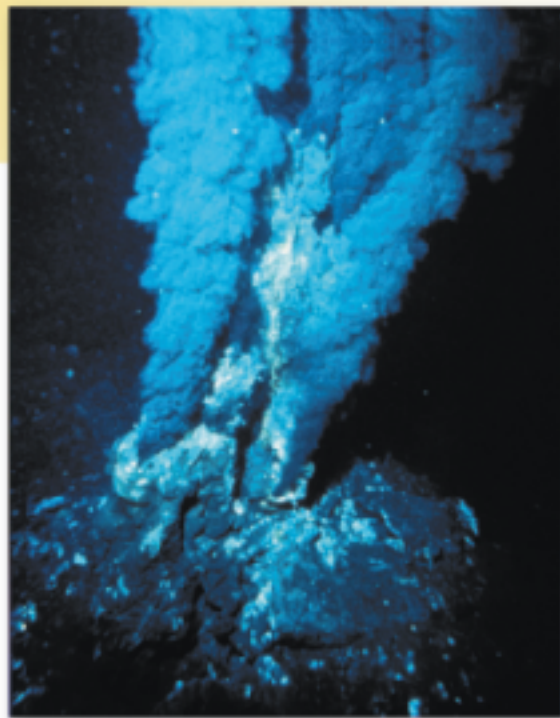


# Chapter 4

## Reactions in Aqueous Solutions



Black smokers form when superheated water, rich in minerals, flows out onto the ocean floor through the lava from an ocean volcano. The hydrogen sulfide present converts the metal ions to insoluble metal sulfides.

### Chapter Outline

- 4.1 General Properties of Aqueous Solutions
- 4.2 Precipitation Reactions
- 4.3 Acid-Base Reactions
- 4.4 Oxidation-Reduction Reactions
- 4.5 Concentration of Solutions
- 4.6 Gravimetric Analysis
- 4.7 Acid-Base Titrations
- 4.8 Redox Titrations

### A Look Ahead

- We begin by studying the properties of solutions prepared by dissolving substances in water, called aqueous solutions. Aqueous solutions can be classified as nonelectrolyte or electrolyte, depending on their ability to conduct electricity. (4.1)
- We will see that precipitation reactions are those in which the product is an insoluble compound. We learn to represent these reactions using ionic equations and net ionic equations. (4.2)
- Next, we learn acid-base reactions, which involve the transfer of proton ( $\text{H}^+$ ) from an acid to a base. (4.3)
- We then learn oxidation-reduction (redox) reactions in which electrons are transferred between reactants. We will see that there are several types of redox reactions. (4.4)
- To carry out quantitative studies of solutions, we learn how to express the concentration of a solution in molarity. (4.5)
- Finally, we will apply our knowledge of the mole method from Chapter 3 to the three types of reactions studied here. We will see how gravimetric analysis is used to study precipitation reactions, and the titration technique is used to study acid-base and redox reactions. (4.6, 4.7, and 4.8)

Many chemical reactions and virtually all biological processes take place in water. In this chapter, we will discuss three major categories of reactions that occur in aqueous solutions: precipitation reactions, acid-base reactions, and redox reactions. In later chapters, we will study the structural characteristics and properties of water—the so-called *universal solvent*—and its solutions.

## 4.1 General Properties of Aqueous Solutions

A **solution** is a *homogeneous mixture of two or more substances*. The **solute** is the *substance present in a smaller amount*, and the **solvent** is the *substance present in a larger amount*. A solution may be gaseous (such as air), solid (such as an alloy), or liquid (seawater, for example). In this section we will discuss only **aqueous solutions**, in which the *solute initially is a liquid or a solid and the solvent is water*.

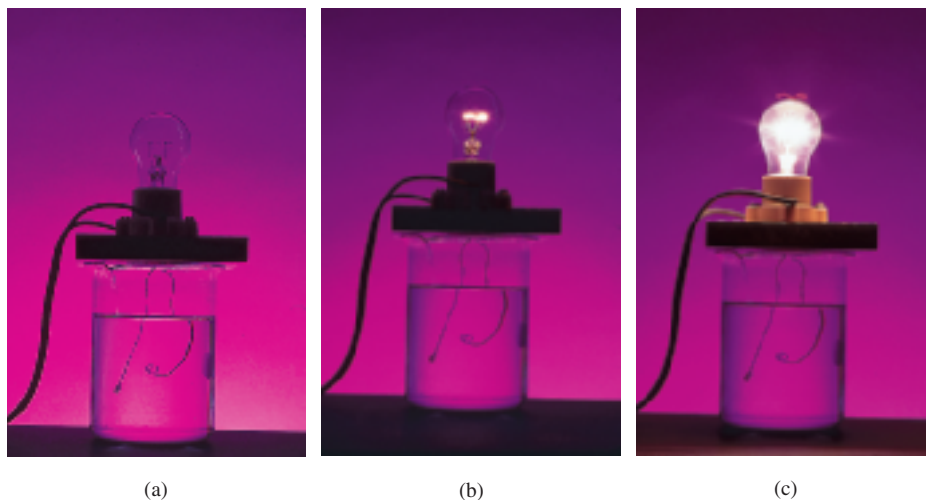
### Electrolytic Properties

All solutes that dissolve in water fit into one of two categories: electrolytes and nonelectrolytes. An **electrolyte** is a *substance that, when dissolved in water, results in a solution that can conduct electricity*. A **nonelectrolyte** does not conduct electricity when dissolved in water. Figure 4.1 shows an easy and straightforward method of distinguishing between electrolytes and nonelectrolytes. A pair of inert electrodes (copper or platinum) is immersed in a beaker of water. To light the bulb, electric current must flow from one electrode to the other, thus completing the circuit. Pure water is a very poor conductor of electricity. However, if we add a small amount of sodium chloride (NaCl), the bulb will glow as soon as the salt dissolves in the water. Solid NaCl, an ionic compound, breaks up into  $\text{Na}^+$  and  $\text{Cl}^-$  ions when it dissolves in water. The  $\text{Na}^+$  ions are attracted to the negative electrode, and the  $\text{Cl}^-$  ions to the positive electrode. This movement sets up an electric current that is equivalent to the flow of electrons along a metal wire. Because the NaCl solution conducts electricity, we say that NaCl is an electrolyte. Pure water contains very few ions, so it cannot conduct electricity.

Comparing the lightbulb's brightness for the same molar amounts of dissolved substances helps us distinguish between strong and weak electrolytes. A characteristic of strong electrolytes is that the solute is assumed to be 100 percent dissociated into

Tap water does conduct electricity because it contains many dissolved ions.

 Animation  
Strong Electrolytes, Weak Electrolytes, and Nonelectrolytes



**Figure 4.1** An arrangement for distinguishing between electrolytes and nonelectrolytes. A solution's ability to conduct electricity depends on the number of ions it contains. (a) A nonelectrolyte solution does not contain ions, and the lightbulb is not lit. (b) A weak electrolyte solution contains a small number of ions, and the lightbulb is dimly lit. (c) A strong electrolyte solution contains a large number of ions, and the lightbulb is brightly lit. The molar amounts of the dissolved solutes are equal in all three cases.

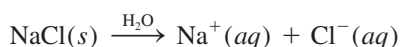
**Table 4.1** Classification of Solutes in Aqueous Solution

Strong Electrolyte	Weak Electrolyte	Nonelectrolyte
HCl	CH <sub>3</sub> COOH	(NH <sub>2</sub> ) <sub>2</sub> CO (urea)
HNO <sub>3</sub>	HF	CH <sub>3</sub> OH (methanol)
HClO <sub>4</sub>	HNO <sub>2</sub>	C <sub>2</sub> H <sub>5</sub> OH (ethanol)
H <sub>2</sub> SO <sub>4</sub> *	NH <sub>3</sub>	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> (glucose)
NaOH	H <sub>2</sub> O <sup>†</sup>	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> (sucrose)
Ba(OH) <sub>2</sub>		
Ionic compounds		

\*H<sub>2</sub>SO<sub>4</sub> has two ionizable H<sup>+</sup> ions, but only one of the H<sup>+</sup> ions is totally ionized.

†Pure water is an extremely weak electrolyte.

ions in solution. (By *dissociation* we mean the breaking up of the compound into cations and anions.) Thus, we can represent sodium chloride dissolving in water as



This equation says that all sodium chloride that enters the solution ends up as Na<sup>+</sup> and Cl<sup>-</sup> ions; there are no undissociated NaCl units in solution.

Table 4.1 lists examples of strong electrolytes, weak electrolytes, and nonelectrolytes. Ionic compounds, such as sodium chloride, potassium iodide (KI), and calcium nitrate [Ca(NO<sub>3</sub>)<sub>2</sub>], are strong electrolytes. It is interesting to note that human body fluids contain many strong and weak electrolytes.

Water is a very effective solvent for ionic compounds. Although water is an electrically neutral molecule, it has a positive region (the H atoms) and a negative region (the O atom), or positive and negative “poles”; for this reason it is a *polar* solvent. When an ionic compound such as sodium chloride dissolves in water, the three-dimensional network of ions in the solid is destroyed. The Na<sup>+</sup> and Cl<sup>-</sup> ions are separated from each other and undergo **hydration**, the process in which an ion is surrounded by water molecules arranged in a specific manner. Each Na<sup>+</sup> ion is surrounded by a number of water molecules orienting their negative poles toward the cation. Similarly, each Cl<sup>-</sup> ion is surrounded by water molecules with their positive poles oriented toward the anion (Figure 4.2). Hydration helps to stabilize ions in solution and prevents cations from combining with anions.

Acids and bases are also electrolytes. Some acids, including hydrochloric acid (HCl) and nitric acid (HNO<sub>3</sub>), are strong electrolytes. These acids are assumed to ionize completely in water; for example, when hydrogen chloride gas dissolves in water, it forms hydrated H<sup>+</sup> and Cl<sup>-</sup> ions:



In other words, *all* the dissolved HCl molecules separate into hydrated H<sup>+</sup> and Cl<sup>-</sup> ions. Thus, when we write HCl(aq), it is understood that it is a solution of only H<sup>+</sup>(aq)

 Animation  
Hydration

**Figure 4.2** Hydration of Na<sup>+</sup> and Cl<sup>-</sup> ions.

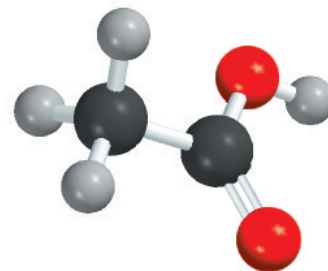


and  $\text{Cl}^-(aq)$  ions and that there are no hydrated HCl molecules present. On the other hand, certain acids, such as acetic acid ( $\text{CH}_3\text{COOH}$ ), which gives vinegar its tart flavor, do not ionize completely and are weak electrolytes. We represent the ionization of acetic acid as



where  $\text{CH}_3\text{COO}^-$  is called the acetate ion. We use the term *ionization* to describe the separation of acids and bases into ions. By writing the formula of acetic acid as  $\text{CH}_3\text{COOH}$ , we indicate that the ionizable proton is in the COOH group.

The ionization of acetic acid is written with a double arrow to show that it is a **reversible reaction**; that is, *the reaction can occur in both directions*. Initially, a number of  $\text{CH}_3\text{COOH}$  molecules break up into  $\text{CH}_3\text{COO}^-$  and  $\text{H}^+$  ions. As time goes on, some of the  $\text{CH}_3\text{COO}^-$  and  $\text{H}^+$  ions recombine into  $\text{CH}_3\text{COOH}$  molecules. Eventually, a state is reached in which the acid molecules ionize as fast as the ions recombine. Such a chemical state, in which no net change can be observed (although activity is continuous on the molecular level), is called *chemical equilibrium*. Acetic acid, then, is a weak electrolyte because its ionization in water is incomplete. By contrast, in a hydrochloric acid solution the  $\text{H}^+$  and  $\text{Cl}^-$  ions have no tendency to recombine and form molecular HCl. We use a single arrow to represent complete ionizations.

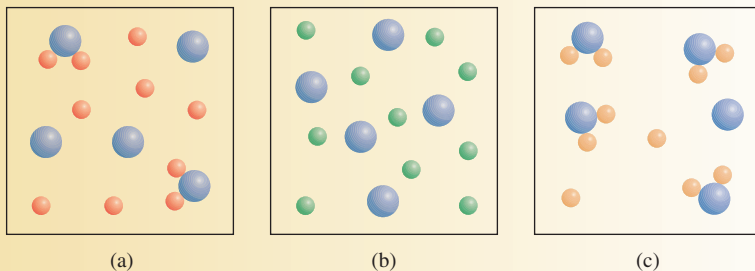


$\text{CH}_3\text{COOH}$

There are different types of chemical equilibrium. We will return to this very important topic in Chapter 14.

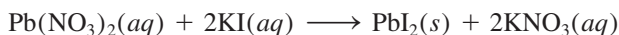
### Review of Concepts

The diagrams here show three compounds  $\text{AB}_2$  (a),  $\text{AC}_2$  (b), and  $\text{AD}_2$  (c) dissolved in water. Which is the strongest electrolyte and which is the weakest? (For simplicity, water molecules are not shown.)



## 4.2 Precipitation Reactions

One common type of reaction that occurs in aqueous solution is the **precipitation reaction**, which *results in the formation of an insoluble product, or precipitate*. A **precipitate** is an insoluble solid that separates from the solution. Precipitation reactions usually involve ionic compounds. For example, when an aqueous solution of lead(II) nitrate [ $\text{Pb}(\text{NO}_3)_2$ ] is added to an aqueous solution of potassium iodide (KI), a yellow precipitate of lead(II) iodide ( $\text{PbI}_2$ ) is formed:

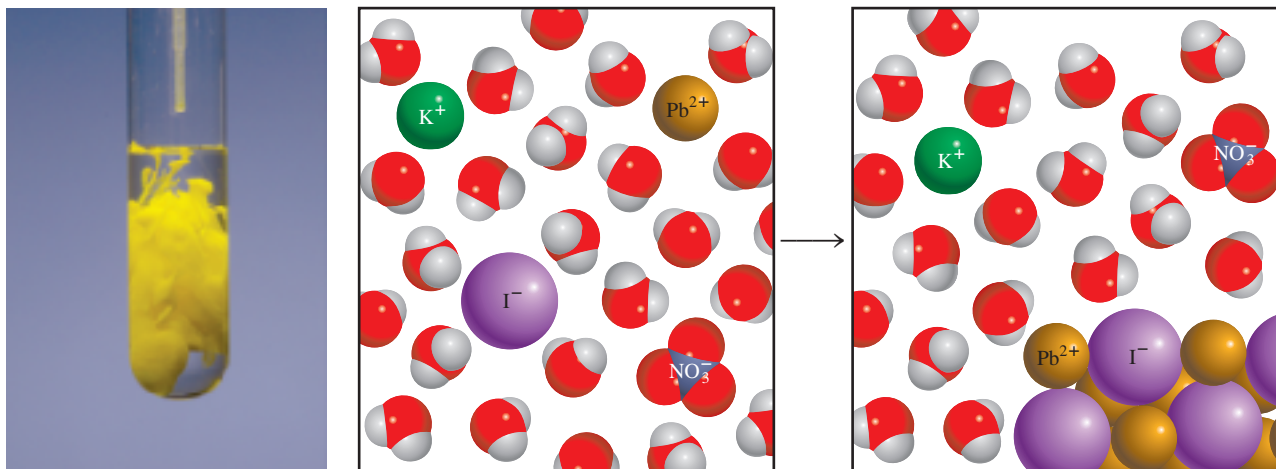


Potassium nitrate remains in solution. Figure 4.3 shows this reaction in progress.

