ to moles of $CaC_2O_4$ titrated:

$$\text{Moles of CaC}_2\text{O}_4 = 1.00\times10^{-6} \text{ mol KMnO}_4 \times \frac{5 \text{ mol CaC}_2\text{O}_4}{2 \text{ mol KMnO}_4}$$
$$= 2.50\times10^{-6} \text{ mol CaC}_2\text{O}_4$$

Finding moles of $Ca^{2+}$ present:

$$\text{Moles of Ca}^{2+} = 2.50\times10^{-6} \text{ mol CaC}_2\text{O}_4 \times \frac{1 \text{ mol Ca}^{2+}}{1 \text{ mol CaC}_2\text{O}_4}$$
$$= \boxed{2.50\times10^{-6} \text{ mol Ca}^{2+}}$$

**Check** A very small volume of dilute $KMnO_4$ is needed, so $10^{-6}$ mol of $KMnO_4$ seems reasonable. The molar ratio of $5CaC_2O_4/2KMnO_4$ gives $2.5\times10^{-6}$ mol of $CaC_2O_4$ and thus $2.5\times10^{-6}$ mol of $Ca^{2+}$.

**(b) Expressing the $Ca^{2+}$ concentration as mg/100 mL blood**

**Plan** The amount in part (a) is the moles of $Ca^{2+}$ ion present in 1.00 mL of blood. We multiply by 100 to obtain the moles of $Ca^{2+}$ ion in 100 mL of blood and then use the atomic mass of Ca to convert to grams and then milligrams of $Ca^{2+}$/100 mL blood.

| Volume (L) of KMnO₄ solution |
| :---: |

multiply by $M$ (mol/L)

| Amount (mol) of KMnO₄ |
| :---: |

molar ratio

| Amount (mol) of CaC₂O₄ |
| :---: |

ratio of elements in chemical formula

| Amount (mol) of Ca²⁺ |
| :---: |

Amount (mol) of $Ca^{2+}$/1 mL blood

multiply by 100

Amount (mol) of $Ca^{2+}$/100 mL blood

multiply by $\mathcal{M}$ (g/mol)

Mass (g) of $Ca^{2+}$/100 mL blood

1 g = 1000 mg

Mass (mg) of $Ca^{2+}$/100 mL blood
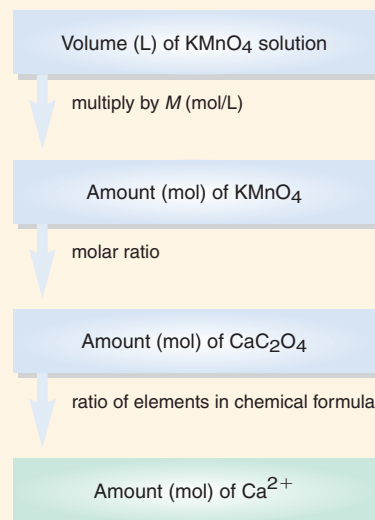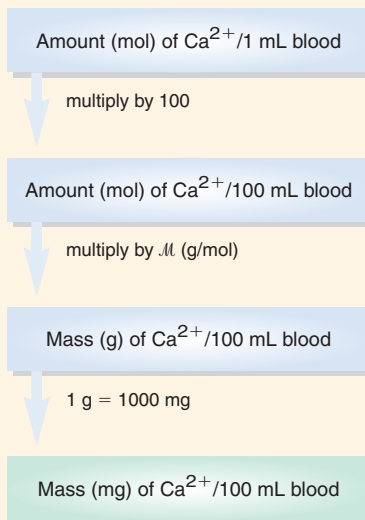
**Solution** Finding moles of $Ca^{2+}$/100 mL blood:

$$\text{Moles of } Ca^{2+}/100 \text{ mL blood} = \frac{2.50 \times 10^{-6} \text{ mol } Ca^{2+}}{1.00 \text{ mL blood}} \times 100$$
$$= 2.50 \times 10^{-4} \text{ mol } Ca^{2+}/100 \text{ mL blood}$$

Converting from moles of $Ca^{2+}$ to milligrams:

$$\text{Mass (mg) } Ca^{2+}/100 \text{ mL blood} = \frac{2.50 \times 10^{-4} \text{ mol } Ca^{2+}}{100 \text{ mL blood}} \times \frac{40.08 \text{ g } Ca^{2+}}{1 \text{ mol } Ca^{2+}} \times \frac{1000 \text{ mg}}{1 \text{ g}}$$
$$= 10.0 \text{ mg } Ca^{2+}/100 \text{ mL blood}$$

**Check** The relative amounts of $Ca^{2+}$ make sense. If there is $2.5 \times 10^{-6}$ mol/mL blood, there is $2.5 \times 10^{-4}$ mol/100 mL blood. A molar mass of about 40 g/mol for $Ca^{2+}$ gives $100 \times 10^{-4}$ g, or $10 \times 10^{-3}$ g/100 mL blood. It is easy to make an order-of-magnitude (power of 10) error in this type of calculation, so be sure to include all units.

**Comment 1.** The normal range of $Ca^{2+}$ concentration in a human adult is 9.0 to 11.5 mg $Ca^{2+}$/100 mL blood, so our value seems reasonable.

**2.** When blood is donated, the receiving bag contains $Na_2C_2O_4$ solution, which precipitates the $Ca^{2+}$ ion and, thus, prevents clotting.

**3.** A redox titration is analogous to an acid-base titration: in redox processes, electrons are lost and gained, whereas in acid-base processes, $H^+$ ions are lost and gained.

**FOLLOW-UP PROBLEM 4.9** A 2.50-mL sample of low-fat milk was treated with sodium oxalate, and the precipitate was filtered and dissolved in $H_2SO_4$. This solution required 6.53 mL of $4.56 \times 10^{-3}$ $M$ $KMnO_4$ to reach the end point.
**(a)** Calculate the molarity of $Ca^{2+}$ in the milk.
**(b)** What is the concentration of $Ca^{2+}$ in g/L? Is this value consistent with the typical value in milk of about 1.2 g $Ca^{2+}$/L?

## SECTION SUMMARY

When there is a net movement of electron charge from one reactant to another, a redox process takes place. The greater attraction of the electrons by one reactant over the other drives the reaction. Electron gain (reduction) and electron loss (oxidation) occur simultaneously. The redox process is tracked by assigning oxidation numbers to each atom in a reaction. The species that is oxidized (contains an atom that increases in oxidation number) is the reducing agent; the species that is reduced (contains an atom that decreases in oxidation number) is the oxidizing agent. Redox reactions can be balanced by keeping track of the changes in oxidation number. A redox titration is used to determine the concentration of either the oxidizing or the reducing agent from the known concentration of the other.

## 4.6 ELEMENTAL SUBSTANCES IN REDOX REACTIONS

As you've seen in this chapter, the modern approach to classifying reactions is based on the underlying chemical process—precipitation, acid-base, or redox. An older method that was once very common classified reactions by comparing the number of reactants with the number of products. By that approach, three types of reactions were recognized:

- *Combination reactions* were those in which two or more reactants formed one product:
$$X + Y \longrightarrow Z$$
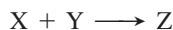
- *Decomposition reactions* were those in which one reactant formed two or more products:
$$Z \longrightarrow X + Y$$

- *Displacement reactions* were those in which the same number of substances were on both sides of the equation, but the atoms (or ions) exchanged places:
$$X + YZ \longrightarrow XZ + Y$$

One feature of this older classification that is especially relevant to oxidation-reduction processes is that *whenever an elemental substance appears as either reactant or product, the change is a redox reaction.*

There are many redox reactions that do *not* involve free elements, such as the one between $MnO_4^-$ and $C_2O_4^{2-}$ that we saw earlier, but we'll focus here on those types that *do* involve elements as free, uncombined substances.

**Combining Two Elements** Two elements may react to form binary ionic or covalent compounds. In every case, there is a net change in the distribution of electron charge, and so the elements change their oxidation numbers. Here are some important examples:

1. *Metal and nonmetal form an ionic compound.* Figure 4.14 shows the reaction between an alkali metal and a halogen on the observable and atomic scales. Note the change in oxidation numbers. As you can see, K is oxidized, so it is the reducing agent; $Cl_2$ is reduced, so it is the oxidizing agent.

Aluminum reacts with $O_2$, as does nearly every metal, to form ionic oxides:

$$\overset{0}{4Al}(s) + \overset{0}{3O_2}(g) \longrightarrow \overset{+3 \; -2}{2Al_2O_3}(s)$$



$$\overset{0}{2K(s)} \quad + \quad \overset{0}{Cl_2(g)} \quad \longrightarrow \quad \overset{+1 \; -1}{2KCl(s)}$$
Potassium          Chlorine                          Potassium chloride
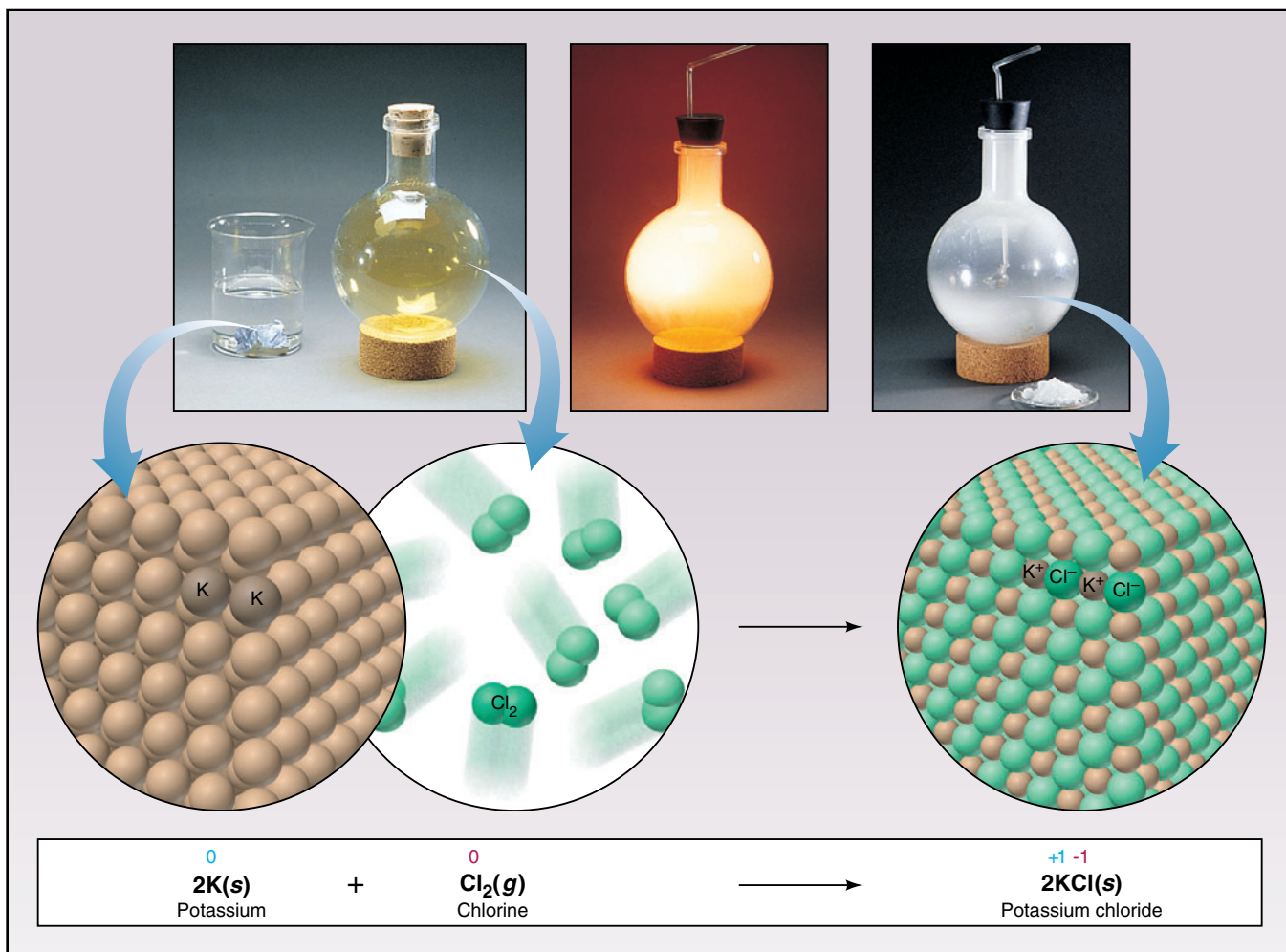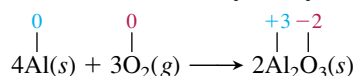
**Figure 4.14 Combining elements to form an ionic compound.** When the metal potassium and the nonmetal chlorine react, they form the solid ionic compound potassium chloride. The photos *(top)* present the view the chemist sees in the laboratory. The blow-up arrows lead to an atomic-scale view *(middle);* the stoichiometry is indicated by the more darkly colored spheres. The balanced redox equation is shown with oxidation numbers *(bottom).*

2. *Two nonmetals form a covalent compound.* In one of thousands of examples, ammonia forms from nitrogen and hydrogen in a reaction that occurs in industry on an enormous scale:

$$\overset{0}{N_2}(g) + 3\overset{0}{H_2}(g) \longrightarrow 2\overset{-3}{\underset{}{N}}\overset{+1}{H_3}(g)$$
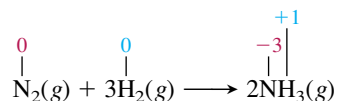
Halogens form many compounds with other nonmetals, as in the formation of phosphorus trichloride, a major reactant in the production of pesticides and other organic compounds:

$$\overset{0}{P_4}(s) + 6\overset{0}{Cl_2}(g) \longrightarrow 4\overset{+3}{P}\overset{-1}{Cl_3}(l)$$
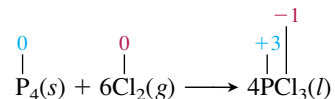
Nearly every nonmetal reacts with $O_2$ to form a covalent oxide, as when nitrogen monoxide forms at the very high temperatures created in air by lightning:

$$\overset{0}{N_2}(g) + \overset{0}{O_2}(g) \longrightarrow 2\overset{+2}{N}\overset{-2}{O}(g)$$
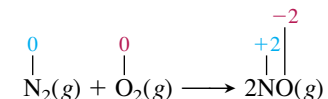
**Combining Compound and Element** Many binary covalent compounds react with nonmetals to form larger compounds. Many nonmetal oxides react with additional $O_2$ to form "higher" oxides (those with more O atoms in each molecule). For example, a key step in the generation of urban smog is

$$2\overset{+2}{N}\overset{-2}{O}(g) + \overset{0}{O_2}(g) \longrightarrow 2\overset{+4}{N}\overset{-2}{O_2}(g)$$
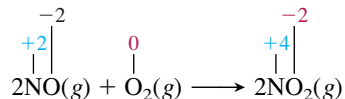
Similarly, many nonmetal halides combine with additional halogen:

$$\overset{+3}{P}\overset{-1}{Cl_3}(l) + \overset{0}{Cl_2}(g) \longrightarrow \overset{+5}{P}\overset{-1}{Cl_5}(s)$$
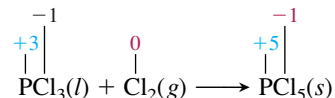
**Decomposing Compounds into Elements** A decomposition reaction occurs when a reactant absorbs enough energy for one or more of its bonds to break. The energy can take many forms—heat, electricity, light, mechanical, and so forth—but we'll focus in this discussion on heat and electricity. The products are either elements or elements and smaller compounds. Here are some common examples:

1. *Thermal decomposition.* When the energy absorbed is heat, the reaction is a thermal decomposition. (A Greek *delta*, $\Delta$, above a reaction arrow indicates that heat is required for the reaction.) Many metal oxides, chlorates, and perchlorates release oxygen when strongly heated. Figure 4.15 shows the decomposition, on the macroscopic and atomic scales, of mercury(II) oxide, used by Lavoisier and Priestley in their classic experiments. Heating potassium chlorate is a modern method for forming small amounts of oxygen in the laboratory:

$$2\overset{+1}{K}\overset{+5}{Cl}\overset{-2}{O_3}(s) \overset{\Delta}{\longrightarrow} 2\overset{+1}{K}\overset{-1}{Cl}(s) + 3\overset{0}{O_2}(g)$$
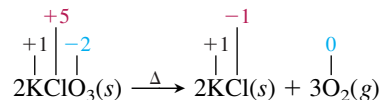
Notice that, in these cases, the lone reactant is the oxidizing *and* the reducing agent. For example, with HgO, $O^{2-}$ reduces $Hg^{2+}$ (and $Hg^{2+}$ oxidizes $O^{2-}$).
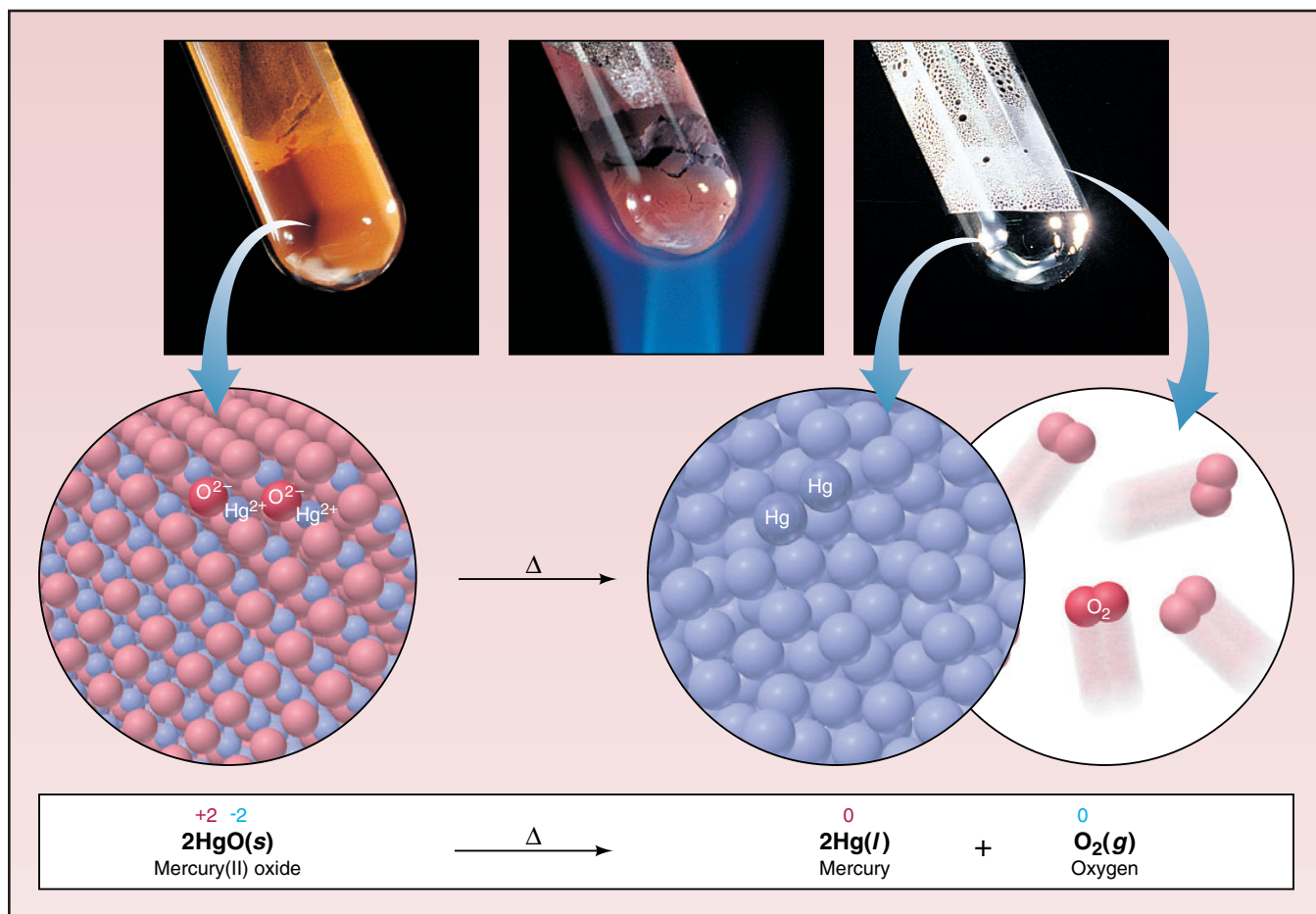
**Figure 4.15 Decomposing a compound to its elements.** Heating solid mercury(II) oxide decomposes it to liquid mercury and gaseous oxygen: the macroscopic (laboratory) view *(top);* the atomic-scale view, with the more darkly colored spheres showing the stoichiometry *(middle);* and the balanced redox equation *(bottom).*

2. *Electrolytic decomposition.* In many cases, a compound can absorb electrical energy and decompose into its elements, in a process known as *electrolysis.* Observation of the electrolysis of water was crucial in the establishment of atomic masses:

$$\overset{+1-2}{2H_2O}(l) \xrightarrow{\text{electricity}} \overset{0}{2H_2}(g) + \overset{0}{O_2}(g)$$
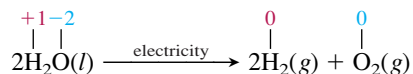
Many active metals, such as sodium, magnesium, and calcium, are produced industrially by electrolysis of their molten halides:

$$\overset{+2-1}{MgCl_2}(l) \xrightarrow{\text{electricity}} \overset{0}{Mg}(l) + \overset{0}{Cl_2}(g)$$
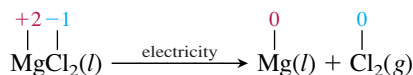
(We'll examine the details of electrolysis in Chapters 21 and 22.)

**Displacing One Element by Another; Activity Series** As was pointed out earlier, displacement reactions have the same number of reactants as products. We mentioned double-displacement (metathesis) reactions in discussing precipitation and acid-base reactions. Here we consider so-called *single-displacement* reactions, which are all oxidation-reduction processes. They occur when one atom displaces the ion of a different atom from solution. When the reaction involves metals, the atom reduces the ion; when it involves nonmetals (specifically halogens), the atom oxidizes the ion. Chemists rank various elements into activity series—one for metals and one for halogens—in order of their ability to displace one another.

1. *The activity series of the metals*. Metals can be ranked by their ability to displace $H_2$ from various sources or to displace one another from solution.

(a) *A metal displaces $H_2$ from water or acid*. The most reactive metals, such as those from Group 1A(1) and Ca, Sr, and Ba from Group 2A(2), displace $H_2$ from water, and they do so vigorously. Figure 4.16 shows this reaction for lithium. Heat is needed to speed the reaction of slightly less reactive metals, such as Al and Zn, so these displace $H_2$ from steam:

$$\overset{0}{2Al}(s) + \overset{+1\,-2}{6H_2O}(g) \longrightarrow \overset{+3\,-2\quad\overset{+1}{\phantom{|}}}{2Al(OH)_3}(s) + \overset{0}{3H_2}(g)$$



$$\overset{0}{\textbf{2Li}(s)} \quad + \quad \overset{+1\ -2}{\textbf{2H}_2\textbf{O}(l)} \quad \longrightarrow \quad \overset{+1\ -2+1}{\textbf{2LiOH}(aq)} \quad + \quad \overset{0}{\textbf{H}_2(g)}$$

Lithium             Water                          Lithium hydroxide          Hydrogen
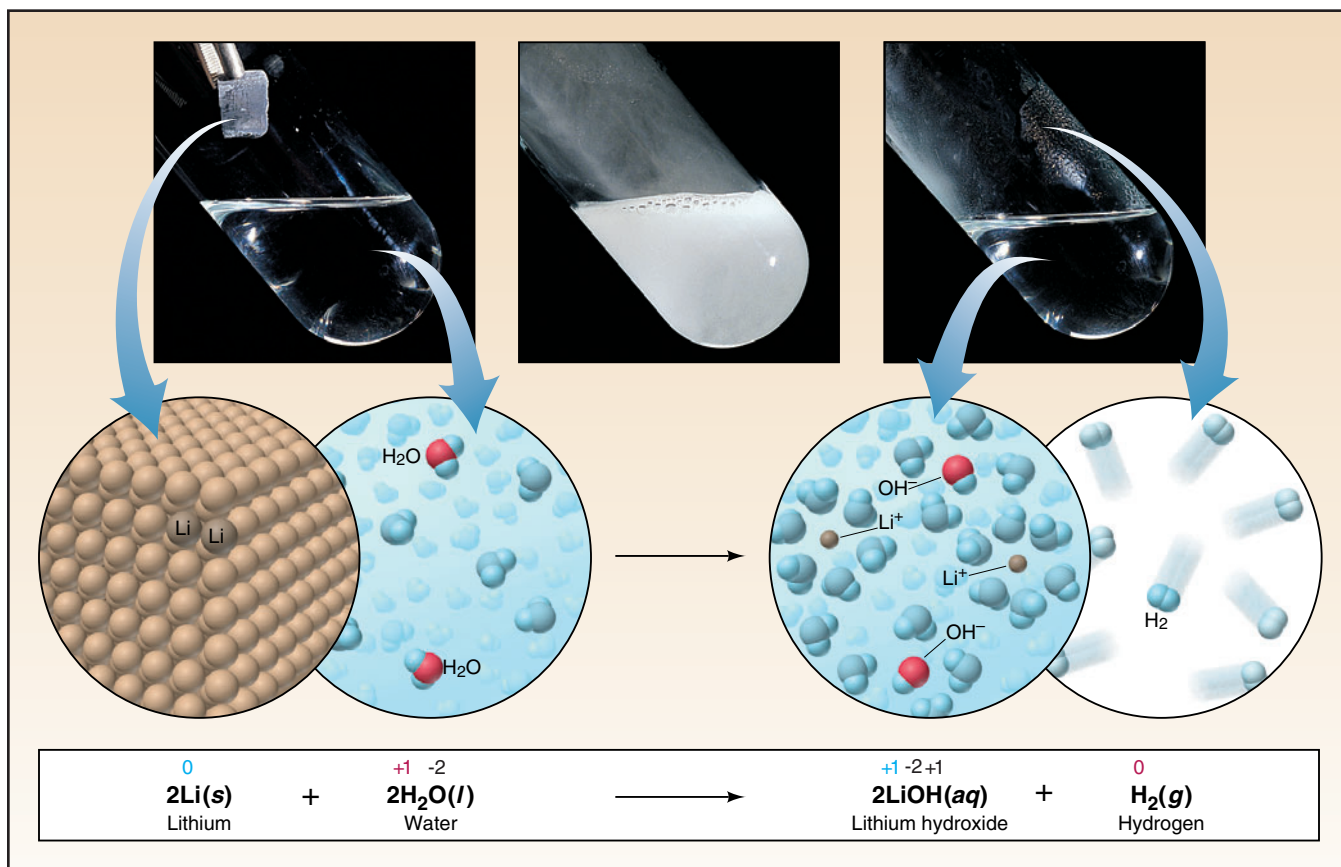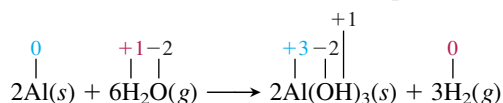
**Figure 4.16** **An active metal displacing hydrogen from water.** Lithium displaces hydrogen from water in a vigorous reaction that yields an aqueous solution of lithium hydroxide and hydrogen gas, as shown on the macroscopic scale *(top),* at the atomic scale *(middle),* and as a balanced equation *(bottom).* (For clarity, the atomic-scale view of water has been greatly simplified, and only water molecules involved in the reaction are colored red and blue.)