The preceding reaction is an example of a **metathesis reaction** (also called a double-displacement reaction), *a reaction that involves the exchange of parts between the two compounds*. (In this case, the cations in the two compounds exchange anions, so  $\text{Pb}^{2+}$  ends up with  $\text{I}^-$  as  $\text{PbI}_2$  and  $\text{K}^+$  ends up with  $\text{NO}_3^-$  as  $\text{KNO}_3$ .) As we will see, the precipitation reactions discussed in this chapter are examples of metathesis reactions.

 Animation  
Precipitation Reactions





**Figure 4.3** Formation of yellow  $PbI_2$  precipitate as a solution of  $Pb(NO_3)_2$  is added to a solution of  $KI$ .

### Solubility

How can we predict whether a precipitate will form when a compound is added to a solution or when two solutions are mixed? It depends on the **solubility** of the solute, which is defined as *the maximum amount of solute that will dissolve in a given quantity of solvent at a specific temperature*. Chemists refer to substances as soluble, slightly soluble, or insoluble in a qualitative sense. A substance is said to be soluble if a fair amount of it visibly dissolves when added to water. If not, the substance is described as slightly soluble or insoluble. All ionic compounds are strong electrolytes, but they are not equally soluble.

Table 4.2 classifies a number of common ionic compounds as soluble or insoluble. Keep in mind, however, that even insoluble compounds dissolve to a certain extent. Figure 4.4 shows several precipitates.

**Table 4.2** Solubility Rules for Common Ionic Compounds in Water at 25°C

Soluble Compounds	Insoluble Exceptions
Compounds containing alkali metal ions ( $Li^+$ , $Na^+$ , $K^+$ , $Rb^+$ , $Cs^+$ ) and the ammonium ion ( $NH_4^+$ )	
Nitrates ( $NO_3^-$ ), acetates ( $CH_3COO^-$ ), bicarbonates ( $HCO_3^-$ ), chlorates ( $ClO_3^-$ ), and perchlorates ( $ClO_4^-$ )	
Halides ( $Cl^-$ , $Br^-$ , $I^-$ )	Halides of $Ag^+$ , $Hg_2^{2+}$ , and $Pb^{2+}$
Sulfates ( $SO_4^{2-}$ )	Sulfates of $Ag^+$ , $Ca^{2+}$ , $Sr^{2+}$ , $Ba^{2+}$ , $Hg_2^{2+}$ , and $Pb^{2+}$
Insoluble Compounds	Soluble Exceptions
Carbonates ( $CO_3^{2-}$ ), phosphates ( $PO_4^{3-}$ ), chromates ( $CrO_4^{2-}$ ), sulfides ( $S^{2-}$ )	Compounds containing alkali metal ions and the ammonium ion
Hydroxides ( $OH^-$ )	Compounds containing alkali metal ions and the $Ba^{2+}$ ion



**Figure 4.4** Appearance of several precipitates. From left to right:  $\text{CdS}$ ,  $\text{PbS}$ ,  $\text{Ni(OH)}_2$ , and  $\text{Al(OH)}_3$ .

Example 4.1 applies the solubility rules in Table 4.2.

### Example 4.1

Classify the following ionic compounds as soluble or insoluble: (a) silver sulfate ( $\text{Ag}_2\text{SO}_4$ ), (b) calcium carbonate ( $\text{CaCO}_3$ ), (c) sodium phosphate ( $\text{Na}_3\text{PO}_4$ ).

**Strategy** Although it is not necessary to memorize the solubilities of compounds, you should keep in mind the following useful rules: All ionic compounds containing alkali metal cations; the ammonium ion; and the nitrate, bicarbonate, and chlorate ions are soluble. For other compounds, we need to refer to Table 4.2.

**Solution** (a) According to Table 4.2,  $\text{Ag}_2\text{SO}_4$  is insoluble.

(b) This is a carbonate and Ca is a Group 2A metal. Therefore,  $\text{CaCO}_3$  is insoluble.

(c) Sodium is an alkali metal (Group 1A) so  $\text{Na}_3\text{PO}_4$  is soluble.

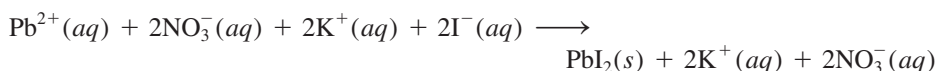
**Practice Exercise** Classify the following ionic compounds as soluble or insoluble: (a)  $\text{CuS}$ , (b)  $\text{Ca(OH)}_2$ , (c)  $\text{Zn(NO}_3)_2$ .

Similar problems: 4.19, 4.20.

## Molecular Equations, Ionic Equations, and Net Ionic Equations

The equation describing the precipitation of lead(II) iodide on page 121 is called a **molecular equation** because *the formulas of the compounds are written as though all species existed as molecules or whole units*. A molecular equation is useful because it identifies the reagents [that is, lead(II) nitrate and potassium iodide]. If we wanted to bring about this reaction in the laboratory, we would use the molecular equation. However, a molecular equation does not describe in detail what actually is happening in solution.

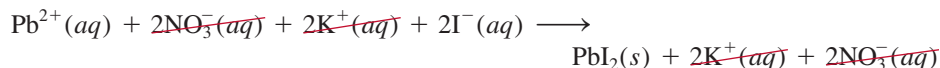
As pointed out earlier, when ionic compounds dissolve in water, they break apart into their component cations and anions. To be more realistic, the equations should show the dissociation of dissolved ionic compounds into ions. Therefore, returning to the reaction between potassium iodide and lead(II) nitrate, we would write



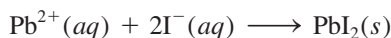


**Figure 4.5** Formation of  $\text{BaSO}_4$  precipitate.

The preceding equation is an example of an **ionic equation**, which shows dissolved species as free ions. To see whether a precipitate might form from this solution, we first combine the cation and anion from different compounds; that is,  $\text{PbI}_2$  and  $\text{KNO}_3$ . Referring to Table 4.2, we see that  $\text{PbI}_2$  is an insoluble compound and  $\text{KNO}_3$  is soluble. Therefore, the dissolved  $\text{KNO}_3$  remains in solution as separate  $\text{K}^+$  and  $\text{NO}_3^-$  ions, which are called **spectator ions**, or ions that are not involved in the overall reaction. Because spectator ions appear on both sides of an equation, they can be eliminated from the ionic equation



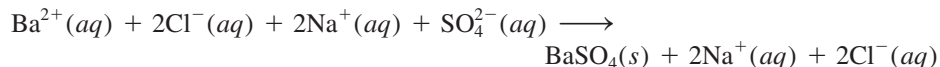
Finally, we end up with the **net ionic equation**, which shows only the species that actually take part in the reaction:



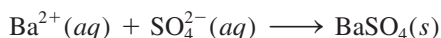
Looking at another example, we find that when an aqueous solution of barium chloride ( $\text{BaCl}_2$ ) is added to an aqueous solution of sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), a white precipitate is formed (Figure 4.5). Treating this as a metathesis reaction, the products are  $\text{BaSO}_4$  and  $\text{NaCl}$ . From Table 4.2 we see that only  $\text{BaSO}_4$  is insoluble. Therefore, we write the molecular equation as



The ionic equation for the reaction is



Canceling the spectator ions ( $\text{Na}^+$  and  $\text{Cl}^-$ ) on both sides of the equation gives us the net ionic equation



The following four steps summarize the procedure for writing ionic and net ionic equations:

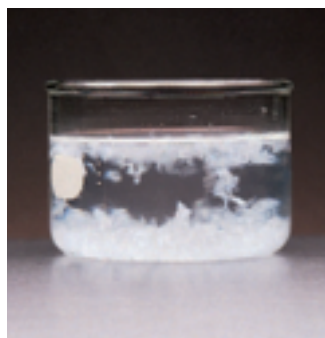
1. Write a balanced molecular equation for the reaction, using the correct formulas for the reactant and product ionic compounds. Refer to Table 4.2 to decide which of the products is insoluble and therefore will appear as a precipitate.
2. Write the ionic equation for the reaction. The compound that does not appear as the precipitate should be shown as free ions.
3. Identify and cancel the spectator ions on both sides of the equation. Write the net ionic equation for the reaction.
4. Check that the charges and number of atoms balance in the net ionic equation.

These steps are applied in Example 4.2.

### Example 4.2

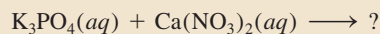
Predict what happens when a potassium phosphate ( $\text{K}_3\text{PO}_4$ ) solution is mixed with a calcium nitrate [ $\text{Ca}(\text{NO}_3)_2$ ] solution. Write a net ionic equation for the reaction.

(Continued)



Precipitate formed by the reaction between  $\text{K}_3\text{PO}_4(aq)$  and  $\text{Ca}(\text{NO}_3)_2(aq)$ .

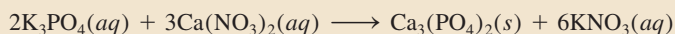
**Strategy** From the given information, it is useful to first write the unbalanced equation



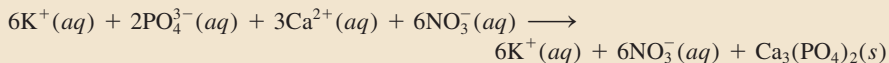
What happens when ionic compounds dissolve in water? What ions are formed from the dissociation of  $\text{K}_3\text{PO}_4$  and  $\text{Ca}(\text{NO}_3)_2$ ? What happens when the cations encounter the anions in solution?

**Solution** In solution,  $\text{K}_3\text{PO}_4$  dissociates into  $\text{K}^+$  and  $\text{PO}_4^{3-}$  ions and  $\text{Ca}(\text{NO}_3)_2$  dissociates into  $\text{Ca}^{2+}$  and  $\text{NO}_3^-$  ions. According to Table 4.2, calcium ions ( $\text{Ca}^{2+}$ ) and phosphate ions ( $\text{PO}_4^{3-}$ ) will form an insoluble compound, calcium phosphate [ $\text{Ca}_3(\text{PO}_4)_2$ ], while the other product,  $\text{KNO}_3$ , is soluble and remains in solution. Therefore, this is a precipitation reaction. We follow the stepwise procedure just outlined.

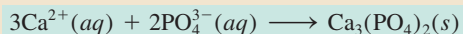
*Step 1:* The balanced molecular equation for this reaction is



*Step 2:* To write the ionic equation, the soluble compounds are shown as dissociated ions:



*Step 3:* Canceling the spectator ions ( $\text{K}^+$  and  $\text{NO}_3^-$ ) on each side of the equation, we obtain the net ionic equation:



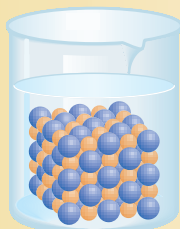
*Step 4:* Note that because we balanced the molecular equation first, the net ionic equation is balanced as to the number of atoms on each side and the number of positive (+6) and negative (−6) charges on the left-hand side is the same.

**Practice Exercise** Predict the precipitate produced by mixing an  $\text{Al}(\text{NO}_3)_3$  solution with a  $\text{NaOH}$  solution. Write the net ionic equation for the reaction.

Similar problems: 4.21, 4.22.

## Review of Concepts

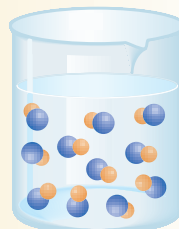
Which of the diagrams here accurately describes the reaction between  $\text{Ca}(\text{NO}_3)_2(aq)$  and  $\text{Na}_2\text{CO}_3(aq)$ ? For simplicity, only the  $\text{Ca}^{2+}$  (yellow) and  $\text{CO}_3^{2-}$  (blue) ions are shown.



(a)



(b)

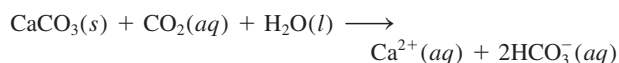


(c)

The Chemistry in Action essay on p. 126 discusses some practical problems associated with precipitation reactions.

## An Undesirable Precipitation Reaction

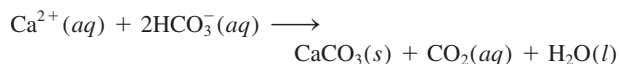
Limestone ( $\text{CaCO}_3$ ) and dolomite ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ ), which are widespread on Earth's surface, often enter the water supply. According to Table 4.2, calcium carbonate is insoluble in water. However, in the presence of dissolved carbon dioxide (from the atmosphere), calcium carbonate is converted to soluble calcium bicarbonate [ $\text{Ca}(\text{HCO}_3)_2$ ]:



where  $\text{HCO}_3^-$  is the bicarbonate ion.

Water containing  $\text{Ca}^{2+}$  and/or  $\text{Mg}^{2+}$  ions is called *hard water*, and water that is mostly free of these ions is called *soft water*. Hard water is unsuitable for some household and industrial uses.

When water containing  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  ions is heated or boiled, the solution reaction is reversed to produce the  $\text{CaCO}_3$  precipitate



and gaseous carbon dioxide is driven off:

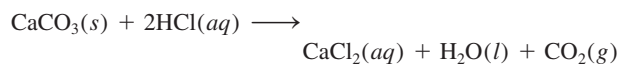


Solid calcium carbonate formed in this way is the main component of the scale that accumulates in boilers, water heaters, pipes, and teakettles. A thick layer of scale reduces heat transfer and decreases the efficiency and durability of boilers, pipes, and appliances. In household hot-water pipes it can restrict or totally



Boiler scale almost fills this hot-water pipe. The deposits consist mostly of  $\text{CaCO}_3$  with some  $\text{MgCO}_3$ .

block the flow of water. A simple method used by plumbers to remove scale deposits is to introduce a small amount of hydrochloric acid, which reacts with (and therefore dissolves)  $\text{CaCO}_3$ :



In this way,  $\text{CaCO}_3$  is converted to soluble  $\text{CaCl}_2$ .