Still less reactive metals, such as nickel and tin, do not react with water but *do* react with acids, from which $H_2$ is displaced more easily (Figure 4.17). Here is the net ionic equation:

$$\overset{0}{Ni}(s) + 2\overset{+1}{H^+}(aq) \longrightarrow \overset{+2}{Ni^{2+}}(aq) + \overset{0}{H_2}(g)$$
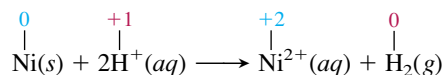
Notice that in all such reactions, the metal is the reducing agent (O.N. of metal increases), and water or acid is the oxidizing agent (O.N. of H decreases). The least reactive metals, such as silver and gold, cannot displace $H_2$ from any source.

(b) *A metal displaces another metal ion from solution.* Direct comparisons of metal reactivity are clearest in these reactions. For example, zinc metal displaces copper(II) ion from copper(II) sulfate solution, as the total ionic equation shows:

$$\overset{+2}{Cu^{2+}}(aq) + \overset{+6}{\underset{-2}{SO_4}}{}^{2-}(aq) + \overset{0}{Zn}(s) \longrightarrow \overset{0}{Cu}(s) + \overset{+2}{Zn^{2+}}(aq) + \overset{+6}{\underset{-2}{SO_4}}{}^{2-}(aq)$$
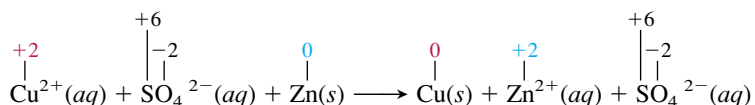
Figure 4.18 demonstrates in atomic detail that copper metal can displace silver ion from solution. Thus, zinc is more reactive than copper, which is more reactive than silver.



**Figure 4.17** The displacement of $H_2$ from acid by nickel.
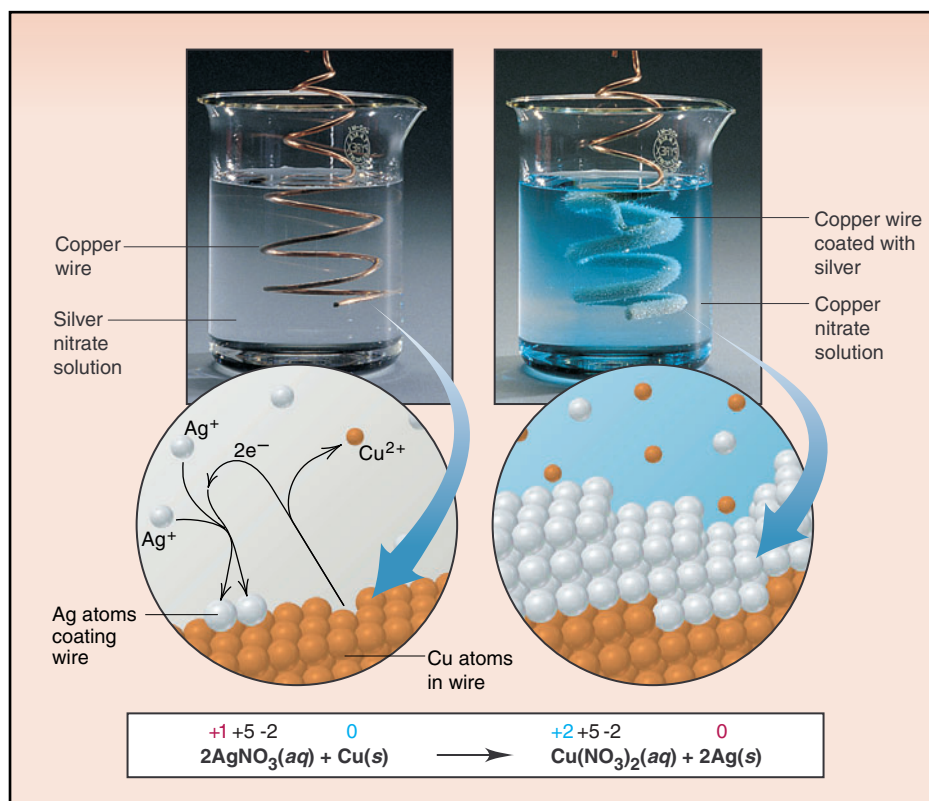


**Figure 4.18** **Displacing one metal with another.** More reactive metals can displace less reactive metals from solution. In this reaction, Cu atoms become $Cu^{2+}$ ions and leave the wire, as they transfer electrons to two $Ag^+$ ions that become Ag atoms and coat the wire. The reaction is depicted as the laboratory view *(top),* the atomic-scale view *(middle),* and the balanced redox equation *(bottom).*

**Figure 4.19** **The activity series of the metals.** This list of metals (and $H_2$) is arranged with the most active metal (strongest reducing agent) at the top and the least active metal (weakest reducing agent) at the bottom. The four metals below $H_2$ cannot displace it from any source. (The ranking refers to behavior in aqueous solution.)

The results of many such reactions between metals and water, aqueous acids, and metal-ion solutions form the basis of the **activity series of the metals.** It is shown in Figure 4.19 as a list of elements arranged such that elements higher on the list are stronger reducing agents than elements lower down. In other words, for those that are stable in water, elements higher on the list can reduce aqueous ions of elements lower down. The list also shows whether the metal can displace $H_2$ and, if so, from which source. Using just the examples we've discussed, you can see that Li, Al, and Ni lie above $H_2$, while Ag lies below it, and that Zn lies above Cu, which lies above Ag.

2. *The activity series of the halogens*. Reactivity decreases down Group 7A(17), so we can arrange the halogens into their own activity series:

$$F_2 > Cl_2 > Br_2 > I_2$$
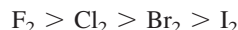
A halogen higher in the periodic table is a stronger oxidizing agent than one lower down. Thus, chlorine can oxidize bromide ions or iodide ions from solution, and bromine can oxidize iodide ions. Here, chlorine displaces bromine:

$$\overset{-1}{2Br^-}(aq) + \overset{0}{Cl_2}(aq) \longrightarrow \overset{0}{Br_2}(aq) + \overset{-1}{2Cl^-}(aq)$$
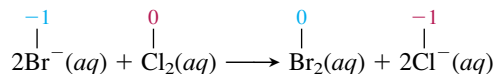
**Combustion Reactions** Combustion is the process of combining with oxygen, usually with the release of large amounts of heat and light, often as a flame. 🔴 Burning in air is a common example. Even though they do not always fall neatly into classes based on the number of reactants and products, *all combustion reactions are redox processes* because elemental oxygen is a reactant:

$$S_8(s) + 8O_2(g) \longrightarrow 8SO_2(g)$$
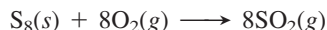
The combustion reactions we use to produce energy involve organic mixtures such as coal, gasoline, and natural gas as reactants. These mixtures consist of sub-

stances with many carbon-carbon and carbon-hydrogen bonds. During the reaction, these bonds break, and each C and H atom combines with oxygen. Therefore, the products typically consist of $CO_2$ and $H_2O$. The combustion of the hydrocarbon butane, which is used in cigarette lighters, is typical:

$$2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(g)$$
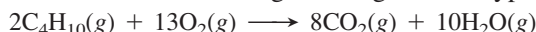
Cellular *respiration* can be thought of as a combustion process that occurs within our bodies' cells—fortunately without flame—when we "burn" organic food-stuffs, such as glucose, for energy:

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(g) + energy$$

---

**SAMPLE PROBLEM 4.10** Identifying the Type of Redox Reaction

**Problem** Classify each of the following redox reactions as a combination, decomposition, or displacement reaction, write a balanced molecular equation for each, as well as total and net ionic equations for part (c), and identify the oxidizing and reducing agents:
(a) Magnesium(s) + nitrogen(g) $\longrightarrow$ magnesium nitride(s)
(b) Hydrogen peroxide(l) $\longrightarrow$ water + oxygen gas
(c) Aluminum(s) + lead(II) nitrate(aq) $\longrightarrow$ aluminum nitrate(aq) + lead(s)
**Plan** To decide on reaction type, recall that combination reactions produce fewer products than reactants, decomposition reactions produce more products, and displacement reactions have the same number of reactants and products. The oxidizing number (O.N.) becomes more positive for the reducing agent and less positive for the oxidizing agent.
**Solution (a)** Combination: two substances form one. This reaction occurs, along with formation of magnesium oxide, when magnesium burns in air:

$$\overset{0}{3Mg}(s) + \overset{0}{N_2}(g) \longrightarrow \overset{+2\ -3}{Mg_3N_2}(s)$$
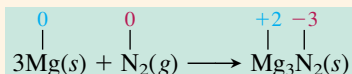
Mg is the reducing agent; $N_2$ is the oxidizing agent.

**(b)** Decomposition: one substance forms two. This reaction occurs within every bottle of this common household antiseptic. Hydrogen peroxide is very unstable and breaks down from heat, light, or just shaking:

$$\overset{+1\ -1}{2H_2O_2}(l) \longrightarrow \overset{+1\ -2}{2H_2O}(l) + \overset{0}{O_2}(g)$$
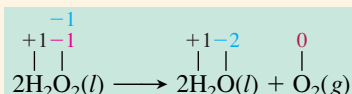
$H_2O_2$ is both the oxidizing *and* the reducing agent. The O.N. of O in peroxides is $-1$. It increases to 0 in $O_2$ and decreases to $-2$ in $H_2O$.

**(c)** Displacement: two substances form two. As Figure 4.19 shows, Al is more active than Pb and, thus, displaces it from aqueous solution:

$$\overset{0}{2Al}(s) + \overset{+2\ +5\ -2}{3Pb(NO_3)_2}(aq) \longrightarrow \overset{+3\ +5\ -2}{2Al(NO_3)_3}(aq) + \overset{0}{3Pb}(s)$$
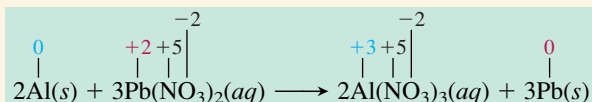
Al is the reducing agent; $Pb(NO_3)_2$ is the oxidizing agent.
The total ionic equation is

$$2Al(s) + 3Pb^{2+}(aq) + 6NO_3^-(aq) \longrightarrow 2Al^{3+}(aq) + 6NO_3^-(aq) + 3Pb(s)$$

The net ionic equation is

$$2Al(s) + 3Pb^{2+}(aq) \longrightarrow 2Al^{3+}(aq) + 3Pb(s)$$
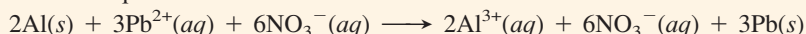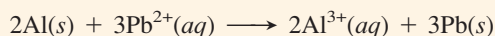
**FOLLOW-UP PROBLEM 4.10** Classify each of the following redox reactions as a combination, decomposition, or displacement reaction, write a balanced molecular equation for each, as well as total and net ionic equations for parts (b) and (c), and identify the oxidizing and reducing agents:
(a) $S_8(s) + F_2(g) \longrightarrow SF_4(g)$
(b) $CsI(aq) + Cl_2(aq) \longrightarrow CsCl(aq) + I_2(aq)$
(c) $Ni(NO_3)_2(aq) + Cr(s) \longrightarrow Cr(NO_3)_3(aq) + Ni(s)$

**SECTION SUMMARY**
Any reaction that includes a free element as reactant or product is a redox reaction. In combination reactions, elements combine to form a compound, or a compound and an element combine. Decomposition of compounds by absorption of heat or electricity can form elements or a compound and an element. In displacement reactions, one element displaces another from solution. Activity series rank elements in order of reactivity. The activity series of the metals ranks metals by their ability to displace $H_2$ from water, steam, acid or to displace one another from solution. Combustion typically releases heat and light energy through reaction of a substance with $O_2$.

## 4.7 REVERSIBLE REACTIONS: AN INTRODUCTION TO CHEMICAL EQUILIBRIUM

So far, we have viewed reactions as occurring from "left to right," from reactants to products and continuing until they are complete, that is, until the limiting reactant is used up. However, many reactions seem to stop before this happens. The reason is that another reaction, the reverse of the first one, is also taking place. The forward (left-to-right) reaction has not stopped, but the reverse (right-to-left) reaction is taking place at the same rate. Therefore, *no further changes occur in the amounts of reactants or products.* At this point, the reaction mixture has reached **dynamic equilibrium.** On the macroscopic scale, the reaction is *static,* but it is *dynamic* on the molecular scale. In principle, all reactions are reversible and will eventually reach dynamic equilibrium as long as all products remain available for the reverse reaction.

Let's examine equilibrium with a particular set of substances. Calcium carbonate breaks down when heated to calcium oxide and carbon dioxide:

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g) \quad \text{[breakdown]}$$
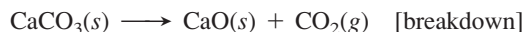
It can also form when calcium oxide and carbon dioxide react:

$$CaO(s) + CO_2(g) \longrightarrow CaCO_3(s) \quad \text{[formation]}$$
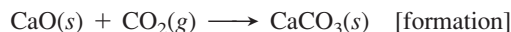
The formation is just the reverse of the breakdown. Suppose we place 10 g of $CaCO_3$ in an *open* steel reaction flask and heat it to around 900°C, as shown in Figure 4.20A. The $CaCO_3$ starts breaking down to CaO and $CO_2$, and the $CO_2$ escapes from the open flask. The reaction goes to completion because the reverse reaction (formation) can occur only if $CO_2$ is present.

In Figure 4.20B, we perform the same experiment in a *closed* steel flask, so that the $CO_2$ remains in contact with the CaO. The breakdown (forward reaction) begins, but at first, when very little $CaCO_3$ has broken down, very little $CO_2$ and CaO are present; thus, the formation (reverse reaction) just barely begins. As the $CaCO_3$ continues to break down, the amounts of $CO_2$ and CaO in the flask increase. They react with each other more frequently, and the formation occurs a bit faster. As the amounts of CaO and $CO_2$ increase, the formation reaction gradually speeds up. Eventually, the reverse reaction (formation) happens just as fast as the forward reaction (breakdown), and the amounts of $CaCO_3$, CaO, and $CO_2$ no longer change: the system has



**A Nonequilibrium system**

$CaCO_3(s)$ → $CaO(s) + CO_2(g)$

**B Equilibrium system**

$CaCO_3(s)$ → $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
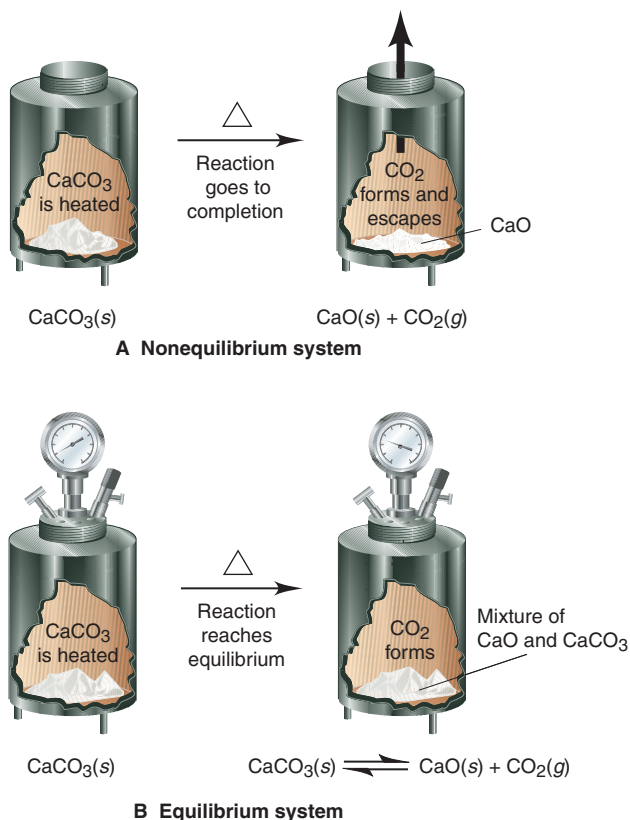
**Figure 4.20 The equilibrium state. A,** In an *open* steel reaction chamber, strong heating breaks down $CaCO_3$ completely because the product $CO_2$ escapes and is not present to react with the other product, CaO. **B,** When $CaCO_3$ breaks down in a *closed* chamber, the $CO_2$ *is* present to react with CaO and re-form $CaCO_3$ in a reaction that is the reverse of the breakdown. At a given temperature, no further change in the amounts of products and reactants means that the reaction has reached equilibrium.

reached equilibrium. We indicate this with a pair of arrows pointing in opposite directions:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Bear in mind that equilibrium can be established only when *all the substances involved are kept in contact with each other.* The breakdown of $CaCO_3$ goes to completion in the open flask because the $CO_2$ escapes.

Aqueous acid-base reactions that form a gaseous product go to completion in an open flask for the same reason: the gas escapes, so the reverse reaction cannot take place. Precipitation and other acid-base reactions also go largely to completion, even though all the products remain in the reaction vessel. In those cases, the *ions* are not available to any appreciable extent to participate in the reverse process, because they are tied up either as an insoluble solid (precipitation) or as water molecules (acid-base).

The concept of reaction reversibility also relates to the behavior of acids and bases that are weak electrolytes, that is, those that dissociate into ions only to a small extent. The dissociation quickly becomes balanced by a reassociation, such that equilibrium is reached with very few ions present. For example, when acetic acid dissolves in water, some of the $CH_3COOH$ molecules transfer a proton to $H_2O$ and form $H_3O^+$ and $CH_3COO^-$ ions. As more of these ions form, they react with each other more often to re-form acetic acid and water:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

In fact, in 0.1 *M* $CH_3COOH$ at 25°C, only about 1.3% of the acid molecules are dissociated at any given moment. Similarly, the weak base ammonia reacts with water to form ions. As the product ions interact, they re-form ammonia and water again, and the rates of the reverse and forward reactions soon balance:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Thus, as you've seen, some reactions proceed very little before they reach equilibrium, while others proceed essentially to completion. And even two reactions that proceed very little, such as those we've just discussed between acetic acid or ammonia and water, proceed to different extents. So, a fundamental question arises: why does each process, even under the same conditions, reach equilibrium with its own particular ratio of product concentrations to reactant concentrations? The full answer will have to wait until later chapters, but we can hint at the factors here. The energy available for a reaction to occur is called its *free energy*. The point at which a process reaches equilibrium occurs when the reaction mixture has its lowest free energy. Two components of this free energy are the heat that a reaction releases (or absorbs) and the change in orderliness of the particles—solids are more orderly than gases, pure substances are more orderly than solutions, and so forth. A particular combination of these factors, discussed quantitatively in Chapter 20, determines the free energy and, thus, the equilibrium point for a given mixture of reactants and products at a given temperature.

Many aspects of dynamic equilibrium are relevant to natural systems, from the cycling of water in the environment to the balance of lion and antelope on the plains of Africa to the nuclear processes occurring in stars. We examine equilibrium in chemical and physical systems in Chapters 12, 13, and 17 through 21.

## SECTION SUMMARY

Every reaction is reversible if all the substances are kept in contact with one another. As the amounts of products increase, the reactants begin to re-form. When the reverse reaction happens as rapidly as the forward reaction, the amounts of the substances no longer change, and the reaction mixture has reached dynamic equilibrium. A reaction goes to completion if a product is removed from the system (as a gas) or exists in a form that prevents it from reacting (precipitate or undissociated molecule). Weak acids and bases reach equilibrium in water with a very small proportion of their molecules dissociated.

## Chapter Perspective

*Classifying facts is the first step toward understanding them, and this chapter classified many of the most important facts of reaction chemistry into three major processes—precipitation, acid-base, and oxidation-reduction. We also examined the great influence that water has on reaction chemistry and introduced the state of dynamic equilibrium, which is related to the central question of why physical and chemical changes occur. All these topics appear again at many places in the text.*

*In the next chapter, our focus changes to the physical behavior of gases. You'll find that your growing appreciation of events on the molecular level has become indispensable for understanding the nature of the three physical states.*

# For Review and Reference (Numbers in parentheses refer to pages, unless noted otherwise.)

## Learning Objectives

**Relevant section and/or sample problem (SP) numbers appear in parentheses.**

### Understand These Concepts

1. How water dissolves ionic compounds and dissociates them into ions (4.1)
2. Distinguish between the species present when ionic and covalent compounds dissolve in water; distinguish between strong and weak electrolytes (4.1)
3. The use of ionic equations to specify the essential nature of an aqueous reaction (4.2)
4. The driving force for aqueous ionic reactions (4.3, 4.4, 4.5)
5. How to decide whether a precipitation reaction occurs (4.3)
6. The main distinction between strong and weak aqueous acids and bases (4.4)
7. The essential character of aqueous acid-base reactions as proton-transfer processes (4.4)
8. The importance of net movement of electrons in the redox process (4.5)
9. The relation between change in oxidation number and identity of oxidizing and reducing agents (4.5)
10. The presence of elements in some important types of redox reactions: combination, decomposition, displacement (4.6)

11. The balance between forward and reverse rates of a chemical reaction that leads to dynamic equilibrium; why some acids and bases are weak (4.7)

### Master These Skills

1. Using the formula of a compound to find the number of moles of ions in solution (SP 4.1)
2. Determining the concentration of $H^+$ ion in an aqueous acid solution (SP 4.2)
3. Predicting whether a precipitation reaction occurs (SP 4.3)
4. Writing ionic equations to describe precipitation and acid-base reactions (SPs 4.3 and 4.4)
5. Calculating an unknown concentration from an acid-base or redox titration (SPs 4.5 and 4.9)
6. Determining the oxidation number of any element in a compound (SP 4.6)
7. Identifying the oxidizing and reducing agents in a redox reaction (SP 4.7)
8. Balancing redox equations (SP 4.8)
9. Identifying combination, decomposition, and displacement redox reactions (SP 4.10)

## Key Terms

**Section 4.1**
electrolyte (132)
solvated (132)
polar molecule (134)
nonelectrolyte (135)

**Section 4.2**
molecular equation (137)
total ionic equation (138)
spectator ion (138)
net ionic equation (138)

**Section 4.3**
precipitation reaction (138)
precipitate (138)
metathesis reaction (139)

**Section 4.4**
acid-base reaction (140)
neutralization reaction (140)
acid (141)
base (141)
salt (142)

titration (143)
equivalence point (143)
end point (143)

**Section 4.5**
oxidation-reduction
  (redox) reaction (147)
oxidation (148)
reduction (148)
oxidizing agent (148)
reducing agent (148)

oxidation number (O.N.)
  (or oxidation state) (148)
oxidation number
  method (151)

**Section 4.6**
activity series of the
  metals (160)

**Section 4.7**
dynamic equilibrium (162)

## Highlighted Figures and Tables

These figures (F) and tables (T) provide a quick review of key ideas. Entries in color contain frequently used data.

## Brief Solutions to Follow-up Problems

**4.1** (a) $KClO_4(s) \xrightarrow{H_2O} K^+(aq) + ClO_4^-(aq)$;
2 mol of $K^+$ and 2 mol of $ClO_4^-$
(b) $Mg(C_2H_3O_2)_2(s) \xrightarrow{H_2O} Mg^{2+}(aq) + 2C_2H_3O_2^-(aq)$;
2.49 mol of $Mg^{2+}$ and 4.97 mol of $C_2H_3O_2^-$
(c) $(NH_4)_2CrO_4(s) \xrightarrow{H_2O} 2NH_4^+(aq) + CrO_4^{2-}(aq)$;
6.24 mol of $NH_4^+$ and 3.12 mol of $CrO_4^{2-}$
(d) $NaHSO_4(s) \xrightarrow{H_2O} Na^+(aq) + HSO_4^-(aq)$;
0.73 mol of $Na^+$ and 0.73 mol of $HSO_4^-$

**4.2** Moles of $H^+ = 451 \text{ mL} \times \dfrac{1 \text{ L}}{10^3 \text{ mL}}$

$\times \dfrac{3.20 \text{ mol HBr}}{1 \text{ L soln}} \times \dfrac{1 \text{ mol H}^+}{1 \text{ mol HBr}}$

$= 1.44 \text{ mol H}^+$

**4.3** (a) $Fe^{3+}(aq) + 3Cl^-(aq) + 3Cs^+(aq) + PO_4^{3-}(aq) \longrightarrow$
$FePO_4(s) + 3Cl^-(aq) + 3Cs^+(aq)$
$Fe^{3+}(aq) + PO_4^{3-}(aq) \longrightarrow FePO_4(s)$
(b) $2Na^+(aq) + 2OH^-(aq) + Cd^{2+}(aq) + 2NO_3^-(aq) \longrightarrow$
$2Na^+(aq) + 2NO_3^-(aq) + Cd(OH)_2(s)$
$2OH^-(aq) + Cd^{2+}(aq) \longrightarrow Cd(OH)_2(s)$
(c) No reaction occurs
(d) $2Ag^+(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2Cl^-(aq) \longrightarrow$
$2AgCl(s) + BaSO_4(s)$
Total and net ionic equations are identical.
**4.4** $Ca(OH)_2(aq) + 2HNO_3(aq) \longrightarrow$
$Ca(NO_3)_2(aq) + 2H_2O(l)$
$Ca^{2+}(aq) + 2OH^-(aq) + 2H^+(aq) + 2NO_3^-(aq) \longrightarrow$
$Ca^{2+}(aq) + 2NO_3^-(aq) + 2H_2O(l)$
$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$
**4.5** $Ba(OH)_2(aq) + 2HCl(aq) \longrightarrow BaCl_2(aq) + 2H_2O(l)$
Volume (L) of soln

$= 50.00 \text{ mL HCl soln} \times \dfrac{1 \text{ L}}{10^3 \text{ mL}} \times \dfrac{0.1016 \text{ mol HCl}}{1 \text{ L soln}}$

$\times \dfrac{1 \text{ mol Ba(OH)}_2}{2 \text{ mol HCl}} \times \dfrac{1 \text{ L soln}}{0.1292 \text{ mol Ba(OH)}_2}$

$= 0.01966 \text{ L}$
**4.6** (a) O.N. of Sc $= +3$; O.N. of O $= -2$
(b) O.N. of Ga $= +3$; O.N. of Cl $= -1$

(c) O.N. of H $= +1$; O.N. of P $= +5$; O.N. of O $= -2$
(d) O.N. of I $= +3$; O.N. of F $= -1$
**4.7** (a) Fe is reducing agent; $Cl_2$ is oxidizing agent.
(b) $C_2H_6$ is reducing agent; $O_2$ is oxidizing agent.
(c) CO is reducing agent; $I_2O_5$ is oxidizing agent.
**4.8** $K_2Cr_2O_7(aq) + 14HI(aq) \longrightarrow$
$2KI(aq) + 2CrI_3(aq) + 3I_2(s) + 7H_2O(l)$

**4.9** (a) Moles of $Ca^{2+} = 6.53 \text{ mL soln} \times \dfrac{1 \text{ L}}{10^3 \text{ mL}}$

$\times \dfrac{4.56 \times 10^{-3} \text{ mol KMnO}_4}{1 \text{ L soln}}$

$\times \dfrac{5 \text{ mol CaC}_2\text{O}_4}{2 \text{ mol KMnO}_4} \times \dfrac{1 \text{ mol Ca}^{2+}}{1 \text{ mol CaC}_2\text{O}_4}$

$= 7.44 \times 10^{-5} \text{ mol Ca}^{2+}$

Molarity of $Ca^{2+} = \dfrac{7.44 \times 10^{-2} \text{ mol Ca}^{2+}}{2.50 \text{ mL milk}} \times \dfrac{10^3 \text{ mL}}{1 \text{ L}}$

$= 2.98 \times 10^{-2} \text{ M Ca}^{2+}$
(b) Conc. of $Ca^{2+}$ (g/L)

$= \dfrac{2.98 \times 10^{-2} \text{ mol Ca}^{2+}}{1 \text{ L}} \times \dfrac{40.08 \text{ g Ca}^{2+}}{1 \text{ mol Ca}^{2+}}$

$= \dfrac{1.19 \text{ g Ca}^{2+}}{1 \text{ L}}$

**4.10** (a) Combination:
$S_8(s) + 16F_2(g) \longrightarrow 8SF_4(g)$
$S_8$ is the reducing agent; $F_2$ is the oxidizing agent.
(b) Displacement:
$2CsI(aq) + Cl_2(aq) \longrightarrow 2CsCl(aq) + I_2(aq)$
$Cl_2$ is the oxidizing agent; CsI is the reducing agent
$2Cs^+(aq) + 2I^-(aq) + Cl_2(aq) \longrightarrow$
$2Cs^+(aq) + 2Cl^-(aq) + I_2(aq)$
$2I^-(aq) + Cl_2(aq) \longrightarrow 2Cl^-(aq) + I_2(aq)$
(c) Displacement:
$3Ni(NO_3)_2(aq) + 2Cr(s) \longrightarrow 3Ni(s) + 2Cr(NO_3)_3(aq)$
$3Ni^{2+}(aq) + 6NO_3^-(aq) + 2Cr(s) \longrightarrow$
$3Ni(s) + 2Cr^{3+}(aq) + 6NO_3^-(aq)$
$3Ni^{2+}(aq) + 2Cr(s) \longrightarrow 3Ni(s) + 2Cr^{3+}(aq)$
Cr is the reducing agent; $Ni(NO_3)_2$ is the oxidizing agent.