## 4.3 Acid-Base Reactions

Acids and bases are as familiar as aspirin and milk of magnesia although many people do not know their chemical names—acetylsalicylic acid (aspirin) and magnesium hydroxide (milk of magnesia). In addition to being the basis of many medicinal and household products, acid-base chemistry is important in industrial processes and essential in sustaining biological systems. Before we can discuss acid-base reactions, we need to know more about acids and bases themselves.

### General Properties of Acids and Bases

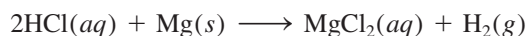
In Section 2.7 we defined acids as substances that ionize in water to produce  $\text{H}^+$  ions and bases as substances that ionize in water to produce  $\text{OH}^-$  ions. These definitions were formulated in the late nineteenth century by the Swedish chemist



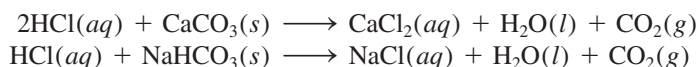
Svante Arrhenius<sup>†</sup> to classify substances whose properties in aqueous solutions were well known.

### Acids

- Acids have a sour taste; for example, vinegar owes its sourness to acetic acid, and lemons and other citrus fruits contain citric acid.
- Acids cause color changes in plant dyes; for example, they change the color of litmus from blue to red.
- Acids react with certain metals, such as zinc, magnesium, and iron, to produce hydrogen gas. A typical reaction is that between hydrochloric acid and magnesium:



- Acids react with carbonates and bicarbonates, such as  $\text{Na}_2\text{CO}_3$ ,  $\text{CaCO}_3$ , and  $\text{NaHCO}_3$ , to produce carbon dioxide gas (Figure 4.6). For example,



- Aqueous acid solutions conduct electricity.

### Bases

- Bases have a bitter taste.
- Bases feel slippery; for example, soaps, which contain bases, exhibit this property.
- Bases cause color changes in plant dyes; for example, they change the color of litmus from red to blue.
- Aqueous base solutions conduct electricity.

## Brønsted Acids and Bases

Arrhenius' definitions of acids and bases are limited in that they apply only to aqueous solutions. Broader definitions were proposed by the Danish chemist Johannes Brønsted<sup>‡</sup> in 1932; a **Brønsted acid** is a *proton donor*, and a **Brønsted base** is a *proton acceptor*. Note that Brønsted's definitions do not require acids and bases to be in aqueous solution.

Hydrochloric acid is a Brønsted acid because it donates a proton in water:



Note that the  $\text{H}^+$  ion is a hydrogen atom that has lost its electron; that is, it is just a bare proton. The size of a proton is about  $10^{-15}$  m, compared to a diameter of  $10^{-10}$  m for an average atom or ion. Such an exceedingly small charged particle cannot exist as a separate entity in aqueous solution owing to its strong attraction for the negative pole

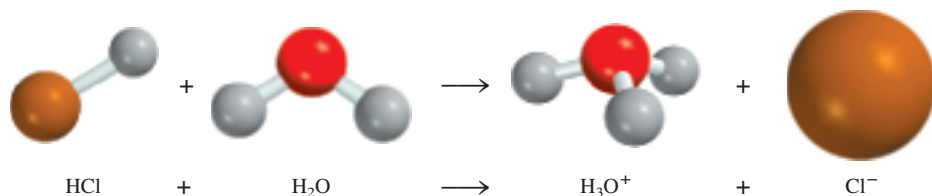


**Figure 4.6** A piece of blackboard chalk, which is mostly  $\text{CaCO}_3$ , reacts with hydrochloric acid.

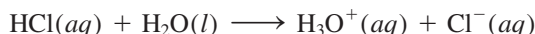
<sup>†</sup>Svante August Arrhenius (1859–1927). Swedish chemist. Arrhenius made important contributions in the study of chemical kinetics and electrolyte solutions. He also speculated that life had come to Earth from other planets, a theory now known as *panspermia*. Arrhenius was awarded the Nobel Prize in Chemistry in 1903.

<sup>‡</sup>Johannes Nicolaus Brønsted (1879–1947). Danish chemist. In addition to his theory of acids and bases, Brønsted worked on thermodynamics and the separation of mercury isotopes. In some texts, Brønsted acids and bases are called Brønsted-Lowry acids and bases. Thomas Martin Lowry (1874–1936). English chemist. Brønsted and Lowry developed essentially the same acid-base theory independently in 1923.

**Figure 4.7** Ionization of HCl in water to form the hydronium ion and the chloride ion.



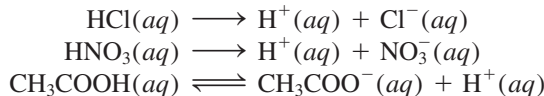
(the O atom) in  $\text{H}_2\text{O}$ . Consequently, the proton exists in the hydrated form, as shown in Figure 4.7. Therefore, the ionization of hydrochloric acid should be written as



The *hydrated proton*,  $\text{H}_3\text{O}^+$ , is called the **hydronium ion**. This equation shows a reaction in which a Brønsted acid (HCl) donates a proton to a Brønsted base ( $\text{H}_2\text{O}$ ).

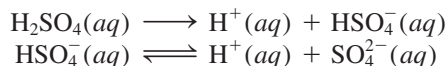
Experiments show that the hydronium ion is further hydrated so that the proton may have several water molecules associated with it. Because the acidic properties of the proton are unaffected by the degree of hydration, in this text we will generally use  $\text{H}^+(aq)$  to represent the hydrated proton. This notation is for convenience, but  $\text{H}_3\text{O}^+$  is closer to reality. Keep in mind that both notations represent the same species in aqueous solution.

Acids commonly used in the laboratory include hydrochloric acid (HCl), nitric acid ( $\text{HNO}_3$ ), acetic acid ( $\text{CH}_3\text{COOH}$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), and phosphoric acid ( $\text{H}_3\text{PO}_4$ ). The first three are **monoprotic acids**; that is, *each unit of the acid yields one hydrogen ion upon ionization*:



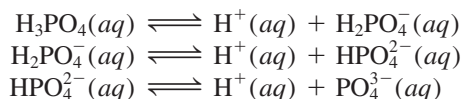
As mentioned earlier, because the ionization of acetic acid is incomplete (note the double arrows), it is a weak electrolyte. For this reason it is called a weak acid (see Table 4.1). On the other hand, HCl and  $\text{HNO}_3$  are strong acids because they are strong electrolytes, so they are completely ionized in solution (note the use of single arrows).

Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is a **diprotic acid** because *each unit of the acid gives up two  $\text{H}^+$  ions*, in two separate steps:

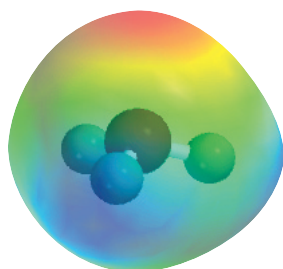


$\text{H}_2\text{SO}_4$  is a strong electrolyte or strong acid (the first step of ionization is complete), but  $\text{HSO}_4^-$  is a weak acid or weak electrolyte, and we need a double arrow to represent its incomplete ionization.

**Triprotic acids**, which yield three  $\text{H}^+$  ions, are relatively few in number. The best known triprotic acid is phosphoric acid, whose ionizations are



All three species ( $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{HPO}_4^{2-}$ ) in this case are weak acids, and we use the double arrows to represent each ionization step. Anions such as  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  are found in aqueous solutions of phosphates such as  $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$ . Table 4.3 lists several common strong and weak acids.



Electrostatic potential map of the  $\text{H}_3\text{O}^+$  ion. In the rainbow color spectrum representation, the most electron-rich region is red and the most electron-poor region is blue.

In most cases, acids start with H in the formula or have a COOH group.

**Table 4.3**

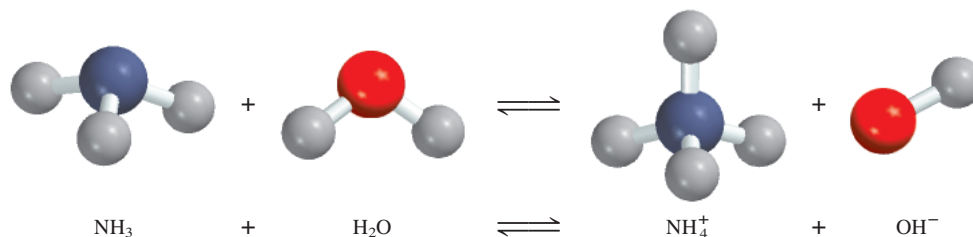
**Some Common Strong and Weak Acids**

**Strong Acids**

Hydrochloric acid	HCl
Hydrobromic acid	HBr
Hydroiodic acid	HI
Nitric acid	$\text{HNO}_3$
Sulfuric acid	$\text{H}_2\text{SO}_4$
Perchloric acid	$\text{HClO}_4$

**Weak Acids**

Hydrofluoric acid	HF
Nitrous acid	$\text{HNO}_2$
Phosphoric acid	$\text{H}_3\text{PO}_4$
Acetic acid	$\text{CH}_3\text{COOH}$



**Figure 4.8** Ionization of ammonia in water to form the ammonium ion and the hydroxide ion.

### Review of Concepts

Which of the following diagrams best represents a weak acid? Which represents a very weak acid? Which represents a strong acid? The proton exists in water as the hydronium ion. All acids are monoprotic. (For simplicity, water molecules are not shown.)

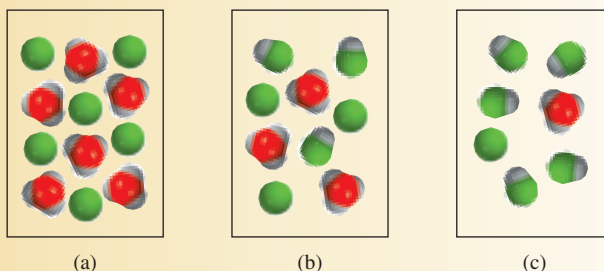
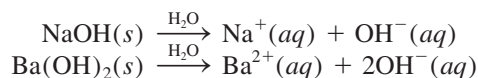
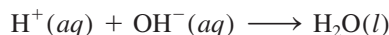


Table 4.1 shows that sodium hydroxide (NaOH) and barium hydroxide [Ba(OH)<sub>2</sub>] are strong electrolytes. This means that they are completely ionized in solution:

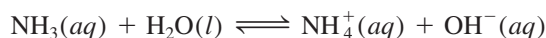


The OH<sup>−</sup> ion can accept a proton as follows:



Thus, OH<sup>−</sup> is a Brønsted base.

Ammonia (NH<sub>3</sub>) is classified as a Brønsted base because it can accept a H<sup>+</sup> ion (Figure 4.8):



Ammonia is a weak electrolyte (and therefore a weak base) because only a small fraction of dissolved NH<sub>3</sub> molecules react with water to form NH<sub>4</sub><sup>+</sup> and OH<sup>−</sup> ions.

The most commonly used strong base in the laboratory is sodium hydroxide. It is cheap and soluble. (In fact, all of the alkali metal hydroxides are soluble.) The most commonly used weak base is aqueous ammonia solution, which is sometimes erroneously called ammonium hydroxide. There is no evidence that the species NH<sub>4</sub>OH actually exists other than the NH<sub>4</sub><sup>+</sup> and OH<sup>−</sup> ions in solution. All of the Group 2A elements form hydroxides of the type M(OH)<sub>2</sub>, where M denotes an alkaline earth



Note that this bottle of aqueous ammonia is erroneously labeled.

metal. Of these hydroxides, only  $\text{Ba}(\text{OH})_2$  is soluble. Magnesium and calcium hydroxides are used in medicine and industry. Hydroxides of other metals, such as  $\text{Al}(\text{OH})_3$  and  $\text{Zn}(\text{OH})_2$  are insoluble and are not used as bases.

Example 4.3 classifies substances as Brønsted acids or Brønsted bases.

### Example 4.3

Classify each of the following species in aqueous solution as a Brønsted acid or base: (a)  $\text{HBr}$ , (b)  $\text{NO}_2^-$ , (c)  $\text{HCO}_3^-$ .

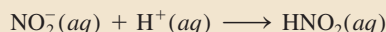
**Strategy** What are the characteristics of a Brønsted acid? Does it contain at least an H atom? With the exception of ammonia, most Brønsted bases that you will encounter at this stage are anions.

**Solution** (a) We know that  $\text{HCl}$  is an acid. Because Br and Cl are both halogens (Group 7A), we expect  $\text{HBr}$ , like  $\text{HCl}$ , to ionize in water as follows:



Therefore  $\text{HBr}$  is a Brønsted acid.

(b) In solution the nitrite ion can accept a proton from water to form nitrous acid:

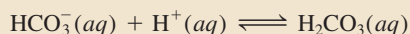


This property makes  $\text{NO}_2^-$  a Brønsted base.

(c) The bicarbonate ion is a Brønsted acid because it ionizes in solution as follows:



It is also a Brønsted base because it can accept a proton to form carbonic acid:



**Comment** The  $\text{HCO}_3^-$  species is said to be *amphoteric* because it possesses both acidic and basic properties. The double arrows show that this is a reversible reaction.

**Practice Exercise** Classify each of the following species as a Brønsted acid or base: (a)  $\text{SO}_4^{2-}$ , (b)  $\text{HI}$ .

Similar problems: 4.31, 4.32.

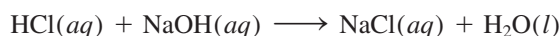
## Acid-Base Neutralization

 Animation  
Neutralization Reactions

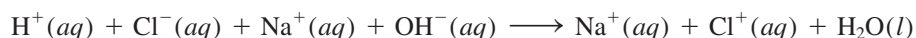
A **neutralization reaction** is a reaction between an acid and a base. Generally, aqueous acid-base reactions produce water and a **salt**, which is an ionic compound made up of a cation other than  $\text{H}^+$  and an anion other than  $\text{OH}^-$  or  $\text{O}^{2-}$ :



The substance we know as table salt,  $\text{NaCl}$ , is a product of the acid-base reaction

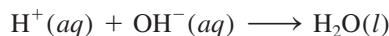


However, because both the acid and the base are strong electrolytes, they are completely ionized in solution. The ionic equation is



Acid-base reactions generally go to completion.

Therefore, the reaction can be represented by the net ionic equation



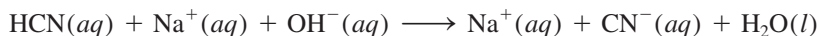
Both  $\text{Na}^+$  and  $\text{Cl}^-$  are spectator ions.

If we had started the preceding reaction with equal molar amounts of the acid and the base, at the end of the reaction we would have only a salt and no leftover acid or base. This is a characteristic of acid-base neutralization reactions.

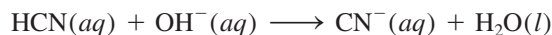
A reaction between a weak acid such as hydrocyanic acid (HCN) and a strong base is



Because HCN is a weak acid, it does not ionize appreciably in solution. Thus, the ionic equation is written as

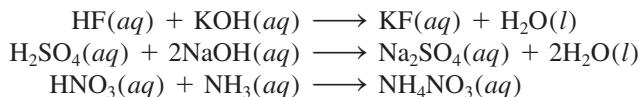


and the net ionic equation is

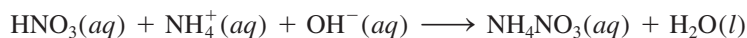


Note that only  $\text{Na}^+$  is a spectator ion;  $\text{OH}^-$  and  $\text{CN}^-$  are not.

The following are also examples of acid-base neutralization reactions, represented by molecular equations:



The last equation looks different because it does not show water as a product. However, if we express  $\text{NH}_3(aq)$  as  $\text{NH}_4^+(aq)$  and  $\text{OH}^-(aq)$ , as discussed earlier, then the equation becomes



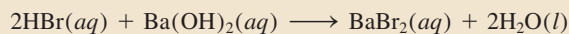
### Example 4.4

Write molecular, ionic, and net ionic equations for each of the following acid-base reactions:

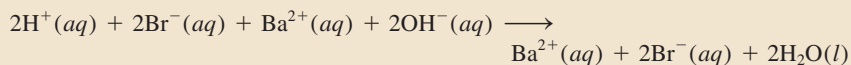
- (a) hydrobromic acid(aq) + barium hydroxide(aq)  $\longrightarrow$   
 (b) sulfuric acid(aq) + potassium hydroxide(aq)  $\longrightarrow$

**Strategy** The first step is to identify the acids and bases as strong or weak. We see that HBr is a strong acid and  $\text{H}_2\text{SO}_4$  is a strong acid for the first step ionization and a weak acid for the second step ionization. Both  $\text{Ba}(\text{OH})_2$  and KOH are strong bases.

**Solution** (a) Molecular equation:



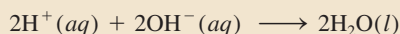
Ionic equation:



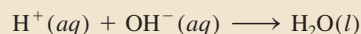
(Continued)



Net ionic equation:

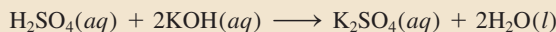


or



Both  $\text{Ba}^{2+}$  and  $\text{Br}^-$  are spectator ions.

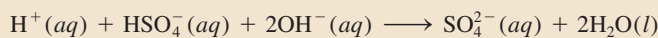
(b) Molecular equation:



Ionic equation:



Net ionic equation:



Note that because  $\text{HSO}_4^-$  is a weak acid and does not ionize appreciably in water, the only spectator ion is  $\text{K}^+$ .

Similar problem: 4.33(b).

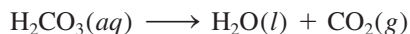
**Practice Exercise** Write a molecular equation, an ionic equation, and a net ionic equation for the reaction between aqueous solutions of phosphoric acid and sodium hydroxide.

## Acid-Base Reactions Leading to Gas Formation

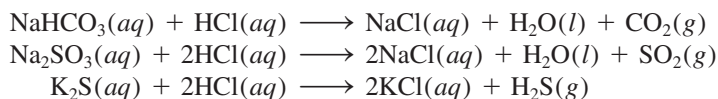
Certain salts like carbonates (containing the  $\text{CO}_3^{2-}$  ion), bicarbonates (containing the  $\text{HCO}_3^-$  ion), sulfites (containing the  $\text{SO}_3^{2-}$  ion), and sulfides (containing the  $\text{S}^{2-}$  ion) react with acids to form gaseous products. For example, the molecular equation for the reaction between sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and  $\text{HCl}(aq)$  is (see Figure 4.6)



Carbonic acid is unstable and if present in solution in sufficient concentrations decomposes as follows:

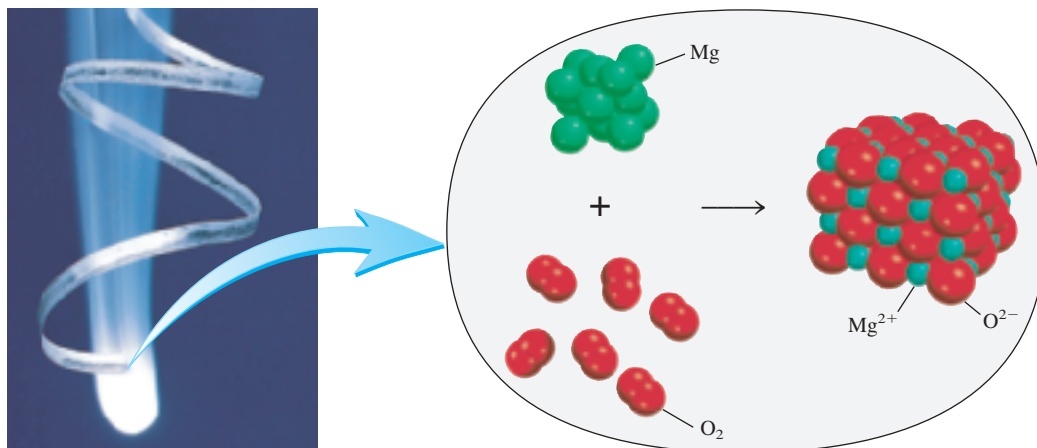


Similar reactions involving other mentioned salts are



## 4.4 Oxidation-Reduction Reactions

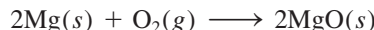
Whereas acid-base reactions can be characterized as proton-transfer processes, the class of reactions called **oxidation-reduction**, or **redox reactions** are considered *electron-transfer reactions*. Oxidation-reduction reactions are very much a part of the world around us. They range from the burning of fossil fuels to the action of household



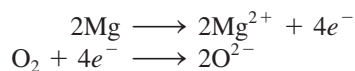
**Figure 4.9** Magnesium burns in oxygen to form magnesium oxide.

bleach. Additionally, most metallic and nonmetallic elements are obtained from their ores by the process of oxidation or reduction.

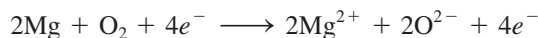
Many important redox reactions take place in water, but not all redox reactions occur in aqueous solution. We begin our discussion with a reaction in which two elements combine to form a compound. Consider the formation of magnesium oxide (MgO) from magnesium and oxygen (Figure 4.9):



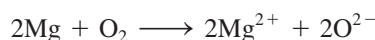
Magnesium oxide (MgO) is an ionic compound made up of  $\text{Mg}^{2+}$  and  $\text{O}^{2-}$  ions. In this reaction, two Mg atoms give up or transfer four electrons to two O atoms (in  $\text{O}_2$ ). For convenience, we can think of this process as two separate steps, one involving the loss of four electrons by the two Mg atoms and the other being the gain of four electrons by an  $\text{O}_2$  molecule:



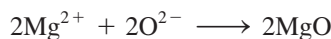
Each of these steps is called a **half-reaction**, which *explicitly shows the electrons involved in a redox reaction*. The sum of the half-reactions gives the overall reaction:



or, if we cancel the electrons that appear on both sides of the equation,




Finally, the  $\text{Mg}^{2+}$  and  $\text{O}^{2-}$  ions combine to form MgO:



The term **oxidation reaction** refers to the *half-reaction that involves loss of electrons*. Chemists originally used “oxidation” to denote the combination of elements with oxygen. However, it now has a broader meaning that includes reactions not involving oxygen. A **reduction reaction** is a *half-reaction that involves gain of electrons*. In the formation of magnesium oxide, magnesium is oxidized. It is said to act

 **Animation**  
Reaction of Magnesium and Oxygen

 **Animation**  
Formation of  $\text{Ag}_2\text{S}$  by Oxidation-Reduction

Note that in an oxidation half-reaction, electrons appear as the product; in a reduction half-reaction, electrons appear as the reactant.

A useful mnemonic for redox is OILRIG: Oxidation Is Loss (of electrons) and Reduction Is Gain (of electrons).

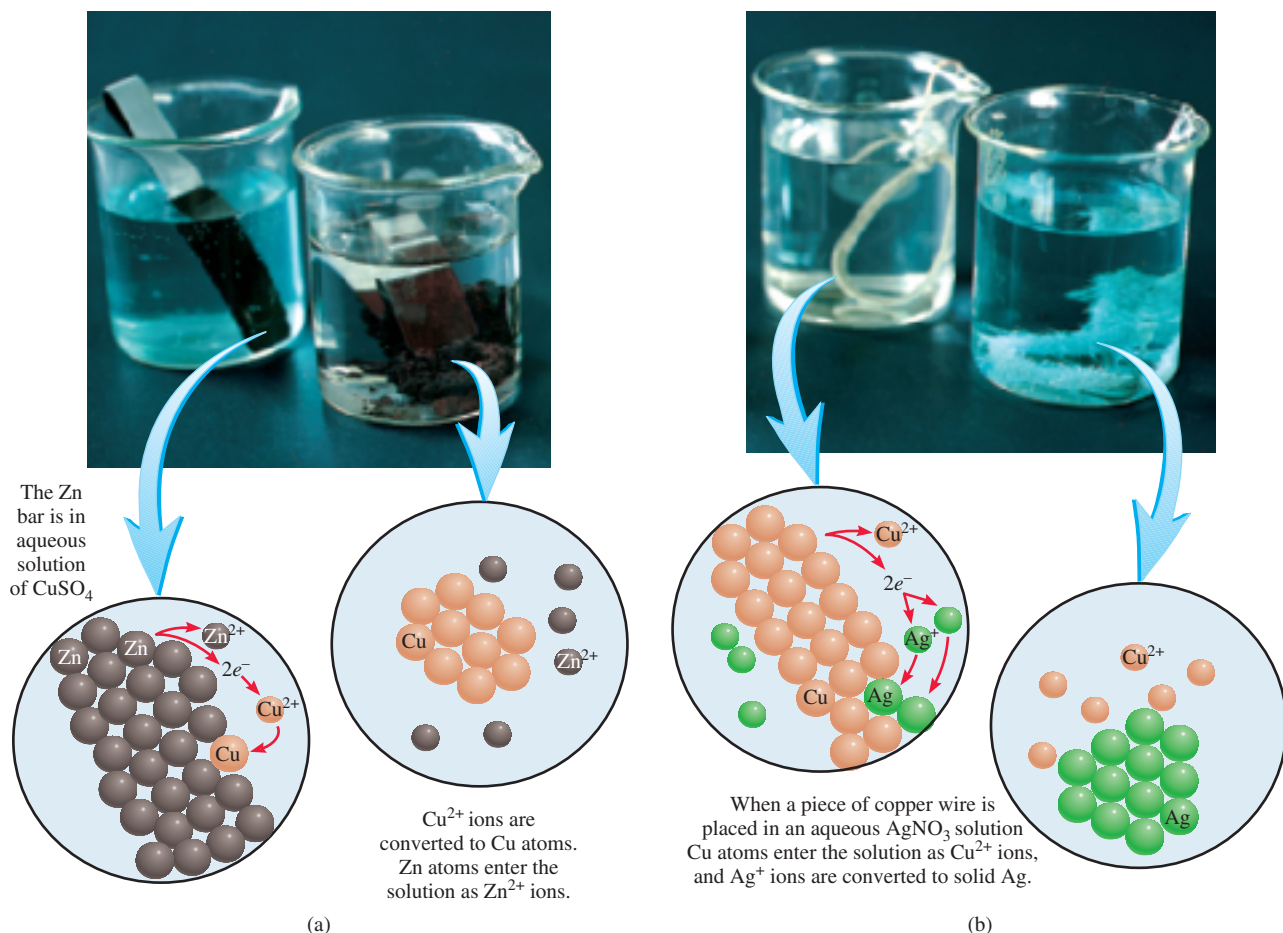
Oxidizing agents are always reduced and reducing agents are always oxidized. This statement may be somewhat confusing, but it is simply a consequence of the definitions of the two processes.

as a **reducing agent** because it *donates electrons* to oxygen and causes oxygen to be reduced. Oxygen is reduced and acts as an **oxidizing agent** because it *accepts electrons* from magnesium, causing magnesium to be oxidized. Note that the extent of oxidation in a redox reaction must be equal to the extent of reduction; that is, the number of electrons lost by a reducing agent must be equal to the number of electrons gained by an oxidizing agent.

The occurrence of electron transfer is more apparent in some redox reactions than others. When metallic zinc is added to a solution containing copper(II) sulfate ( $\text{CuSO}_4$ ), zinc reduces  $\text{Cu}^{2+}$  by donating two electrons to it:

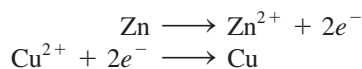


In the process, the solution loses the blue color that characterizes the presence of hydrated  $\text{Cu}^{2+}$  ions (Figure 4.10):



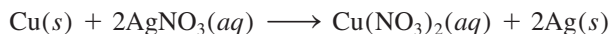
**Figure 4.10** Metal displacement reactions in solution. (a) First beaker: A zinc strip is placed in a blue  $\text{CuSO}_4$  solution. Immediately  $\text{Cu}^{2+}$  ions are reduced to metallic Cu in the form of a dark layer. Second beaker: In time, most of the  $\text{Cu}^{2+}$  ions are reduced and the solution becomes colorless. (b) First beaker: A piece of Cu wire is placed in a colorless  $\text{AgNO}_3$  solution.  $\text{Ag}^+$  ions are reduced to metallic Ag. Second beaker: As time progresses, most of the  $\text{Ag}^+$  ions are reduced and the solution acquires the characteristic blue color due to the presence of hydrated  $\text{Cu}^{2+}$  ions.

The oxidation and reduction half-reactions are

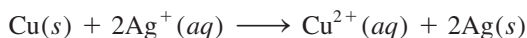


Similarly, metallic copper reduces silver ions in a solution of silver nitrate ( $\text{AgNO}_3$ ):

 Animation  
Reaction of Cu with  $\text{AgNO}_3$

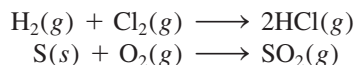


or



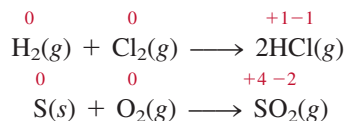
## Oxidation Number

The definitions of oxidation and reduction in terms of loss and gain of electrons apply to the formation of ionic compounds such as  $\text{MgO}$  and the reduction of  $\text{Cu}^{2+}$  ions by  $\text{Zn}$ . However, these definitions do not accurately characterize the formation of hydrogen chloride ( $\text{HCl}$ ) and sulfur dioxide ( $\text{SO}_2$ ):



Because  $\text{HCl}$  and  $\text{SO}_2$  are not ionic but molecular compounds, no electrons are actually transferred in the formation of these compounds, as they are in the case of  $\text{MgO}$ . Nevertheless, chemists find it convenient to treat these reactions as redox reactions because experimental measurements show that there is a partial transfer of electrons (from  $\text{H}$  to  $\text{Cl}$  in  $\text{HCl}$  and from  $\text{S}$  to  $\text{O}$  in  $\text{SO}_2$ ).