# Problems

Problems with **colored** numbers are answered at the back of the text. Sections match the text and provide the number(s) of relevant sample problems. Most offer Concept Review Questions, Skill-Building Exercises (in similar pairs), and Problems in Context. Then Comprehensive Problems, based on material from any section or previous chapter, follow.

## The Role of Water as a Solvent
(Sample Problems 4.1 and 4.2)

● **Concept Review Questions**

**4.1** What two factors cause water to be polar?

**4.2** What types of substances are most likely to be soluble in water?

**4.3** What must be present in an aqueous solution for it to conduct an electric current? What general classes of compounds form solutions that conduct?

**4.4** What occurs on the molecular level when an ionic compound dissolves in water?

**4.5** Examine each of the following aqueous solutions and determine which represents: (a) $CaCl_2$; (b) $Li_2SO_4$; (c) $NH_4Br$.
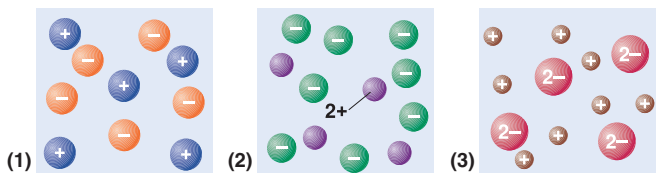


**4.6** Which of the following best represents a volume from a solution of magnesium nitrate?
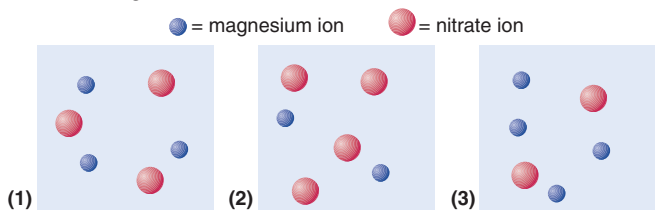


**4.7** Why are some ionic compounds soluble in water and others are not?

**4.8** Why are some covalent compounds soluble in water and others are not?

**4.9** Some covalent compounds dissociate into ions when they dissolve in water. What atom do these compounds have in their structures? What type of aqueous solution do they form? Name three examples of such an aqueous solution.

● **Skill-Building Exercises** *(paired)*

**4.10** State whether each of the following substances is likely to be very soluble in water. Explain.
(a) Benzene, $C_6H_6$ (b) Sodium hydroxide
(c) Ethanol, $CH_3CH_2OH$ (d) Potassium acetate

**4.11** State whether each of the following substances is likely to be very soluble in water. Explain.
(a) Lithium nitrate (b) Glycine, $H_2NCH_2COOH$
(c) Pentane (d) Ethylene glycol, $HOCH_2CH_2OH$

**4.12** State whether an aqueous solution of each of the following substances conducts an electric current. Explain your reasoning.
(a) Cesium iodide (b) Hydrogen bromide

**4.13** State whether an aqueous solution of each of the following substances conducts an electric current. Explain your reasoning.
(a) Sodium hydroxide (b) Glucose, $C_6H_{12}O_6$

**4.14** How many total moles of ions are released when each of the following samples dissolves completely in water?
(a) 0.25 mol of $NH_4Cl$ (b) 26.4 g of $Ba(OH)_2 \cdot 8H_2O$
(c) $1.78 \times 10^{20}$ formula units of LiCl

**4.15** How many total moles of ions are released when each of the following samples dissolves completely in water?
(a) 0.805 mol of $Cs_2SO_4$ (b) $1.55 \times 10^{-3}$ g of $Ca(NO_3)_2$
(c) $3.85 \times 10^{27}$ formula units of $Sr(HCO_3)_2$

**4.16** How many total moles of ions are released when each of the following samples dissolves completely in water?
(a) 0.15 mol of $Na_3PO_4$ (b) 47.9 g of $NiBr_2 \cdot 3H_2O$
(c) $4.23 \times 10^{22}$ formula units of $FeCl_3$

**4.17** How many total moles of ions are released when each of the following samples dissolves completely in water?
(a) 0.382 mol of $K_2HPO_4$ (b) 6.80 g of $MgSO_4 \cdot 7H_2O$
(c) $6.188 \times 10^{21}$ formula units of $NiCl_2$

**4.18** How many moles and numbers of ions of each type are present in the following aqueous solutions?
(a) 95.5 mL of 2.45 *M* aluminum chloride
(b) 2.50 L of a solution containing 4.59 g/L sodium sulfate
(c) 80.5 mL of a solution containing $2.68 \times 10^{22}$ formula units of magnesium bromide per liter

**4.19** How many moles and numbers of ions of each type are present in the following aqueous solutions?
(a) 3.8 mL of 1.88 *M* magnesium chloride
(b) 345 mL of a solution containing 4.22 g/L aluminum sulfate
(c) 2.66 L of a solution containing $6.63 \times 10^{21}$ formula units of lithium nitrate per liter

**4.20** How many moles of $H^+$ ions are present in the following aqueous solutions?
(a) 0.140 L of 2.5 *M* perchloric acid
(b) 6.8 mL of 0.52 *M* nitric acid
(c) 2.5 L of 0.056 *M* hydrochloric acid

**4.21** How many moles of $H^+$ ions are present in the following aqueous solutions?
(a) 1.4 L of 0.48 *M* hydrobromic acid
(b) 47 mL of 1.8 *M* hydriodic acid
(c) 425 mL of 0.27 *M* nitric acid

● **Problems in Context**

**4.22** In laboratory studies of ocean-dwelling organisms, marine biologists use salt mixtures that simulate the ion concentrations in seawater. A 1.00-kg sample of simulated seawater is prepared by mixing 26.5 g of NaCl, 2.40 g of $MgCl_2$, 3.35 g of $MgSO_4$, 1.20 g of $CaCl_2$, 1.05 g of KCl, 0.315 g of $NaHCO_3$, and 0.098 g of NaBr in distilled water.
(a) If the density of this solution is 1.04 g/cm³, what is the molarity of each ion?
(b) What is the total molarity of alkali metal ions?
(c) What is the total molarity of alkaline earth metal ions?
(d) What is the total molarity of anions?

**4.23** Water "softeners" remove metal ions such as $Fe^{2+}$, $Fe^{3+}$, $Ca^{2+}$, and $Mg^{2+}$ (which make water "hard") by replacing them

with enough $Na^+$ ions to maintain the same number of positive charges in the solution. If $1.0 \times 10^3$ L of hard water is 0.015 $M$ $Ca^{2+}$ and 0.0010 $M$ $Fe^{3+}$, how many moles of $Na^+$ are needed to replace these ions?

## Writing Equations for Aqueous Ionic Reactions

● **Concept Review Questions**

**4.24** Which ions do not appear in a net ionic equation? Why?
**4.25** Write two equations (both molecular and total ionic) with different reactants to obtain the same net ionic equation as the following aqueous ionic equation:

$Ba(NO_3)_2(aq) + Na_2CO_3(aq) \longrightarrow BaCO_3(s) + 2NaNO_3(aq)$
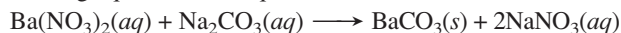
## Precipitation Reactions
(Sample Problem 4.3)

● **Concept Review Questions**

**4.26** Why do some pairs of ions precipitate and others do not?

**4.27** Use Table 4.1 to determine which of the following combinations leads to a reaction. How can you identify the spectator ions in the reaction?
(a) Calcium nitrate($aq$) + potassium chloride($aq$) $\longrightarrow$
(b) Sodium chloride($aq$) + lead(II) nitrate($aq$) $\longrightarrow$

**4.28** The beakers represent the aqueous reaction of $AgNO_3$ and NaCl. Silver ions are gray. What colors are used to represent $NO_3^-$, $Na^+$, and $Cl^-$? Write molecular, total ionic, and net ionic equations for the reaction.
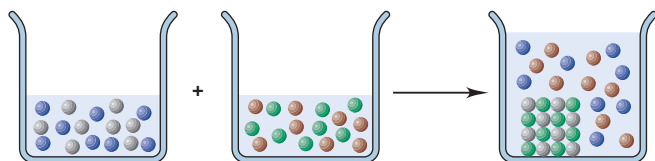


● **Skill-Building Exercises (paired)**

**4.29** When each of the following pairs of aqueous solutions is mixed, does a precipitation reaction occur? If so, write the formula and name of the precipitate:
(a) Sodium nitrate + copper(II) sulfate
(b) Ammonium iodide + silver nitrate
**4.30** When each of the following pairs of aqueous solutions is mixed, does a precipitation reaction occur? If so, write the formula and name of the precipitate:
(a) Potassium carbonate + barium hydroxide
(b) Aluminum nitrate + sodium phosphate

**4.31** When each of the following pairs of aqueous solutions is mixed, does a precipitation reaction occur? If so, write the formula and name of the precipitate:
(a) Potassium chloride + iron(II) nitrate
(b) Ammonium sulfate + barium chloride
**4.32** When each of the following pairs of aqueous solutions is mixed, does a precipitation reaction occur? If so, write the formula and name of the precipitate:
(a) Sodium sulfide + nickel(II) sulfate
(b) Lead(II) nitrate + potassium bromide

**4.33** Complete the following precipitation reactions with balanced molecular, total ionic, and net ionic equations, and identify the spectator ions:

(a) $Hg_2(NO_3)_2(aq) + KI(aq) \longrightarrow$
(b) $FeSO_4(aq) + Ba(OH)_2(aq) \longrightarrow$
**4.34** Complete the following precipitation reactions with balanced molecular, total ionic, and net ionic equations, and identify the spectator ions:
(a) $CaCl_2(aq) + Cs_3PO_4(aq) \longrightarrow$
(b) $Na_2S(aq) + ZnSO_4(aq) \longrightarrow$

**4.35** If 35.0 mL of lead(II) nitrate solution reacts completely with excess sodium iodide solution to yield 0.628 g of precipitate, what is the molarity of lead(II) ion in the original solution?
**4.36** If 25.0 mL of silver nitrate solution reacts with excess potassium chloride solution to yield 0.842 g of precipitate, what is the molarity of silver ion in the original solution?

● **Problems in Context**

**4.37** The mass percent of $Cl^-$ in a seawater sample is determined by titrating 25.00 mL of seawater with $AgNO_3$ solution, causing a precipitation reaction. An indicator is used to detect the end point, which occurs when free $Ag^+$ ion is present in solution after all the $Cl^-$ has reacted. If 43.63 mL of 0.3020 $M$ $AgNO_3$ is required to reach the end point, what is the mass percent of $Cl^-$ in the seawater ($d$ of seawater = 1.04 g/mL)?
**4.38** Aluminum sulfate, known as cake alum, has a remarkably wide range of uses, from dyeing leather and cloth to purifying sewage. In aqueous solution, it reacts with base to form a white precipitate. (a) Write balanced total and net ionic equations for its reaction with aqueous NaOH. (b) What mass of precipitate forms when 135.5 mL of 0.633 $M$ NaOH is added to 517 mL of a solution that contains 12.8 g of aluminum sulfate per liter?

## Acid-Base Reactions
(Sample Problems 4.4 and 4.5)

● **Concept Review Questions**

**4.39** Is the total ionic equation the same as the net ionic equation when $Sr(OH)_2(aq)$ and $H_2SO_4(aq)$ react? Explain.
**4.40** State a general equation for a neutralization reaction.
**4.41** (a) Name three common strong acids. (b) Name three common strong bases. (c) What is a characteristic behavior of a strong acid or a strong base?
**4.42** (a) Name three common weak acids. (b) Name one common weak base. (c) What is the major difference between a weak acid and a strong acid or between a weak base and a strong base, and what experiment would you perform to observe it?
**4.43** Do either of the following reactions go to completion? If so, what factor(s) drives each to completion?
(a) $MgSO_3(s) + 2HCl(aq) \longrightarrow$
$$MgCl_2(aq) + SO_2(g) + H_2O(l)$$
(b) $3Ba(OH)_2(aq) + 2H_3PO_4(aq) \longrightarrow Ba_3(PO_4)_2(s) + 6H_2O(l)$
**4.44** The net ionic equation for the aqueous neutralization reaction between acetic acid and sodium hydroxide is different from that for the reaction between hydrochloric acid and sodium hydroxide. Explain by writing balanced net ionic equations.