To keep track of electrons in redox reactions, it is useful to assign oxidation numbers to the reactants and products. An atom's **oxidation number**, also called **oxidation state**, signifies the *number of charges the atom would have in a molecule (or an ionic compound) if electrons were transferred completely*. For example, we can rewrite the previous equations for the formation of  $\text{HCl}$  and  $\text{SO}_2$  as follows:



The numbers above the element symbols are the oxidation numbers. In both of the reactions shown, there is no charge on the atoms in the reactant molecules. Thus, their oxidation number is zero. For the product molecules, however, it is assumed that complete electron transfer has taken place and that atoms have gained or lost electrons. The oxidation numbers reflect the number of electrons “transferred.”

Oxidation numbers enable us to identify elements that are oxidized and reduced at a glance. The elements that show an increase in oxidation number—hydrogen and sulfur in the preceding examples—are oxidized. Chlorine and oxygen are reduced, so their oxidation numbers show a decrease from their initial values. Note that the sum of the oxidation numbers of  $\text{H}$  and  $\text{Cl}$  in  $\text{HCl}$  (+1 and  $-1$ ) is zero.

Likewise, if we add the oxidation numbers of S (+4) and two atoms of O [ $2 \times (-2)$ ], the total is zero. The reason is that the HCl and SO<sub>2</sub> molecules are neutral, so the charges must cancel.

We use the following rules to assign oxidation numbers:

1. In free elements (that is, in the uncombined state), each atom has an oxidation number of zero. Thus, each atom in H<sub>2</sub>, Br<sub>2</sub>, Na, Be, K, O<sub>2</sub>, and P<sub>4</sub> has the same oxidation number: zero.
2. For ions composed of only one atom (that is, monatomic ions), the oxidation number is equal to the charge on the ion. Thus, Li<sup>+</sup> ion has an oxidation number of +1; Ba<sup>2+</sup> ion, +2; Fe<sup>3+</sup> ion, +3; I<sup>-</sup> ion, -1; O<sup>2-</sup> ion, -2; and so on. All alkali metals have an oxidation number of +1 and all alkaline earth metals have an oxidation number of +2 in their compounds. Aluminum has an oxidation number of +3 in all its compounds.
3. The oxidation number of oxygen in most compounds (for example, MgO and H<sub>2</sub>O) is -2, but in hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and peroxide ion (O<sub>2</sub><sup>2-</sup>), it is -1.
4. The oxidation number of hydrogen is +1, except when it is bonded to metals in binary compounds. In these cases (for example, LiH, NaH, CaH<sub>2</sub>), its oxidation number is -1.
5. Fluorine has an oxidation number of -1 in *all* its compounds. Other halogens (Cl, Br, and I) have negative oxidation numbers when they occur as halide ions in their compounds. When combined with oxygen—for example in oxoacids and oxoanions (see Section 2.7)—they have positive oxidation numbers.
6. In a neutral molecule, the sum of the oxidation numbers of all the atoms must be zero. In a polyatomic ion, the sum of oxidation numbers of all the elements in the ion must be equal to the net charge of the ion. For example, in the ammonium ion, NH<sub>4</sub><sup>+</sup>, the oxidation number of N is -3 and that of H is +1. Thus, the sum of the oxidation numbers is  $-3 + 4(+1) = +1$ , which is equal to the net charge of the ion.
7. Oxidation numbers do not have to be integers. For example, the oxidation number of O in the superoxide ion, O<sub>2</sub><sup>-</sup>, is  $-\frac{1}{2}$ .

We apply the preceding rules to assign oxidation numbers in Example 4.5.

### Example 4.5

Assign oxidation numbers to all the elements in the following compounds and ion:  
(a) Li<sub>2</sub>O, (b) HNO<sub>3</sub>, (c) Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>.

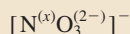
**Strategy** In general, we follow the rules just listed for assigning oxidation numbers. Remember that all alkali metals have an oxidation number of +1, and in most cases hydrogen has an oxidation number of +1 and oxygen has an oxidation number of -2 in their compounds.

**Solution** (a) By rule 2 we see that lithium has an oxidation number of +1 (Li<sup>+</sup>) and oxygen's oxidation number is -2 (O<sup>2-</sup>).  
(b) This is the formula for nitric acid, which yields a H<sup>+</sup> ion and a NO<sub>3</sub><sup>-</sup> ion in solution. From rule 4 we see that H has an oxidation number of +1. Thus the other group (the nitrate ion) must have a net oxidation number of -1. Oxygen has an

(Continued)



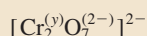
oxidation number of  $-2$ , and if we use  $x$  to represent the oxidation number of nitrogen, then the nitrate ion can be written as



so that  $x + 3(-2) = -1$

or  $x = +5$

- (c) From rule 6 we see that the sum of the oxidation numbers in the dichromate ion  $\text{Cr}_2\text{O}_7^{2-}$  must be  $-2$ . We know that the oxidation number of O is  $-2$ , so all that remains is to determine the oxidation number of Cr, which we call  $y$ . The dichromate ion can be written as



so that  $2(y) + 7(-2) = -2$

or  $y = +6$

**Check** In each case, does the sum of the oxidation numbers of all the atoms equal the net charge on the species?

**Practice Exercise** Assign oxidation numbers to all the elements in the following compound and ion: (a)  $\text{PF}_3$ , (b)  $\text{MnO}_4^-$ .

Similar problems: 4.47, 4.49.

Figure 4.11 shows the known oxidation numbers of the familiar elements, arranged according to their positions in the periodic table. We can summarize the content of this figure as follows:

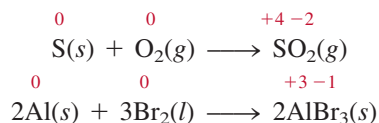
- Metallic elements have only positive oxidation numbers, whereas nonmetallic elements may have either positive or negative oxidation numbers.
- The highest oxidation number an element in Groups 1A–7A can have is its group number. For example, the halogens are in Group 7A, so their highest possible oxidation number is  $+7$ .
- The transition metals (Groups 1B, 3B–8B) usually have several possible oxidation numbers.

## Types of Redox Reactions

Among the most common oxidation-reduction reactions are combination, decomposition, combustion, and displacement reactions. A more involved type is called disproportionation reactions, which will also be discussed in this section.

### Combination Reactions

A **combination reaction** is a reaction in which two or more substances combine to form a single product. Figure 4.12 shows some combination reactions. For example,



Not all combination reactions are redox in nature. The same holds for decomposition reactions.

1 1A <b>H</b> +1 -1																	18 8A <b>He</b>	
2 2A												13 3A	14 4A	15 5A	16 6A	17 7A	10 <b>Ne</b>	
3 <b>Li</b> +1	4 <b>Be</b> +2											5 <b>B</b> +3	6 <b>C</b> +4 +2 -4	7 <b>N</b> +5 +4 +3 +2 +1 -3	8 <b>O</b> +2 -1 -2	9 <b>F</b> -1	18 <b>Ar</b>	
11 <b>Na</b> +1	12 <b>Mg</b> +2											13 <b>Al</b> +3	14 <b>Si</b> +4 -4	15 <b>P</b> +5 +3 -3	16 <b>S</b> +6 +4 +2 -2	17 <b>Cl</b> +7 +6 +5 +4 +3 +1 -1	18 <b>Ar</b>	
		3 3B	4 4B	5 5B	6 6B	7 7B	8 8B		9	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
19 <b>K</b> +1	20 <b>Ca</b> +2	21 <b>Sc</b> +3	22 <b>Ti</b> +4 +3 +2	23 <b>V</b> +5 +4 +3 +2	24 <b>Cr</b> +6 +5 +4 +3 +2	25 <b>Mn</b> +7 +6 +4 +3 +2	26 <b>Fe</b> +3 +2	27 <b>Co</b> +3 +2	28 <b>Ni</b> +2	29 <b>Cu</b> +2 +1	30 <b>Zn</b> +2	31 <b>Ga</b> +3	32 <b>Ge</b> +4 -4	33 <b>As</b> +5 +3 -3	34 <b>Se</b> +6 +4 -2	35 <b>Br</b> +5 +3 +1 -1	36 <b>Kr</b> +4 +2	36 <b>Kr</b>
37 <b>Rb</b> +1	38 <b>Sr</b> +2	39 <b>Y</b> +3	40 <b>Zr</b> +4	41 <b>Nb</b> +5 +4	42 <b>Mo</b> +6 +4 +3	43 <b>Tc</b> +7 +6 +4	44 <b>Ru</b> +8 +6 +4 +3	45 <b>Rh</b> +4 +3 +2	46 <b>Pd</b> +4 +2	47 <b>Ag</b> +1	48 <b>Cd</b> +2	49 <b>In</b> +3	50 <b>Sn</b> +4 +2	51 <b>Sb</b> +5 +3 -3	52 <b>Te</b> +6 +4 -2	53 <b>I</b> +7 +5 +1 -1	54 <b>Xe</b> +6 +4 +2	54 <b>Xe</b>
55 <b>Cs</b> +1	56 <b>Ba</b> +2	57 <b>La</b> +3	72 <b>Hf</b> +4	73 <b>Ta</b> +5	74 <b>W</b> +6 +4	75 <b>Re</b> +7 +6 +4	76 <b>Os</b> +8 +4	77 <b>Ir</b> +4 +3	78 <b>Pt</b> +4 +2	79 <b>Au</b> +3 +1	80 <b>Hg</b> +2 +1	81 <b>Tl</b> +3 +1	82 <b>Pb</b> +4 +2	83 <b>Bi</b> +5 +3	84 <b>Po</b> +2	85 <b>At</b> -1	86 <b>Rn</b>	86 <b>Rn</b>

**Figure 4.11** The oxidation numbers of elements in their compounds. The more common oxidation numbers are in color.



(a)

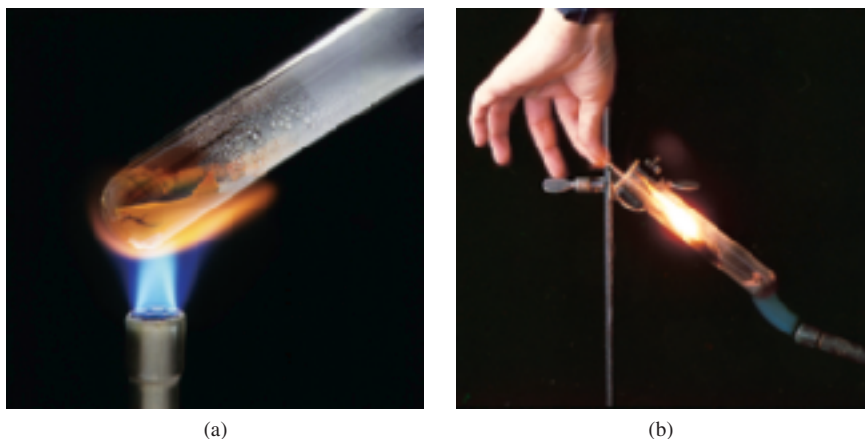


(b)



(c)

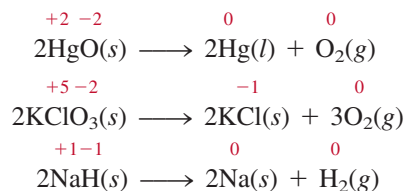
**Figure 4.12** Some simple combination redox reactions. (a) Sulfur burning in air to form sulfur dioxide. (b) Sodium burning in chlorine to form sodium chloride. (c) Aluminum reacting with bromine to form aluminum bromide.



**Figure 4.13** (a) On heating, mercury(II) oxide ( $\text{HgO}$ ) decomposes to form mercury and oxygen. (b) Heating potassium chlorate ( $\text{KClO}_3$ ) produces oxygen, which supports the combustion of the wood splint.

### Decomposition Reactions

Decomposition reactions are the opposite of combination reactions. Specifically, a **decomposition reaction** is the breakdown of a compound into two or more components (Figure 4.13). For example,

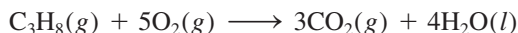


We show oxidation numbers only for elements that are oxidized or reduced.

All combustion reactions are redox processes.

### Combustion Reactions

A **combustion reaction** is a reaction in which a substance reacts with oxygen, usually with the release of heat and light to produce a flame. The reactions between magnesium and sulfur with oxygen described earlier are combustion reactions. Another example is the burning of propane ( $\text{C}_3\text{H}_8$ ), a component of natural gas that is used for domestic heating and cooking:

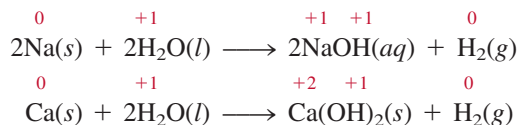


Assigning an oxidation number to C atoms in organic compounds is more involved. Here, we focus only on the oxidation number of O atoms, which changes from 0 to  $-2$ .

### Displacement Reactions

In a **displacement reaction**, an ion (or atom) in a compound is replaced by an ion (or atom) of another element: Most displacement reactions fit into one of three sub-categories: hydrogen displacement, metal displacement, or halogen displacement.