● **Skill-Building Exercises (paired)**

**4.45** Complete the following acid-base reactions with balanced molecular, total ionic, and net ionic equations, and identify the spectator ions:
(a) Potassium hydroxide($aq$) + hydriodic acid($aq$) $\longrightarrow$
(b) Ammonia($aq$) + hydrochloric acid($aq$) $\longrightarrow$

**4.46** Complete the following acid-base reactions with balanced molecular, total ionic, and net ionic equations, and identify the spectator ions:
(a) Cesium hydroxide($aq$) + nitric acid($aq$) $\longrightarrow$
(b) Calcium hydroxide($aq$) + acetic acid($aq$) $\longrightarrow$

**4.47** Limestone (calcium carbonate) is insoluble in water but dissolves when a hydrochloric acid solution is added. Why? Write balanced total ionic and net ionic equations, showing hydrochloric acid as it actually exists in water and the reaction as a proton-transfer process.

**4.48** Zinc hydroxide is insoluble in water but dissolves when a nitric acid solution is added. Why? Write balanced total ionic and net ionic equations, showing nitric acid as it actually exists in water and the reaction as a proton-transfer process.

**4.49** If 15.98 mL of a standard 0.1080 $M$ KOH solution reacts with 52.00 mL of $CH_3COOH$ solution, what is the molarity of the acid solution?

**4.50** If 26.35 mL of a standard 0.1650 $M$ NaOH solution is required to neutralize 35.00 mL of $H_2SO_4$, what is the molarity of the acid solution?

● **Problems in Context**

**4.51** An auto mechanic spills 85 mL of 2.6 $M$ $H_2SO_4$ solution from a rebuilt auto battery. How many milliliters of 2.5 $M$ $NaHCO_3$ must be poured on the spill to react completely with the sulfuric acid?

**4.52** Sodium hydroxide is used extensively in acid-base titrations because it is a strong, inexpensive base. A sodium hydroxide solution was standardized by titrating 25.00 mL of 0.1528 $M$ standard hydrochloric acid. The initial buret reading of the sodium hydroxide was 2.24 mL, and the final reading was 39.21 mL. What was the molarity of the base solution?

**4.53** One of the first steps in the enrichment of uranium for use in nuclear power plants involves a displacement reaction between $UO_2$ and aqueous HF:
$$UO_2(s) + 4HF(aq) \longrightarrow UF_4(s) + 2H_2O(l)$$
How many liters of 6.50 $M$ HF are needed to react with 3.25 kg of $UO_2$?

## Oxidation-Reduction (Redox) Reactions
(Sample Problems 4.6 to 4.9)

● **Concept Review Questions**

**4.54** Describe how to determine the oxidation number of sulfur in (a) $H_2S$ and (b) $SO_3$.

**4.55** Is the following a redox reaction? Explain.
$$NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)$$
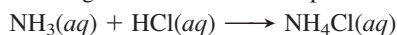
**4.56** Explain why an oxidizing agent undergoes reduction.

**4.57** Why must every redox reaction involve an oxidizing agent and a reducing agent?

**4.58** In which of the following equations does sulfuric acid act as an oxidizing agent? In which does it act as an acid? Explain.
(a) $4H^+(aq) + SO_4^{2-}(aq) + 2NaI(s) \longrightarrow$
$$2Na^+(aq) + I_2(s) + SO_2(g) +> 2H_2O(l)$$
(b) $BaF_2(s) + 2H^+(aq) + SO_4^{2-}(aq) \longrightarrow$
$$2HF(aq) + BaSO_4(s)$$
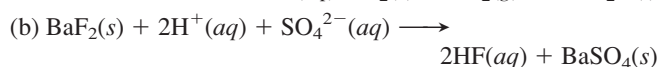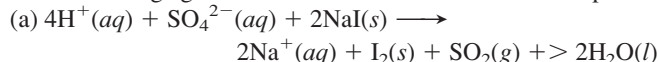
**4.59** Identify the oxidizing agent and the reducing agent in the following reaction, and explain your answer:
$$8NH_3(g) + 6NO_2(g) \longrightarrow 7N_2(g) + 12H_2O(l)$$
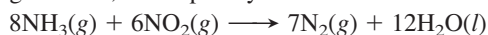
● **Skill-Building Exercises** *(paired)*

**4.60** Give the oxidation number of carbon in the following:
(a) $CF_2Cl_2$    (b) $Na_2C_2O_4$    (c) $HCO_3^-$    (d) $C_2H_6$

**4.61** Give the oxidation number of bromine in the following:
(a) KBr    (b) $BrF_3$    (c) $HBrO_3$    (d) $CBr_4$

**4.62** Give the oxidation number of nitrogen in the following:
(a) $NH_2OH$    (b) $N_2H_4$    (c) $NH_4^+$    (d) $HNO_2$

**4.63** Give the oxidation number of sulfur in the following:
(a) $SOCl_2$    (b) $H_2S_2$    (c) $H_2SO_3$    (d) $Na_2S$

**4.64** Give the oxidation number of arsenic in the following:
(a) $AsH_3$    (b) $H_3AsO_4$    (c) $AsCl_3$

**4.65** Give the oxidation number of phosphorus in the following:
(a) $H_2P_2O_7^{2-}$    (b) $PH_4^+$    (c) $PCl_5$
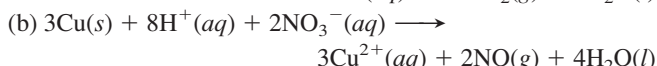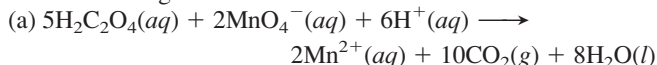
**4.66** Give the oxidation number of manganese in the following:
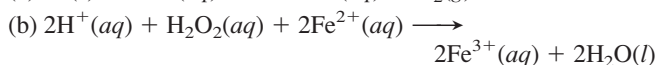(a) $MnO_4^{2-}$    (b) $Mn_2O_3$    (c) $KMnO_4$

**4.67** Give the oxidation number of chromium the following:
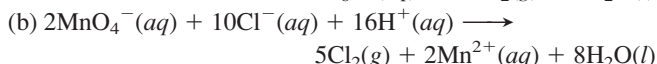(a) $CrO_3$    (b) $Cr_2O_7^{2-}$    (c) $Cr_2(SO_4)_3$

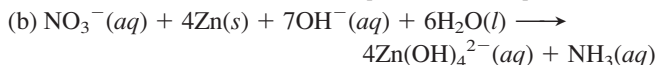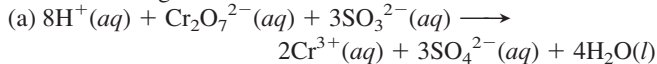**4.68** Identify the oxidizing agent and the reducing agent in each of the following:
(a) $5H_2C_2O_4(aq) + 2MnO_4^-(aq) + 6H^+(aq) \longrightarrow$
$$2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$
(b) $3Cu(s) + 8H^+(aq) + 2NO_3^-(aq) \longrightarrow$
$$3Cu^{2+}(aq) + 2NO(g) + 4H_2O(l)$$

**4.69** Identify the oxidizing agent and the reducing agent in each of the following:
(a) $Sn(s) + 2H^+(aq) \longrightarrow Sn^{2+}(aq) + H_2(g)$
(b) $2H^+(aq) + H_2O_2(aq) + 2Fe^{2+}(aq) \longrightarrow$
$$2Fe^{3+}(aq) + 2H_2O(l)$$

**4.70** Identify the oxidizing agent and the reducing agent in each of the following:
(a) $8H^+(aq) + 6Cl^-(aq) + Sn(s) + 4NO_3^-(aq) \longrightarrow$
$$SnCl_6^{2-}(aq) + 4NO_2(g) + 4H_2O(l)$$
(b) $2MnO_4^-(aq) + 10Cl^-(aq) + 16H^+(aq) \longrightarrow$
$$5Cl_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$$

**4.71** Identify the oxidizing agent and the reducing agent in each of the following:
(a) $8H^+(aq) + Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) \longrightarrow$
$$2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + 4H_2O(l)$$
(b) $NO_3^-(aq) + 4Zn(s) + 7OH^-(aq) + 6H_2O(l) \longrightarrow$
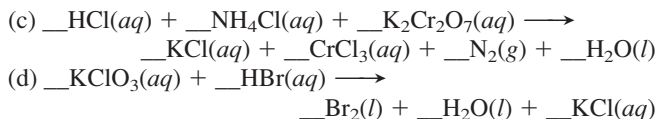$$4Zn(OH)_4^{2-}(aq) + NH_3(aq)$$
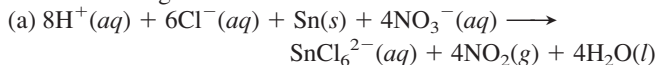
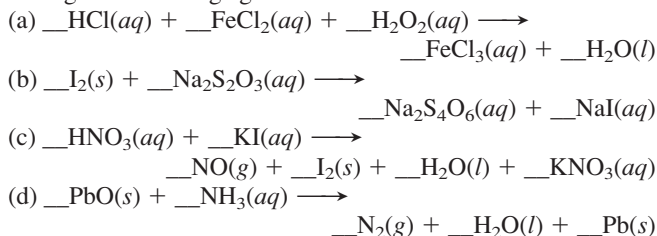**4.72** Discuss each conclusion from a study of redox reactions:
(a) The sulfide ion functions only as a reducing agent.
(b) The sulfate ion functions only as an oxidizing agent.
(c) Sulfur dioxide functions as an oxidizing or a reducing agent.

**4.73** Discuss each conclusion from a study of redox reactions:
(a) The nitride ion functions only as a reducing agent.
(b) The nitrate ion functions only as an oxidizing agent.
(c) The nitrite ion functions as an oxidizing or a reducing agent.

**4.74** Use the oxidation number method to balance the following equations by placing coefficients in the blanks. Identify the reducing and oxidizing agents:
(a) __$HNO_3(aq)$ + __$K_2CrO_4(aq)$ + __$Fe(NO_3)_2(aq)$ $\longrightarrow$
__$KNO_3(aq)$ + __$Fe(NO_3)_3(aq)$ + __$Cr(NO_3)_3(aq)$ + __$H_2O(l)$
(b) __$HNO_3(aq)$ + __$C_2H_6O(l)$ + __$K_2Cr_2O_7(aq)$ $\longrightarrow$
__$KNO_3(aq)$ + __$C_2H_4O(l)$ + __$H_2O(l)$ + __$Cr(NO_3)_3(aq)$

(c) $\_\_HCl(aq) + \_\_NH_4Cl(aq) + \_\_K_2Cr_2O_7(aq) \longrightarrow$
$\_\_KCl(aq) + \_\_CrCl_3(aq) + \_\_N_2(g) + \_\_H_2O(l)$
(d) $\_\_KClO_3(aq) + \_\_HBr(aq) \longrightarrow$
$\_\_Br_2(l) + \_\_H_2O(l) + \_\_KCl(aq)$
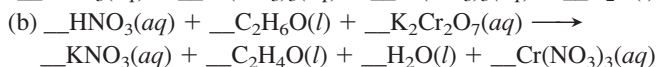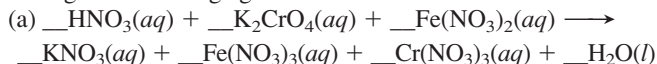
**4.75** Use the oxidation number method to balance the following equations by placing coefficients in the blanks. Identify the reducing and oxidizing agents:
(a) $\_\_HCl(aq) + \_\_FeCl_2(aq) + \_\_H_2O_2(aq) \longrightarrow$
$\_\_FeCl_3(aq) + \_\_H_2O(l)$
(b) $\_\_I_2(s) + \_\_Na_2S_2O_3(aq) \longrightarrow$
$\_\_Na_2S_4O_6(aq) + \_\_NaI(aq)$
(c) $\_\_HNO_3(aq) + \_\_KI(aq) \longrightarrow$
$\_\_NO(g) + \_\_I_2(s) + \_\_H_2O(l) + \_\_KNO_3(aq)$
(d) $\_\_PbO(s) + \_\_NH_3(aq) \longrightarrow$
$\_\_N_2(g) + \_\_H_2O(l) + \_\_Pb(s)$

● **Problems in Context**

**4.76** The active agent in many hair bleaches is hydrogen peroxide. The amount of hydrogen peroxide in 13.8 g of hair bleach was determined by titration with a standard potassium permanganate solution:

$2MnO_4^-(aq) + 5H_2O_2(aq) + 6H^+(aq) \longrightarrow$
$5O_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$
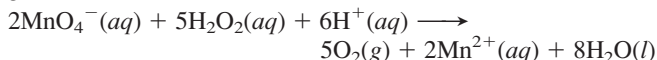
(a) How many moles of $MnO_4^-$ were required for the titration if 43.2 mL of 0.105 $M$ $KMnO_4$ was needed to reach the end point?
(b) How many moles of $H_2O_2$ were present in the 13.8-g sample of bleach?
(c) How many grams of $H_2O_2$ were in the sample?
(d) What is the mass percent of $H_2O_2$ in the sample?
(e) What is the reducing agent in the redox reaction?

**4.77** A person's blood alcohol ($C_2H_5OH$) level can be determined by titrating a sample of blood plasma with a potassium dichromate solution. The balanced equation is

$16H^+(aq) + 2Cr_2O_7^{2-}(aq) + C_2H_5OH(aq) \longrightarrow$
$4Cr^{3+}(aq) + 2CO_2(g) + 11H_2O(l)$
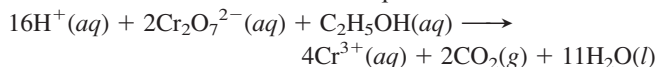
If 35.46 mL of 0.05961 $M$ $Cr_2O_7^{2-}$ is required to titrate 28.00 g of plasma, what is the mass percent of alcohol in the blood?

**Elemental Substances in Redox Reactions**
(Sample Problem 4.10)

● **Concept Review Questions**

**4.78** What is the name of the type of reaction that leads to the following?
(a) An increase in the number of substances
(b) A decrease in the number of substances
(c) No change in the number of substances

**4.79** Why do decomposition reactions typically have compounds as reactants, whereas combination and displacement reactions have one or more elements?
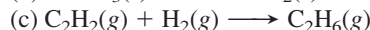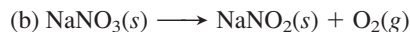
**4.80** Which of the three types of reactions discussed in this section commonly produce one or more compounds?

**4.81** Give an example of a combination reaction that is a redox reaction. Give an example of a combination reaction that is not a redox reaction.
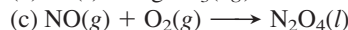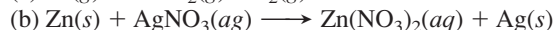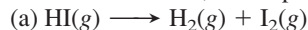
**4.82** Are all combustion reactions redox reactions? Explain.

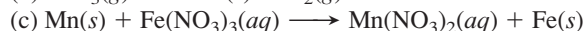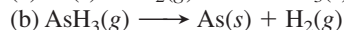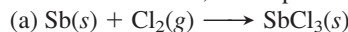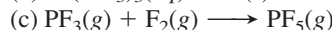● **Skill-Building Exercises** *(paired)*

**4.83** Balance each of the following redox reactions and classify it as a combination, decomposition, or displacement reaction:
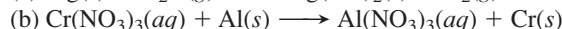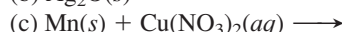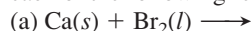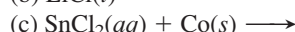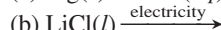(a) $Ca(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq) + H_2(g)$

(b) $NaNO_3(s) \longrightarrow NaNO_2(s) + O_2(g)$
(c) $C_2H_2(g) + H_2(g) \longrightarrow C_2H_6(g)$

**4.84** Balance each of the following redox reactions and classify it as a combination, decomposition, or displacement reaction:
(a) $HI(g) \longrightarrow H_2(g) + I_2(g)$
(b) $Zn(s) + AgNO_3(ag) \longrightarrow Zn(NO_3)_2(aq) + Ag(s)$
(c) $NO(g) + O_2(g) \longrightarrow N_2O_4(l)$

**4.85** Balance each of the following redox reactions and classify it as a combination, decomposition, or displacement reaction:
(a) $Sb(s) + Cl_2(g) \longrightarrow SbCl_3(s)$
(b) $AsH_3(g) \longrightarrow As(s) + H_2(g)$
(c) $Mn(s) + Fe(NO_3)_3(aq) \longrightarrow Mn(NO_3)_2(aq) + Fe(s)$

**4.86** Balance each of the following redox reactions and classify it as a combination, decomposition, or displacement reaction:
(a) $Mg(s) + H_2O(g) \longrightarrow Mg(OH)_2(s) + H_2(g)$
(b) $Cr(NO_3)_3(aq) + Al(s) \longrightarrow Al(NO_3)_3(aq) + Cr(s)$
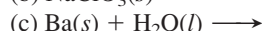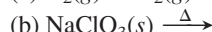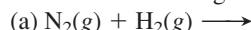(c) $PF_3(g) + F_2(g) \longrightarrow PF_5(g)$

**4.87** Predict the product(s) and write a balanced equation for each of the following redox reactions:
(a) $Ca(s) + Br_2(l) \longrightarrow$
(b) $Ag_2O(s) \xrightarrow{\Delta}$
(c) $Mn(s) + Cu(NO_3)_2(aq) \longrightarrow$

**4.88** Predict the product(s) and write a balanced equation for each of the following redox reactions:
(a) $Mg(s) + HCl(aq) \longrightarrow$
(b) $LiCl(l) \xrightarrow{electricity}$
(c) $SnCl_2(aq) + Co(s) \longrightarrow$

**4.89** Predict the product(s) and write a balanced equation for each of the following redox reactions:
(a) $N_2(g) + H_2(g) \longrightarrow$
(b) $NaClO_3(s) \xrightarrow{\Delta}$
(c) $Ba(s) + H_2O(l) \longrightarrow$

**4.90** Predict the product(s) and write a balanced equation for each of the following redox reactions:
(a) $Fe(s) + HClO_4(aq) \longrightarrow$
(b) $S_8(s) + O_2(g) e \longrightarrow$
(c) $BaCl_2(aq) \xrightarrow{electricity}$

**4.91** Predict the product(s) and write a balanced equation for each of the following redox reactions:
(a) Cesium + iodine $\longrightarrow$
(b) Aluminum + aqueous manganese(II) sulfate $\longrightarrow$
(c) Sulfur dioxide + oxygen $\longrightarrow$
(d) Propane and oxygen $\longrightarrow$
(e) Write a balanced net ionic equation for (b).

**4.92** Predict the product(s) and write a balanced equation for each of the following redox reactions:
(a) Pentane and oxygen $\longrightarrow$
(b) Phosphorus trichloride + chlorine $\longrightarrow$
(c) Zinc + hydrobromic acid $\longrightarrow$
(d) Aqueous potassium iodide + bromine $\longrightarrow$
(e) Write a balanced net ionic equation for (d).
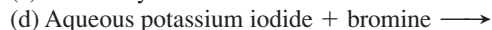
**4.93** How many grams of $O_2$ can be prepared from the complete decomposition of 4.27 kg of HgO? Name and calculate the mass (in kg) of the other product.

**4.94** How many grams of lime (CaO) can be produced from the complete decomposition of 114.52 g of limestone ($CaCO_3$)? Name and calculate the mass (in grams) of the other product.

**4.95** In a combination reaction, 1.62 g of lithium is mixed with 6.00 g of oxygen.
(a) Which reactant is present in excess?
(b) How many moles of product are formed?
(c) After reaction, how many grams of each reactant and product are present?

**4.96** In a combination reaction, 2.22 g of magnesium is heated with 3.75 g of nitrogen.
(a) Which reactant is present in excess?
(b) How many moles of product are formed?
(c) After reaction, how many grams of each reactant and product are present?

**4.97** A mixture of $KClO_3$ and $KCl$ with a mass of 0.900 g was heated to produce $O_2$. After heating, the mass of residue was 0.700 g. Assuming all the $KClO_3$ decomposed to $KCl$ and $O_2$, calculate the mass percent of $KClO_3$ in the original mixture.

**4.98** A mixture of $CaCO_3$ and $CaO$ weighing 0.693 g was heated to produce $CO_2$. After heating, the remaining solid weighed 0.508 g. Assuming all the $CaCO_3$ decomposed to $CaO$ and $CO_2$, calculate the mass percent of $CaCO_3$ in the original mixture.

● **Problems in Context**

**4.99** Before arc welding was developed, a displacement reaction involving aluminum and iron(III) oxide was commonly used to produce molten iron (the thermite process; see photo). This reaction was used, for example, to connect sections of iron railroad track. Calculate the mass of molten iron produced when 1.00 kg of aluminum reacts with 2.00 mol of iron(III) oxide.

**4.100** Iron reacts rapidly with chlorine gas to form the reddish-brown ionic Compound A, which contains iron in the higher of its two common oxidation states. Strong heating decomposes Compound A to Compound B, another ionic compound, which contains iron in the lower of its two oxidation states. When Compound A is formed by the reaction of 50.6 g of Fe and 83.8 g of $Cl_2$ and then heated, how much Compound B forms?

## Reversible Reactions: An Introduction to Chemical Equilibrium

● **Concept Review Questions**

**4.101** Why is the equilibrium state called "dynamic"?

**4.102** In a decomposition reaction involving a gaseous product, what must be done for the reaction to reach equilibrium?

**4.103** Describe what happens on the molecular level when acetic acid dissolves in water.

**4.104** When either a mixture of NO and $Br_2$ or pure nitrosyl bromide (NOBr) is placed in a reaction vessel, the product mixture contains NO, $Br_2$, and NOBr. Explain.

● **Problems in Context**

**4.105** Ammonia is produced by the millions of tons annually for use as a fertilizer. It is commonly made from $N_2$ and $H_2$ by the Haber process. Because the reaction reaches equilibrium before going completely to product, the stoichiometric amount of ammonia is not obtained. At a particular temperature and pressure, 10.0 g of $H_2$ reacts with 20.0 g of $N_2$ to form ammonia. When equilibrium is reached, 15.0 g of $NH_3$ has formed.
(a) Calculate the percent yield.
(b) How many moles of $N_2$ and $H_2$ are present at equilibrium?

## Comprehensive Problems

Problems with an asterisk (*) are more challenging.

**4.106** Nutritional biochemists have known for decades that acidic foods cooked in cast-iron cookware can supply significant amounts of dietary (ferrous) iron.
(a) Write a balanced net ionic equation, with oxidation numbers, that supports this fact.
(b) Measurements show an increase from 3.3 mg of iron to 49 mg of iron per $\frac{1}{2}$-cup (125-g) serving during the slow preparation of tomato sauce in a cast-iron pot. How many ferrous ions are present in a 26-oz (737-g) jar of the tomato sauce?

**4.107** Limestone ($CaCO_3$) is used to remove acidic pollutants from smokestack flue gases in a sequence of decomposition-combination reactions. It is heated to form lime (CaO), which reacts with sulfur dioxide to form calcium sulfite. Assuming a 70.% yield in the overall reaction, what mass of limestone is required to remove all the sulfur dioxide formed by the combustion of $8.5 \times 10^4$ kg of coal that is 0.33 mass % sulfur?

**4.108** The brewing industry uses yeast microorganisms to convert glucose to ethanol for wine and beer. The baking industry uses the carbon dioxide they produce to make bread rise:

$$C_6H_{12}O_6(s) \xrightarrow{\text{yeast}} 2C_2H_5OH(l) + 2CO_2(g)$$
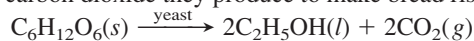
How many grams of ethanol can be produced from the decomposition of 10.0 g of glucose? What volume of $CO_2$ is produced? (Assume 1 mol of gas occupies 22.4 L at the conditions used.)

**4.109** A chemical engineer determines the mass percent of iron in an ore sample by converting the Fe to $Fe^{2+}$ in acid and then titrating the $Fe^{2+}$ with $MnO_4^-$. A 1.1081-g sample was dissolved in acid and then titrated with 39.32 mL of 0.03190 $M$ $KMnO_4$. The balanced equation is

$$8H^+(aq) + 5Fe^{2+}(aq) + MnO_4^-(aq) \longrightarrow$$
$$5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$$
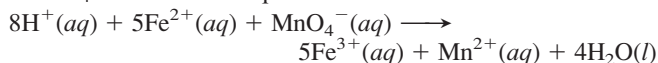
Calculate the mass percent of iron in the ore.

**4.110** Mixtures of $CaCl_2$ and $NaCl$ are used for salting roads to prevent ice formation. A dissolved 1.9348-g sample of such a mixture was analyzed by using excess $Na_2C_2O_4$ to precipitate the $Ca^{2+}$ as $CaC_2O_4$. The $CaC_2O_4$ was separated from the solution and then dissolved with sulfuric acid. The resulting $H_2C_2O_4$ was titrated with 37.68 mL of 0.1019 $M$ $KMnO_4$ solution.
(a) Write the balanced net ionic equation for the precipitation reaction.
(b) Write the balanced net ionic equation for the titration reaction. (See Sample Problem 4.9.)
(c) What is the oxidizing agent?
(d) What is the reducing agent?
(e) Calculate the mass percent of $CaCl_2$ in the original sample.

**\*4.111** A student has three beakers that contain the same volume of solution. The first contains 0.1 $M$ $AgNO_3$, the second 0.02 $M$ CaS, and the third 0.05 $M$ $Na_2SO_4$. While out of the room, her lab partner accidentally mixes the solutions. Assuming complete precipitation of any solids that form, determine which solids form and the concentration of each ion remaining in solution.

**4.112** Precipitation reactions are often used to prepare useful ionic compounds. For example, thousands of tons of silver bromide are prepared annually for use in making black-and-white photographic film. (a) What mass (in kilograms) of silver bromide forms when 5.85 m³ of 1.68 $M$ potassium bromide reacts with 3.51 m³ of 2.04 $M$ silver nitrate? (b) After the solid silver bromide is removed, what ions are present in the remaining solution? Determine the molarity of each ion. (Assume the total volume is the sum of the reactant volumes.)

**4.113** The flask *(right)* depicts the products of the titration of 25 mL of sulfuric acid with 25 mL of sodium hydroxide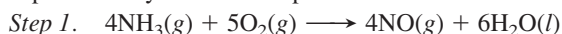. (a) Write balanced molecular, total ionic, and net ionic equations for the reaction. (b) If each orange sphere represents 0.010 mol of sulfate ion, how many moles of acid and of base reacted? (c) What are the molarities of the acid and the base?
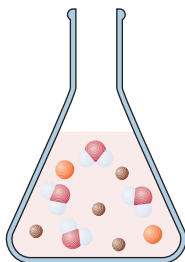
**4.114** To find the mass percent of dolomite [CaMg(CO₃)₂] in a soil sample, a geochemist titrates 12.86 g of the soil with 33.56 mL of 0.2516 $M$ HCl. What is the mass percent of dolomite in the soil?

**4.115** The calcium carbonate impurity in a sample of phosphate rock is removed by treatment with hydrochloric acid; the products are carbon dioxide, water, and aqueous calcium chloride. When 15.5 g of the rock is treated with excess hydrochloric acid, 1.81 g of carbon dioxide is formed. Calculate the mass percent of calcium carbonate in the rock.