**1. Hydrogen Displacement.** All alkali metals and some alkaline earth metals (Ca, Sr, and Ba), which are the most reactive of the metallic elements, will displace hydrogen from cold water (Figure 4.14):

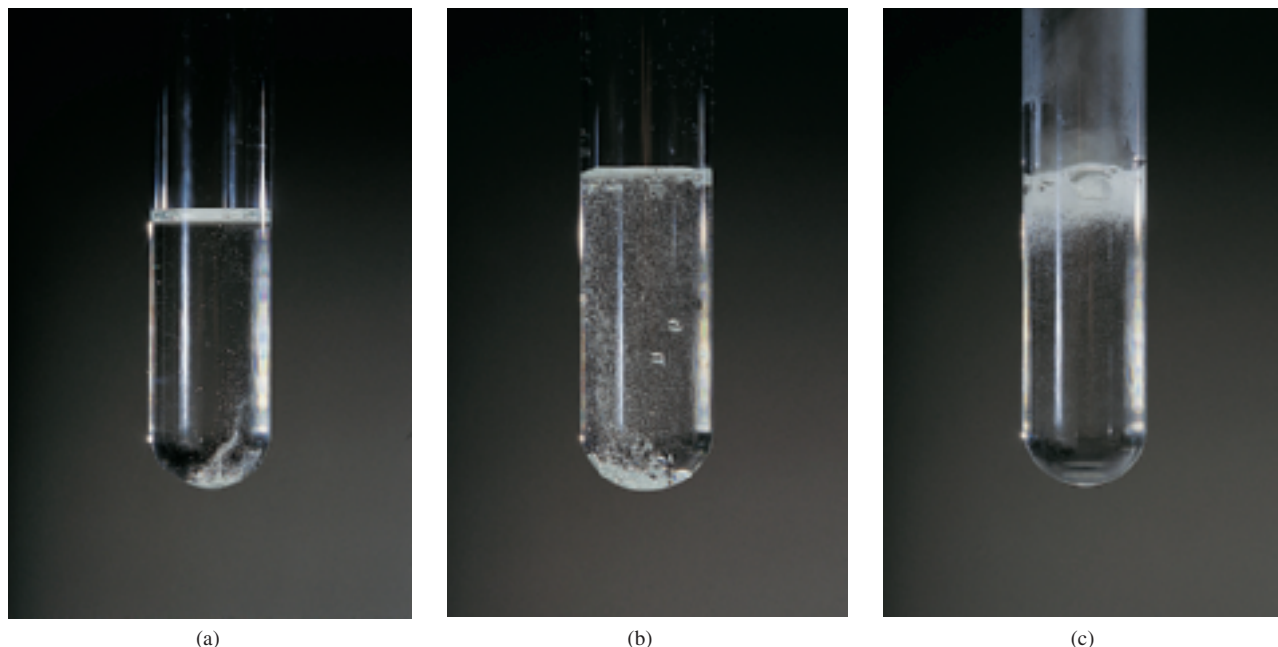


(a)



(b)

**Figure 4.14** Reactions of (a) sodium (Na) and (b) calcium (Ca) with cold water. Note that the reaction is more vigorous with Na than with Ca.



**Figure 4.15** Reactions of (a) iron (Fe), (b) zinc (Zn), and (c) magnesium (Mg) with hydrochloric acid to form hydrogen gas and the metal chlorides ( $\text{FeCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{MgCl}_2$ ). The reactivity of these metals is reflected in the rate of hydrogen gas evolution, which is slowest for the least reactive metal, Fe, and fastest for the most reactive metal, Mg.

Many metals, including those that do not react with water, are capable of displacing hydrogen from acids. For example, zinc (Zn) and magnesium (Mg) do not react with cold water but do react with hydrochloric acid, as follows:

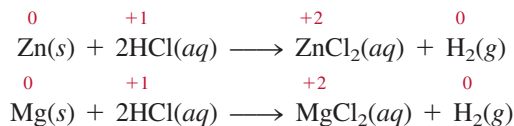


Figure 4.15 shows the reactions between hydrochloric acid (HCl) and iron (Fe), zinc (Zn), and magnesium (Mg). These reactions are used to prepare hydrogen gas in the laboratory.

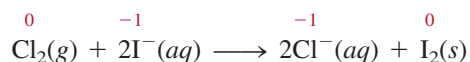
**2. Metal Displacement.** A metal in a compound can be displaced by another metal in the elemental state. We have already seen examples of zinc replacing copper ions and copper replacing silver ions (see p. 134). Reversing the roles of the metals would result in no reaction. Thus, copper metal will not displace zinc ions from zinc sulfate, and silver metal will not displace copper ions from copper nitrate.

An easy way to predict whether a metal or hydrogen displacement reaction will actually occur is to refer to an **activity series** (sometimes called the *electrochemical series*), shown in Figure 4.16. Basically, an activity series is a *convenient summary of the results of many possible displacement reactions* similar to the ones already discussed. According to this series, any metal above hydrogen will displace it from water or from an acid, but metals below hydrogen will not react with either water or an acid. In fact, any metal listed in the series will react with any metal (in a compound) below it. For example, Zn is above Cu, so zinc metal will displace copper ions from copper sulfate.

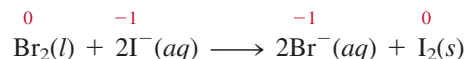




The ionic equations are



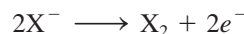
Molecular bromine, in turn, can displace iodide ion in solution:



Reversing the roles of the halogens produces no reaction. Thus, bromine cannot displace chloride ions, and iodine cannot displace bromide and chloride ions.

The halogen displacement reactions have a direct industrial application. The halogens as a group are the most reactive of the nonmetallic elements. They are all strong oxidizing agents. As a result, they are found in nature in the combined state (with metals) as halides and never as free elements. Of these four elements, chlorine is by far the most important industrial chemical. In 2010 the amount of chlorine produced in the United States was about 25 billion pounds, making chlorine the tenth-ranking industrial chemical. The annual production of bromine is only one-hundredth that of chlorine, while the amounts of fluorine and iodine produced are even less.

Recovering the halogens from their halides requires an oxidation process, which is represented by



Bromine is a fuming red liquid.



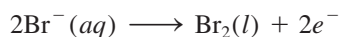
**Figure 4.17** The industrial manufacture of liquid bromine by oxidizing an aqueous solution containing  $\text{Br}^-$  ions with chlorine gas.

												5A	6A	7A
												N	O	
												P	S	Cl
														Br
														I
												Au	Hg	

Elements that are most likely to undergo disproportionation reactions.

where X denotes a halogen element. Seawater and natural brine (for example, underground water in contact with salt deposits) are rich sources of  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  ions. Minerals such as fluorite ( $\text{CaF}_2$ ) and cryolite ( $\text{Na}_3\text{AlF}_6$ ) are used to prepare fluorine. Because fluorine is the strongest oxidizing agent known, there is no way to convert  $\text{F}^-$  ions to  $\text{F}_2$  by chemical means. The only way to carry out the oxidation is by electrolytic means, the details of which will be discussed in Chapter 18. Industrially, chlorine, like fluorine, is produced electrolytically.

Bromine is prepared industrially by oxidizing  $\text{Br}^-$  ions with chlorine, which is a strong enough oxidizing agent to oxidize  $\text{Br}^-$  ions but not water:



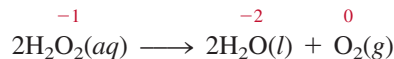
One of the richest sources of  $\text{Br}^-$  ions is the Dead Sea—about 4000 parts per million (ppm) by mass of all dissolved substances in the Dead Sea is Br. Following the oxidation of  $\text{Br}^-$  ions, bromine is removed from the solution by blowing air over the solution, and the air-bromine mixture is then cooled to condense the bromine (Figure 4.17).

Iodine is also prepared from seawater and natural brine by the oxidation of  $\text{I}^-$  ions with chlorine. Because  $\text{Br}^-$  and  $\text{I}^-$  ions are invariably present in the same source, they are both oxidized by chlorine. However, it is relatively easy to separate  $\text{Br}_2$  from  $\text{I}_2$  because iodine is a solid that is sparingly soluble in water. The air-blowing procedure will remove most of the bromine formed but will not affect the iodine present.

### Disproportionation Reaction

A special type of redox reaction is the disproportionation reaction. In a **disproportionation reaction**, an element in one oxidation state is simultaneously oxidized and reduced. One reactant in a disproportionation reaction *always* contains an element that can have at least three oxidation states. The element itself is in an intermediate oxidation state;

that is, both higher and lower oxidation states exist for that element in the products. The decomposition of hydrogen peroxide is an example of a disproportionation reaction:



Note that the oxidation number of H remains unchanged at +1.

Here the oxidation number of oxygen in the reactant (−1) both increases to zero in O<sub>2</sub> and decreases to −2 in H<sub>2</sub>O. Another example is the reaction between molecular chlorine and NaOH solution:



This reaction describes the formation of household bleaching agents, for it is the hypochlorite ion (ClO<sup>−</sup>) that oxidizes the color-bearing substances in stains, converting them to colorless compounds.

Finally, it is interesting to compare redox reactions and acid-base reactions. They are analogous in that acid-base reactions involve the transfer of protons while redox reactions involve the transfer of electrons. However, while acid-base reactions are quite easy to recognize (because they always involve an acid and a base), there is no simple procedure for identifying a redox process. The only sure way is to compare the oxidation numbers of all the elements in the reactants and products. Any change in oxidation number *guarantees* that the reaction is redox in nature.

The classification of different types of redox reactions is illustrated in Example 4.6.

### Example 4.6

Classify the following redox reactions and indicate changes in the oxidation numbers of the elements:

- (a)  $2\text{N}_2\text{O}(g) \longrightarrow 2\text{N}_2(g) + \text{O}_2(g)$
- (b)  $6\text{Li}(s) + \text{N}_2(g) \longrightarrow 2\text{Li}_3\text{N}(s)$
- (c)  $\text{Ni}(s) + \text{Pb}(\text{NO}_3)_2(aq) \longrightarrow \text{Pb}(s) + \text{Ni}(\text{NO}_3)_2(aq)$
- (d)  $2\text{NO}_2(g) + \text{H}_2\text{O}(l) \longrightarrow \text{HNO}_2(aq) + \text{HNO}_3(aq)$

**Strategy** Review the definitions of combination reactions, decomposition reactions, displacement reactions, and disproportionation reactions.

- Solution**
- (a) This is a decomposition reaction because one reactant is converted to two different products. The oxidation number of N changes from +1 to 0, while that of O changes from −2 to 0.
  - (b) This is a combination reaction (two reactants form a single product). The oxidation number of Li changes from 0 to +1 while that of N changes from 0 to −3.
  - (c) This is a metal displacement reaction. The Ni metal replaces (reduces) the Pb<sup>2+</sup> ion. The oxidation number of Ni increases from 0 to +2 while that of Pb decreases from +2 to 0.
  - (d) The oxidation number of N is +4 in NO<sub>2</sub> and it is +3 in HNO<sub>2</sub> and +5 in HNO<sub>3</sub>. Because the oxidation number of the *same* element both increases and decreases, this is a disproportionation reaction.

**Practice Exercise** Identify the following redox reactions by type:

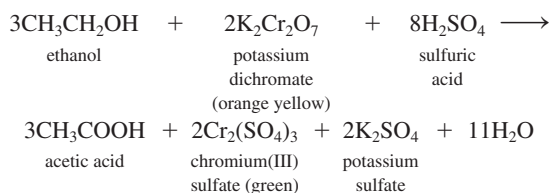
- (a)  $\text{Fe} + \text{H}_2\text{SO}_4 \longrightarrow \text{FeSO}_4 + \text{H}_2$
- (b)  $\text{S} + 3\text{F}_2 \longrightarrow \text{SF}_6$
- (c)  $2\text{CuCl} \longrightarrow \text{Cu} + \text{CuCl}_2$
- (d)  $2\text{Ag} + \text{PtCl}_2 \longrightarrow 2\text{AgCl} + \text{Pt}$

Similar problems: 4.55, 4.56.

## Breathalyzer

Every year in the United States about 25,000 people are killed and 500,000 more are injured as a result of drunk driving. In spite of efforts to educate the public about the dangers of driving while intoxicated and stiffer penalties for drunk driving offenses, law enforcement agencies still have to devote a great deal of work to removing drunk drivers from America's roads.

The police often use a device called a breathalyzer to test drivers suspected of being drunk. The chemical basis of this device is a redox reaction. A sample of the driver's breath is drawn into the breathalyzer, where it is treated with an acidic solution of potassium dichromate. The alcohol (ethanol) in the breath is converted to acetic acid as shown in the following equation:

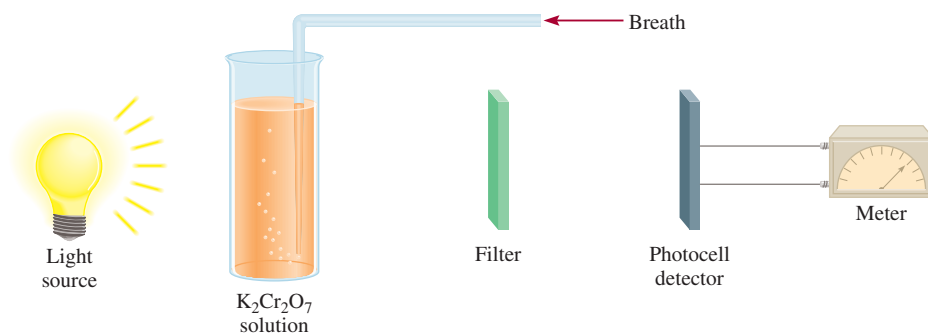


In this reaction, the ethanol is oxidized to acetic acid and the chromium(VI) in the orange-yellow dichromate ion is reduced to



A driver being tested for blood alcohol content with a handheld breathalyzer.

the green chromium(III) ion (see Figure 4.22). The driver's blood alcohol level can be determined readily by measuring the degree of this color change (read from a calibrated meter on the instrument). The current legal limit of blood alcohol content is 0.08 percent by mass. Anything higher constitutes intoxication.



Schematic diagram of a breathalyzer. The alcohol in the driver's breath is reacted with a potassium dichromate solution. The change in the absorption of light due to the formation of chromium(III) sulfate is registered by the detector and shown on a meter, which directly displays the alcohol content in blood. The filter selects only one wavelength of light for measurement.

### Review of Concepts

Which of the following combination reactions is not a redox reaction?

- (a)  $2\text{Mg}(s) + \text{O}_2(g) \longrightarrow 2\text{MgO}(s)$
- (b)  $\text{H}_2(g) + \text{F}_2(g) \longrightarrow 2\text{HF}(g)$
- (c)  $\text{NH}_3(g) + \text{HCl}(g) \longrightarrow \text{NH}_4\text{Cl}(s)$
- (d)  $2\text{Na}(s) + \text{S}(s) \longrightarrow \text{Na}_2\text{S}(s)$

The above Chemistry in Action essay describes how law enforcement makes use of a redox reaction to apprehend drunk drivers.

## 4.5 Concentration of Solutions

To study solution stoichiometry, we must know how much of the reactants are present in a solution and also how to control the amounts of reactants used to bring about a reaction in aqueous solution.

The **concentration of a solution** is the amount of solute present in a given amount of solvent, or a given amount of solution. (For this discussion, we will assume the solute is a liquid or a solid and the solvent is a liquid.) The concentration of a solution can be expressed in many different ways, as we will see in Chapter 12. Here we will consider one of the most commonly used units in chemistry, **molarity (M)**, or **molar concentration**, which is the number of moles of solute per liter of solution. Molarity is defined as

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}} \quad (4.1)$$

Equation (4.1) can also be expressed algebraically as

$$M = \frac{n}{V} \quad (4.2)$$

Keep in mind that volume ( $V$ ) is liters of solution, *not* liters of solvent. Also, the molarity of a solution depends on temperature.