**4.116** Nitric acid is used to make explosives and fertilizers and is produced by the Ostwald process:

*Step 1.*   $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(l)$
*Step 2.*   $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$
*Step 3.*   $3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(l) + NO(g)$
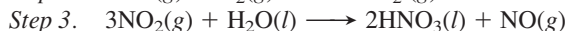
If you start with 72.5 kg of NH₃ and excess O₂: (a) How many grams of HNO₃ can form? (b) How many kilograms of O₂ are used? (c) How many kilograms of H₂O are produced? (d) For each step, determine the substance being oxidized, that being reduced, the oxidizing agent, and the reducing agent.
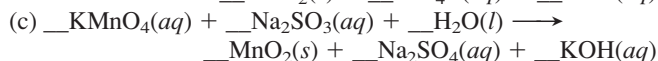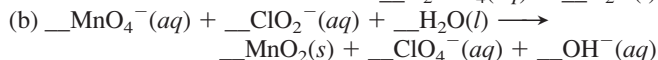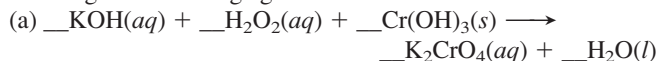
**4.117** Complete each of the following reactions and write the net ionic equation:

1. $NaOH(aq) + HCl(aq) \longrightarrow$
2. $KOH(aq) + HNO_3(aq) \longrightarrow$
3. $Ba(OH)_2(aq) + 2HBr(aq) \longrightarrow$
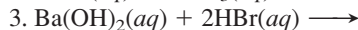
(a) What do you conclude from these equations about the nature of the reactants?
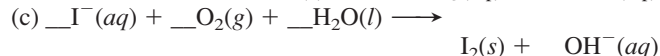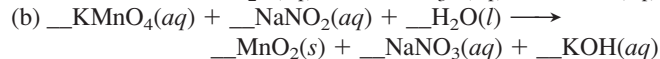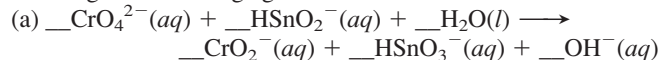(b) What are the spectator ions in each reaction?

**4.118** Use the oxidation number method to balance the following equations by placing coefficients in the blanks. Identify the reducing and oxidizing agents:

(a) __KOH($aq$) + __H₂O₂($aq$) + __Cr(OH)₃($s$) ⟶
        __K₂CrO₄($aq$) + __H₂O($l$)
(b) __MnO₄⁻($aq$) + __ClO₂⁻($aq$) + __H₂O($l$) ⟶
        __MnO₂($s$) + __ClO₄⁻($aq$) + __OH⁻($aq$)
(c) __KMnO₄($aq$) + __Na₂SO₃($aq$) + __H₂O($l$) ⟶
        __MnO₂($s$) + __Na₂SO₄($aq$) + __KOH($aq$)

**4.119** When two solutions of ionic compounds are mixed, a reaction occurs only if ions are removed from solution to form product. (a) What are three ways in which this removal can oc-

cur? (b) What type of reaction is involved in each case? (c) Write a balanced total ionic equation to illustrate each case.

**4.120** Use the oxidation number method to balance the following reactions by placing coefficients in the blanks. Identify the reducing and oxidizing agents:

(a) __CrO₄²⁻($aq$) + __HSnO₂⁻($aq$) + __H₂O($l$) ⟶
        __CrO₂⁻($aq$) + __HSnO₃⁻($aq$) + __OH⁻($aq$)
(b) __KMnO₄($aq$) + __NaNO₂($aq$) + __H₂O($l$) ⟶
        __MnO₂($s$) + __NaNO₃($aq$) + __KOH($aq$)
(c) __I⁻($aq$) + __O₂($g$) + __H₂O($l$) ⟶
        __I₂($s$) + __OH⁻($aq$)

**4.121** Sodium peroxide (Na₂O₂) is often used in self-contained breathing devices, such as those used in fire emergencies, because it reacts with exhaled CO₂ to form Na₂CO₃ and O₂. How many liters of respired air can react with 80.0 g of Na₂O₂ if each liter of respired air contains 0.0720 g of CO₂?

**4.122** Magnesium is used in airplane bodies and other lightweight alloys. The metal is obtained from seawater in a process that includes precipitation, neutralization, evaporation, and electrolysis. How many kilograms of magnesium can be obtained from 1.00 km³ of seawater if the initial Mg²⁺ concentration is 0.13% by mass ($d$ of seawater = 1.04 g/mL)?

*****4.123** A typical formulation for window glass is 75% SiO₂, 15% Na₂O, and 10.% CaO by mass. What masses of sand (SiO₂), sodium carbonate, and calcium carbonate must be combined to produce 1.00 kg of glass after carbon dioxide is driven off by thermal decomposition of the carbonates?

**4.124** The field of sports medicine has become an important specialty, with physicians routinely treating athletes and dancers. Ethyl chloride, a local anesthetic commonly used for simple injuries, is the product of the combination of ethylene with hydrogen chloride:

$$C_2H_4(g) + HCl(g) \longrightarrow C_2H_5Cl(g)$$
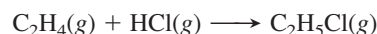
If 0.100 kg of C₂H₄ and 0.100 kg of HCl react:
(a) How many molecules of gas (reactants plus products) are present when the reaction is complete?
(b) How many moles of gas are present when half the product forms?

**4.125** The *salinity* of a solution is defined as the grams of total salts per kilogram of solution. An agricultural chemist uses a solution whose salinity is 35.0 g/kg to test the effect of irrigating farmland with high-salinity river water. The two solutes are NaCl and MgSO₄, and there are twice as many moles of NaCl as MgSO₄. What masses of NaCl and MgSO₄ are contained in 1.00 kg of the solution?

*****4.126** Thyroxine (C₁₅H₁₁I₄NO₄) is a hormone synthesized by the thyroid gland and used to control many metabolic functions in the body. A physiologist determines the mass % of thyroxine in a thyroid extract by igniting 0.4332 g of extract with sodium carbonate, which converts the iodine to iodide. The iodide is dissolved in water, and bromine and hydrochloric acid are added, which convert the iodide to iodate.

(a) How many moles of iodate form per mole of thyroxine?
(b) Excess bromine is boiled off and more iodide is added, which reacts as in the following *unbalanced* equation:

$$IO_3^-(aq) + H^+(aq) + I^-(aq) \longrightarrow I_2(aq) + H_2O(l)$$
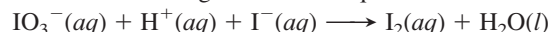
How many moles of iodine are produced per mole of thyroxine? (*Hint:* Be sure to balance the charges as well as the atoms.) What are the oxidizing and reducing agents in the reaction?

(c) The iodine reacts completely with 17.23 mL of 0.1000 $M$ thiosulfate as in the following *unbalanced* equation:

$$I_2(aq) + S_2O_3^{2-}(aq) \longrightarrow I^-(aq) + S_4O_6^{2-}(aq)$$

What is the mass % of thyroxine in the thyroid extract?

**4.127** Carbon dioxide is removed from the atmosphere of space capsules by reaction with a solid metal hydroxide. The products are water and the metal carbonate.
(a) Calculate the mass of $CO_2$ that can be removed by reaction with 3.50 kg of lithium hydroxide.
(b) How many grams of $CO_2$ can be removed by 1.00 g of each of the following: lithium hydroxide, magnesium hydroxide, and aluminum hydroxide?

**\*4.128** Calcium dihydrogen phosphate, $Ca(H_2PO_4)_2$, and sodium hydrogen carbonate, $NaHCO_3$, are ingredients of baking powder that react with each other to produce $CO_2$, which causes dough or batter to rise:

$Ca(H_2PO_4)_2(s) + NaHCO_3(s) \longrightarrow$
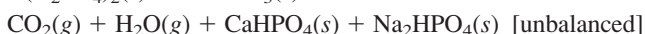
  $CO_2(g) + H_2O(g) + CaHPO_4(s) + Na_2HPO_4(s)$ [unbalanced]
If the baking powder contains 31% $NaHCO_3$ and 35% $Ca(H_2PO_4)_2$ by mass:
(a) How many moles of $CO_2$ are produced from 1.00 g of baking powder?
(b) If 1 mol of $CO_2$ occupies 37.0 L at 350°F (a typical baking temperature), what volume of $CO_2$ is produced from 1.00 g of baking powder?

**4.129** During the process of developing black-and-white film, unexposed silver bromide is removed in a displacement reaction with sodium thiosulfate solution:

$AgBr(s) + 2Na_2S_2O_3(aq) \longrightarrow Na_3Ag(S_2O_3)_2(aq) + NaBr(aq)$

What volume of 0.105 $M$ $Na_2S_2O_3$ solution is needed to remove 2.66 g of AgBr from a roll of film?

**4.130** Ionic hydrates lose their "waters of hydration" when thermally decomposed. When 25.36 g of hydrated copper(II) sulfate is heated, it forms 16.21 g of anhydrous copper(II) sulfate. What is the formula of the hydrate?

**\*4.131** In 1997, at the United Nations Conference on Climate Change, the major industrial nations agreed to expand their research efforts to develop renewable sources of carbon-based fuels. For more than a decade, Brazil has been engaged in a program to replace gasoline with ethanol derived from the root crop manioc (cassava).
(a) Write separate balanced equations for the complete combustion of ethanol ($C_2H_5OH$) and of gasoline (represented by the formula $C_8H_{18}$).
(b) What mass of oxygen is required to burn completely 1.00 L of a mixture that is 90.0% gasoline ($d = 0.742$ g/mL) and 10.0% ethanol ($d = 0.789$ g/mL) by volume?
(c) If 1.00 mol of $O_2$ occupies 22.4 L, what volume of $O_2$ is needed to burn 1.00 L of the mixture?
(d) Air is 20.9% $O_2$ by volume. What volume of air is needed to burn 1.00 L of the mixture?

**\*4.132** In a car engine, gasoline (represented by $C_8H_{18}$) does not burn completely, and some CO, a toxic pollutant, forms along with $CO_2$ and $H_2O$. If 5.0% of the gasoline forms CO:
(a) What is the ratio of $CO_2$ to CO molecules in the exhaust?
(b) What is the mass ratio of $CO_2$ to CO?

(c) What percent of the gasoline must form CO for the mass ratio of $CO_2$ to CO to be exactly 1:1?

**4.133** One of the molecules responsible for atmospheric ozone depletion is the refrigerant and aerosol propellant Freon-12 ($CF_2Cl_2$). It can be prepared in a sequence of two reactions:
1. A combination reaction between hydrogen and fluorine gases
2. A displacement reaction between the product of Reaction 1 and liquid carbon tetrachloride. Hydrogen chloride gas also forms.
(a) Write balanced equations for the two reactions.
(b) What is the maximum mass (in kg) of Freon-12 that can be produced from 0.760 kg of fluorine?

**4.134** In a blast furnace, iron ore is reduced to the free metal, and CO is the reducing agent. For 156.8 g of each of the following iron ores, calculate the mass of CO required: (a) wuestite (FeO); (b) hematite ($Fe_2O_3$); (c) siderite ($FeCO_3$).

**4.135** Interhalogens are covalent compounds of one halogen with another. When 3.299 g of $I_2$ reacts with $F_2$, 5.768 g of $IF_x$ is formed. What is the value of $x$ in the product formula?

**4.136** In the process of *salting-in*, protein solubility in a dilute salt solution is increased by adding more salt. Because the protein solubility depends on the total ion concentration as well as the ion charge, salts yielding divalent ions are often more effective than those yielding monovalent ions. (a) How many grams of $MgCl_2$ must dissolve to equal the ion concentration of 12.4 g of NaCl? (b) How many grams of CaS must dissolve? (c) Which of the three salt solutions would dissolve the most protein?

**4.137** Elemental fluorine is such a strong oxidizing agent that it cannot be produced from the abundant minerals fluorspar ($CaF_2$) and fluorapatite [$Ca_5(PO_4)_3F$]. One method uses potassium hexafluoromanganate(IV) with antimony(V) fluoride to produce $MnF_4$, which spontaneously decomposes into $MnF_3$ and $F_2$:

$$K_2MnF_6(s) + SbF_5(l) \longrightarrow KSbF_6(s) + MnF_3(s) + F_2(g)$$

Balance this equation by the oxidation number method, and identify the oxidizing and reducing agents.

**\*4.138** In the process of *pickling*, rust is removed from newly produced steel by washing in hydrochloric acid:

1. $6HCl(aq) + Fe_2O_3(s) \longrightarrow 2FeCl_3(aq) + 3H_2O(l)$
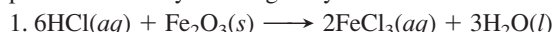
During the process, some iron is lost as well:

2. $2HCl(aq) + Fe(s) \longrightarrow FeCl_2(aq) + H_2(g)$

(a) Which reaction, if either, is a redox process? (b) If Reaction 2 did not occur and all the HCl were used, how many grams of $Fe_2O_3$ could be removed and $FeCl_3$ produced in a $2.50\times10^3$-L bath of 3.00 $M$ HCl? (c) If Reaction 1 did not occur and all the HCl were used, how many grams of Fe could be lost and $FeCl_2$ produced in a $2.50\times10^3$-L bath of 3.00 $M$ HCl? (d) If 0.280 g of Fe is lost per gram of $Fe_2O_3$ removed, what is the mass ratio of $FeCl_2$ to $FeCl_3$?

**4.139** At liftoff, the space shuttle uses a solid mixture of ammonium perchlorate and aluminum powder to obtain great thrust from the volume change of solid to gas. In the presence of a catalyst, the mixture forms solid aluminum oxide and aluminum trichloride and gaseous water and nitric oxide. (a) Write a balanced equation for the reaction, and identify the reducing and oxidizing agents. (b) How many total moles of gas (water vapor and nitric oxide) are produced when 50.0 kg of ammonium perchlorate reacts with a stoichiometric amount of Al? (c) What is the volume change from this reaction? ($d$ of $NH_4ClO_4 = 1.95$ g/cc, Al $= 2.70$ g/cc, $Al_2O_3 = 3.97$ g/cc, and $AlCl_3 = 2.44$ g/cc; assume 1 mol of gas occupies 22.4 L.)