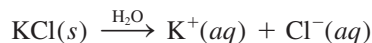
where  $n$  denotes the number of moles of solute and  $V$  is the volume of the solution in liters.

A 1.46 molar glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) solution, written as 1.46  $M$   $\text{C}_6\text{H}_{12}\text{O}_6$ , contains 1.46 moles of the solute ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) in 1 L of the solution. Of course, we do not always work with solution volumes of 1 L. Thus, a 500-mL solution containing 0.730 mole of  $\text{C}_6\text{H}_{12}\text{O}_6$  also has a concentration of 1.46  $M$ :

$$\text{molarity} = \frac{0.730 \text{ mol } \text{C}_6\text{H}_{12}\text{O}_6}{500 \text{ mL soln}} \times \frac{1000 \text{ mL soln}}{1 \text{ L soln}} = 1.46 \text{ M } \text{C}_6\text{H}_{12}\text{O}_6$$

Note that concentration, like density, is an intensive property, so its value does not depend on how much of the solution is present.

It is important to keep in mind that molarity refers only to the amount of solute originally dissolved in water and does not take into account any subsequent processes, such as the dissociation of a salt or the ionization of an acid. Consider what happens when a sample of potassium chloride (KCl) is dissolved in enough water to make a 1  $M$  solution:



Because KCl is a strong electrolyte, it undergoes complete dissociation in solution. Thus, a 1  $M$  KCl solution contains 1 mole of  $\text{K}^+$  ions and 1 mole of  $\text{Cl}^-$  ions, and no KCl units are present. The concentrations of the ions can be expressed as  $[\text{K}^+] = 1 \text{ M}$  and  $[\text{Cl}^-] = 1 \text{ M}$ , where the square brackets [ ] indicate that the concentration is expressed in molarity. Similarly, in a 1  $M$  barium nitrate [ $\text{Ba}(\text{NO}_3)_2$ ] solution

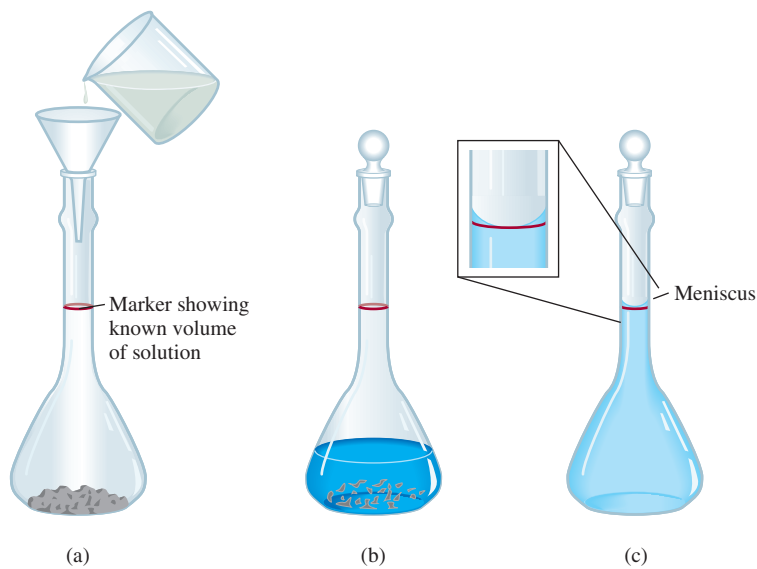


we have  $[\text{Ba}^{2+}] = 1 \text{ M}$  and  $[\text{NO}_3^-] = 2 \text{ M}$  and no  $\text{Ba}(\text{NO}_3)_2$  units at all.

The procedure for preparing a solution of known molarity is as follows. First, the solute is accurately weighed and transferred to a volumetric flask through a funnel (Figure 4.18). Next, water is added to the flask, which is carefully swirled to dissolve

 Animation  
Making a Solution

**Figure 4.18** Preparing a solution of known molarity. (a) A known amount of a solid solute is transferred into the volumetric flask; then water is added through a funnel. (b) The solid is slowly dissolved by gently swirling the flask. (c) After the solid has completely dissolved, more water is added to bring the level of solution to the mark. Knowing the volume of the solution and the amount of solute dissolved in it, we can calculate the molarity of the prepared solution.



the solid. After *all* the solid has dissolved, more water is added slowly to bring the level of solution exactly to the volume mark. Knowing the volume of the solution in the flask and the quantity of compound (the number of moles) dissolved, we can calculate the molarity of the solution using Equation (4.1). Note that this procedure does not require knowing the amount of water added, as long as the volume of the final solution is known.

Examples 4.7 and 4.8 illustrate the applications of Equations (4.1) and (4.2).



A  $\text{K}_2\text{Cr}_2\text{O}_7$  solution.

### Example 4.7

How many grams of potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) are required to prepare a 250-mL solution whose concentration is 2.16  $M$ ?

**Strategy** How many moles of  $\text{K}_2\text{Cr}_2\text{O}_7$  does a 1-L (or 1000 mL) 2.16  $M$   $\text{K}_2\text{Cr}_2\text{O}_7$  solution contain? A 250-mL solution? How would you convert moles to grams?

**Solution** The first step is to determine the number of moles of  $\text{K}_2\text{Cr}_2\text{O}_7$  in 250 mL or 0.250 L of a 2.16  $M$  solution. Rearranging Equation (4.1) gives

$$\text{moles of solute} = \text{molarity} \times \text{L soln}$$

Thus,

$$\begin{aligned} \text{moles of } \text{K}_2\text{Cr}_2\text{O}_7 &= \frac{2.16 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7}{1 \text{ L soln}} \times 0.250 \text{ L soln} \\ &= 0.540 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7 \end{aligned}$$

The molar mass of  $\text{K}_2\text{Cr}_2\text{O}_7$  is 294.2 g, so we write

$$\begin{aligned} \text{grams of } \text{K}_2\text{Cr}_2\text{O}_7 \text{ needed} &= 0.540 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7 \times \frac{294.2 \text{ g } \text{K}_2\text{Cr}_2\text{O}_7}{1 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7} \\ &= 159 \text{ g } \text{K}_2\text{Cr}_2\text{O}_7 \end{aligned}$$

(Continued)

**Check** As a ball-park estimate, the mass should be given by [molarity (mol/L)  $\times$  volume (L)  $\times$  molar mass (g/mol)] or [2 mol/L  $\times$  0.25 L  $\times$  300 g/mol] = 150 g. So the answer is reasonable.

**Practice Exercise** What is the molarity of an 85.0-mL ethanol (C<sub>2</sub>H<sub>5</sub>OH) solution containing 1.77 g of ethanol?

Similar problems: 4.65, 4.68.

### Example 4.8

In a biochemical assay, a chemist needs to add 3.81 g of glucose to a reaction mixture. Calculate the volume in milliliters of a 2.53 M glucose solution she should use for the addition.

**Strategy** We must first determine the number of moles contained in 3.81 g of glucose and then use Equation (4.2) to calculate the volume.

**Solution** From the molar mass of glucose, we write

$$3.81 \text{ g } \cancel{\text{C}_6\text{H}_{12}\text{O}_6} \times \frac{1 \text{ mol } \text{C}_6\text{H}_{12}\text{O}_6}{180.2 \text{ g } \cancel{\text{C}_6\text{H}_{12}\text{O}_6}} = 2.114 \times 10^{-2} \text{ mol } \text{C}_6\text{H}_{12}\text{O}_6$$

Next, we calculate the volume of the solution that contains  $2.114 \times 10^{-2}$  mole of the solute. Rearranging Equation (4.2) gives

$$\begin{aligned} V &= \frac{n}{M} \\ &= \frac{2.114 \times 10^{-2} \text{ mol } \text{C}_6\text{H}_{12}\text{O}_6}{2.53 \text{ mol } \text{C}_6\text{H}_{12}\text{O}_6/\text{L soln}} \times \frac{1000 \text{ mL soln}}{1 \text{ L soln}} \\ &= 8.36 \text{ mL soln} \end{aligned}$$

**Check** One liter of the solution contains 2.53 moles of C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>. Therefore, the number of moles in 8.36 mL or  $8.36 \times 10^{-3}$  L is ( $2.53 \text{ mol} \times 8.36 \times 10^{-3}$ ) or  $2.12 \times 10^{-2}$  mol. The small difference is due to the different ways of rounding off.

**Practice Exercise** What volume (in milliliters) of a 0.315 M NaOH solution contains 6.22 g of NaOH?

Note that we have carried an additional digit past the number of significant figures for the intermediate step.

Similar problem: 4.67.

## Dilution of Solutions

Concentrated solutions are often stored in the laboratory stockroom for use as needed. Frequently we dilute these “stock” solutions before working with them. **Dilution** is the procedure for preparing a less concentrated solution from a more concentrated one.

Suppose that we want to prepare 1 L of a 0.400 M KMnO<sub>4</sub> solution from a solution of 1.00 M KMnO<sub>4</sub>. For this purpose we need 0.400 mole of KMnO<sub>4</sub>. Because there is 1.00 mole of KMnO<sub>4</sub> in 1 L of a 1.00 M KMnO<sub>4</sub> solution, there is 0.400 mole of KMnO<sub>4</sub> in 0.400 L of the same solution:

$$\frac{1.00 \text{ mol}}{1 \text{ L soln}} = \frac{0.400 \text{ mol}}{0.400 \text{ L soln}}$$

Therefore, we must withdraw 400 mL from the 1.00 M KMnO<sub>4</sub> solution and dilute it to 1000 mL by adding water (in a 1-L volumetric flask). This method gives us 1 L of the desired solution of 0.400 M KMnO<sub>4</sub>.

In carrying out a dilution process, it is useful to remember that adding more solvent to a given amount of the stock solution changes (decreases) the concentration

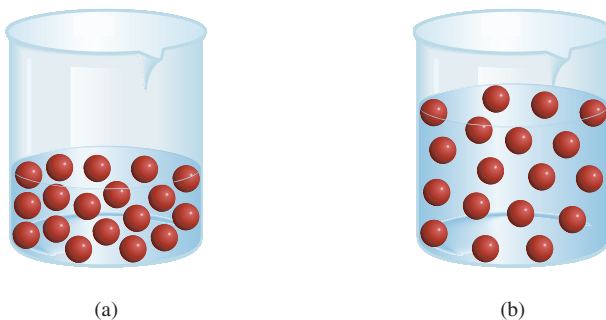
 Animation  
Preparing a Solution by Dilution



Two KMnO<sub>4</sub> solutions of different concentrations.



**Figure 4.19** The dilution of a more concentrated solution (a) to a less concentrated one (b) does not change the total number of solute particles (18).



of the solution without changing the number of moles of solute present in the solution (Figure 4.19). In other words,

$$\text{moles of solute before dilution} = \text{moles of solute after dilution}$$

Molarity is defined as moles of solute in 1 liter of solution, so the number of moles of solute is given by [see Equation (4.2)]

$$\underbrace{\frac{\text{moles of solute}}{\text{liters of soln}}}_M \times \underbrace{\text{volume of soln (in liters)}}_V = \underbrace{\text{moles of solute}}_n$$

or

$$MV = n$$

Because all the solute comes from the original stock solution, we can conclude that  $n$  remains the same; that is,

$$\begin{array}{ccc} M_i V_i & = & M_f V_f \\ \text{moles of solute} & & \text{moles of solute} \\ \text{before dilution} & & \text{after dilution} \end{array} \quad (4.3)$$

where  $M_i$  and  $M_f$  are the initial and final concentrations of the solution in molarity and  $V_i$  and  $V_f$  are the initial and final volumes of the solution, respectively. Of course, the units of  $V_i$  and  $V_f$  must be the same (mL or L) for the calculation to work. To check the reasonableness of your results, be sure that  $M_i > M_f$  and  $V_f > V_i$ .

We apply Equation (4.3) in Example 4.9.

### Example 4.9

Describe how you would prepare  $5.00 \times 10^2$  mL of a  $1.75 M$   $H_2SO_4$  solution, starting with an  $8.61 M$  stock solution of  $H_2SO_4$ .

**Strategy** Because the concentration of the final solution is less than that of the original one, this is a dilution process. Keep in mind that in dilution, the concentration of the solution decreases but the number of moles of the solute remains the same.

**Solution** We prepare for the calculation by tabulating our data:

$$\begin{array}{ll} M_i = 8.61 M & M_f = 1.75 M \\ V_i = ? & V_f = 5.00 \times 10^2 \text{ mL} \end{array}$$

(Continued)

Substituting in Equation (4.3),

$$\begin{aligned}(8.61 M)(V_i) &= (1.75 M)(5.00 \times 10^2 \text{ mL}) \\ V_i &= \frac{(1.75 M)(5.00 \times 10^2 \text{ mL})}{8.61 M} \\ &= 102 \text{ mL}\end{aligned}$$

Thus, we must dilute 102 mL of the 8.61 M H<sub>2</sub>SO<sub>4</sub> solution with sufficient water to give a final volume of 5.00 × 10<sup>2</sup> mL in a 500-mL volumetric flask to obtain the desired concentration.

**Check** The initial volume is less than the final volume, so the answer is reasonable.

**Practice Exercise** How would you prepare 2.00 × 10<sup>2</sup> mL of a 0.866 M NaOH solution, starting with a 5.07 M stock solution?

Similar problems: 4.75, 4.76.

## Review of Concepts

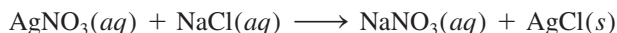
What is the final concentration of a 0.6 M NaCl solution if its volume is doubled and the number of moles of solute is tripled?

Now that we have discussed the concentration and dilution of solutions, we can examine the quantitative aspects of reactions in aqueous solution, or *solution stoichiometry*. Sections 4.6–4.8 focus on two techniques for studying solution stoichiometry: gravimetric analysis and titration. These techniques are important tools of **quantitative analysis**, which is *the determination of the amount or concentration of a substance in a sample*.

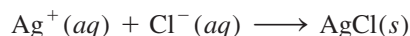
## 4.6 Gravimetric Analysis

**Gravimetric analysis** is an analytical technique based on the measurement of mass. One type of gravimetric analysis experiment involves the formation, isolation, and mass determination of a precipitate. Generally, this procedure is applied to ionic compounds. First, a sample substance of unknown composition is dissolved in water and allowed to react with another substance to form a precipitate. Then the precipitate is filtered off, dried, and weighed. Knowing the mass and chemical formula of the precipitate formed, we can calculate the mass of a particular chemical component (that is, the anion or cation) of the original sample. Finally, from the mass of the component and the mass of the original sample, we can determine the percent composition by mass of the component in the original compound.

A reaction that is often studied in gravimetric analysis, because the reactants can be obtained in pure form, is

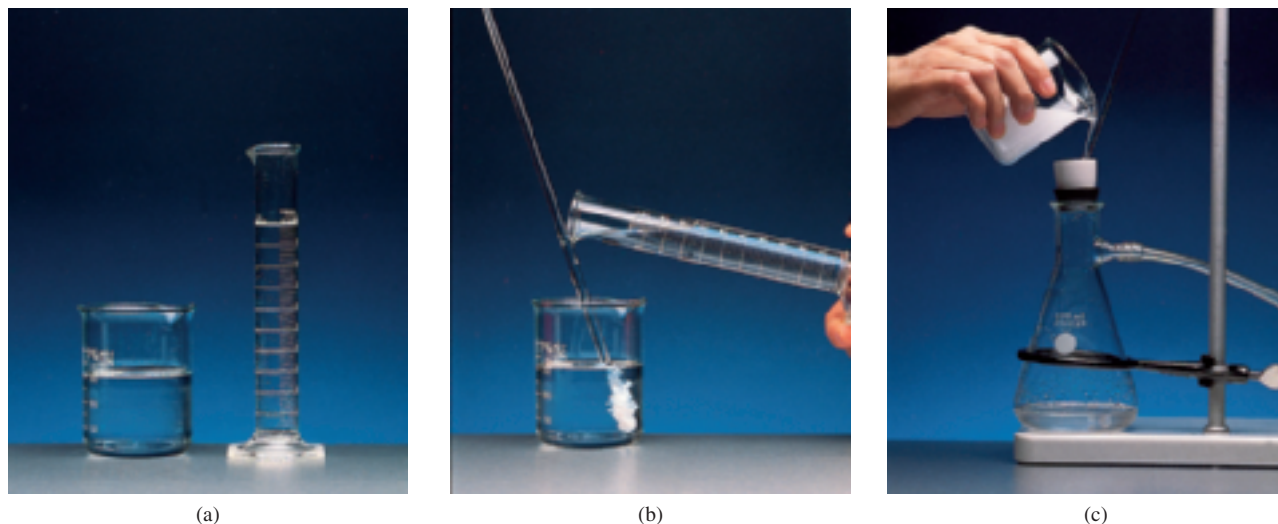


The net ionic equation is



The precipitate is silver chloride (see Table 4.2). As an example, let us say that we wanted to determine *experimentally* the percent by mass of Cl in NaCl. First, we would accurately weigh out a sample of NaCl and dissolve it in water. Next, we would add enough AgNO<sub>3</sub> solution to the NaCl solution to cause the precipitation of all the

This procedure would enable us to determine the purity of the NaCl sample.



**Figure 4.20** Basic steps for gravimetric analysis. (a) A solution containing a known amount of NaCl in a beaker. (b) The precipitation of AgCl upon the addition of AgNO<sub>3</sub> solution from a measuring cylinder. In this reaction, AgNO<sub>3</sub> is the excess reagent and NaCl is the limiting reagent. (c) The solution containing the AgCl precipitate is filtered through a preweighed sintered-disk crucible, which allows the liquid (but not the precipitate) to pass through. The crucible is then removed from the apparatus, dried in an oven, and weighed again. The difference between this mass and that of the empty crucible gives the mass of the AgCl precipitate.

Cl<sup>-</sup> ions present in solution as AgCl. In this procedure, NaCl is the limiting reagent and AgNO<sub>3</sub> the excess reagent. The AgCl precipitate is separated from the solution by filtration, dried, and weighed. From the measured mass of AgCl, we can calculate the mass of Cl using the percent by mass of Cl in AgCl. Because this same amount of Cl was present in the original NaCl sample, we can calculate the percent by mass of Cl in NaCl. Figure 4.20 shows how this procedure is performed.

Gravimetric analysis is a highly accurate technique, because the mass of a sample can be measured accurately. However, this procedure is applicable only to reactions that go to completion, or have nearly 100 percent yield. Thus, if AgCl were slightly soluble instead of being insoluble, it would not be possible to remove all the Cl<sup>-</sup> ions from the NaCl solution and the subsequent calculation would be in error.

Example 4.10 shows the calculations involved in a gravimetric experiment.

### Example 4.10

A 0.5662-g sample of an ionic compound containing chloride ions and an unknown metal is dissolved in water and treated with an excess of AgNO<sub>3</sub>. If 1.0882 g of AgCl precipitate forms, what is the percent by mass of Cl in the original compound?

**Strategy** We are asked to calculate the percent by mass of Cl in the unknown sample, which is

$$\% \text{Cl} = \frac{\text{mass of Cl}}{0.5662 \text{ g sample}} \times 100\%$$

The only source of Cl<sup>-</sup> ions is the original compound. These chloride ions eventually end up in the AgCl precipitate. Can we calculate the mass of the Cl<sup>-</sup> ions if we know the percent by mass of Cl in AgCl?

(Continued)

**Solution** The molar masses of Cl and AgCl are 35.45 g and 143.4 g, respectively. Therefore, the percent by mass of Cl in AgCl is given by

$$\begin{aligned}\% \text{Cl} &= \frac{35.45 \text{ g Cl}}{143.4 \text{ g AgCl}} \times 100\% \\ &= 24.72\%\end{aligned}$$

Next, we calculate the mass of Cl in 1.0882 g of AgCl. To do so we convert 24.72 percent to 0.2472 and write

$$\begin{aligned}\text{mass of Cl} &= 0.2472 \times 1.0882 \text{ g} \\ &= 0.2690 \text{ g}\end{aligned}$$

Because the original compound also contained this amount of  $\text{Cl}^-$  ions, the percent by mass of Cl in the compound is

$$\begin{aligned}\% \text{Cl} &= \frac{0.2690 \text{ g}}{0.5662 \text{ g}} \times 100\% \\ &= 47.51\%\end{aligned}$$

**Check** AgCl is about 25 percent chloride by mass, so the roughly 1 g of AgCl precipitate that formed corresponds to about 0.25 g of chloride, which is a little less than half of the mass of the original sample. Therefore, the calculated percent chloride of 47.51 percent is reasonable.

**Practice Exercise** A sample of 0.3220 g of an ionic compound containing the bromide ion ( $\text{Br}^-$ ) is dissolved in water and treated with an excess of  $\text{AgNO}_3$ . If the mass of the AgBr precipitate that forms is 0.6964 g, what is the percent by mass of Br in the original compound?

Similar problem: 4.82.

Note that gravimetric analysis does not establish the whole identity of the unknown. Thus, in Example 4.10 we still do not know what the cation is. However, knowing the percent by mass of Cl greatly helps us to narrow the possibilities. Because no two compounds containing the same anion (or cation) have the same percent composition by mass, comparison of the percent by mass obtained from gravimetric analysis with that calculated from a series of known compounds would reveal the identity of the unknown.

### Review of Concepts

Calculate the mass of AgBr formed if a solution containing 6.00 g of KBr is treated with an excess of  $\text{AgNO}_3$ .

## 4.7 Acid-Base Titrations

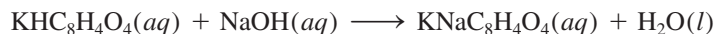
Quantitative studies of acid-base neutralization reactions are most conveniently carried out using a technique known as titration. In **titration**, a solution of accurately known concentration, called a **standard solution**, is added gradually to another solution of unknown concentration, until the chemical reaction between the two solutions is complete. If we know the volumes of the standard and unknown solutions used in the titration, along with the concentration of the standard solution, we can calculate the concentration of the unknown solution.



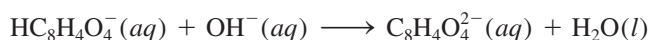
Potassium hydrogen phthalate (KHP).

KHP is a weak acid.

Sodium hydroxide is one of the bases commonly used in the laboratory. However, it is difficult to obtain solid sodium hydroxide in a pure form because it has a tendency to absorb water from air, and its solution reacts with carbon dioxide. For these reasons, a solution of sodium hydroxide must be *standardized* before it can be used in accurate analytical work. We can standardize the sodium hydroxide solution by titrating it against an acid solution of accurately known concentration. The acid often chosen for this task is a monoprotic acid called potassium hydrogen phthalate (KHP), for which the molecular formula is  $\text{KHC}_8\text{H}_4\text{O}_4$  (molar mass = 204.2 g). KHP is a white, soluble solid that is commercially available in highly pure form. The reaction between KHP and sodium hydroxide is



and the net ionic equation is

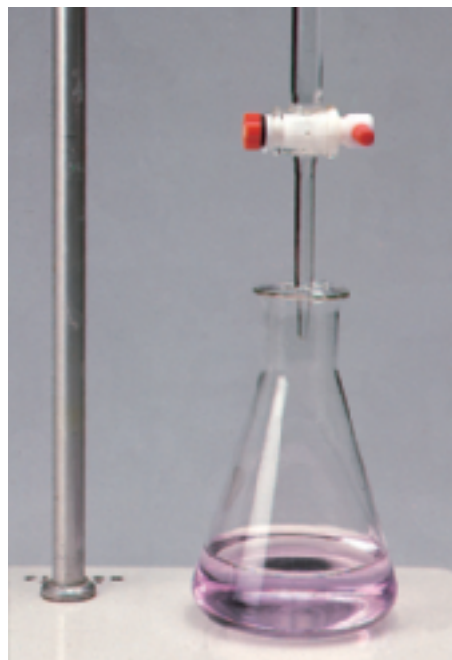


The procedure for the titration is shown in Figure 4.21. First, a known amount of KHP is transferred to an Erlenmeyer flask and some distilled water is added to make up a solution. Next, NaOH solution is carefully added to the KHP solution from a buret until we reach the **equivalence point**, that is, *the point at which the acid has completely reacted with or been neutralized by the base*. The equivalence point is usually signaled by a sharp change in the color of an indicator in the acid solution. In acid-base titrations, **indicators** are *substances that have distinctly different colors in acidic and basic media*. One commonly used indicator is phenolphthalein, which is colorless in acidic and neutral solutions but reddish pink in basic solutions. At the equivalence point, all the KHP present has been neutralized by the added NaOH and the solution is still colorless. However, if we add just one more drop of NaOH solution from the buret, the solution will immediately turn pink because the solution is now basic. Example 4.11 illustrates such a titration.

**Figure 4.21** (a) Apparatus for acid-base titration. A NaOH solution is added from the buret to a KHP solution in an Erlenmeyer flask. (b) A reddish-pink color appears when the equivalence point is reached. The color here has been intensified for visual display.



(a)



(b)

### Example 4.11

In a titration experiment, a student finds that 23.48 mL of a NaOH solution are needed to neutralize 0.5468 g of KHP. What is the concentration (in molarity) of the NaOH solution?

**Strategy** We want to determine the molarity of the NaOH solution. What is the definition of molarity?

$$\text{molarity of NaOH} = \frac{\text{mol NaOH}}{\text{L soln}}$$

↑ want to calculate
↑ need to find  
↑ given

The volume of NaOH solution is given in the problem. Therefore, we need to find the number of moles of NaOH to solve for molarity. From the preceding equation for the reaction between KHP and NaOH shown in the text we see that 1 mole of KHP neutralizes 1 mole of NaOH. How many moles of KHP are contained in 0.5468 g of KHP?

**Solution** First we calculate the number of moles of KHP consumed in the titration:

$$\begin{aligned} \text{moles of KHP} &= 0.5468 \text{ g KHP} \times \frac{1 \text{ mol KHP}}{204.2 \text{ g KHP}} \\ &= 2.678 \times 10^{-3} \text{ mol KHP} \end{aligned}$$

Because 1 mol KHP  $\approx$  1 mol NaOH, there must be  $2.678 \times 10^{-3}$  mole of NaOH in 23.48 mL of NaOH solution. Finally, we calculate the number of moles of NaOH in 1 L of the solution or the molarity as follows:

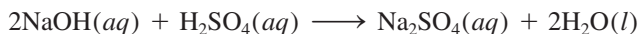
$$\begin{aligned} \text{molarity of NaOH soln} &= \frac{2.678 \times 10^{-3} \text{ mol NaOH}}{23.48 \text{ mL soln}} \times \frac{1000 \text{ mL soln}}{1 \text{ L soln}} \\ &= 0.1141 \text{ mol NaOH/1 L soln} = \mathbf{0.1141 M} \end{aligned}$$

**Practice Exercise** How many grams of KHP are needed to neutralize 18.64 mL of a 0.1004 M NaOH solution?

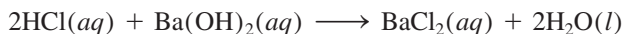
Recall that KHP is  $\text{KHC}_8\text{H}_4\text{O}_4$ .

Similar problems: 4.89, 4.90.

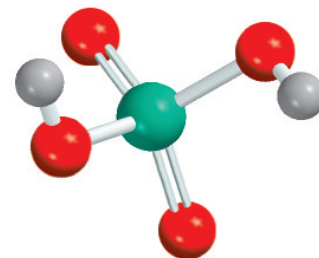
The neutralization reaction between NaOH and KHP is one of the simplest types of acid-base neutralization known. Suppose, though, that instead of KHP, we wanted to use a diprotic acid such as  $\text{H}_2\text{SO}_4$  for the titration. The reaction is represented by



Because 2 mol NaOH  $\approx$  1 mol  $\text{H}_2\text{SO}_4$ , we need twice as much NaOH to react completely with a  $\text{H}_2\text{SO}_4$  solution of the *same* molar concentration and volume as a monoprotic acid like HCl. On the other hand, we would need twice the amount of HCl to neutralize a  $\text{Ba}(\text{OH})_2$  solution compared to a NaOH solution having the same concentration and volume because 1 mole of  $\text{Ba}(\text{OH})_2$  yields 2 moles of  $\text{OH}^-$  ions:



In calculations involving acid-base titrations, regardless of the acid or base that takes place in the reaction, keep in mind that the total number of moles of  $\text{H}^+$  ions that have reacted at the equivalence point must be equal to the total number of moles of  $\text{OH}^-$  ions that have reacted.



$\text{H}_2\text{SO}_4$  has two ionizable protons.



Example 4.12 shows the titration of a NaOH solution with a diprotic acid.

### Example 4.12

How many milliliters (mL) of a 0.610 *M* NaOH solution are needed to neutralize 20.0 mL of a 0.245 *M* H<sub>2</sub>SO<sub>4</sub> solution?

**Strategy** We want to calculate the volume of the NaOH solution. From the definition of molarity [see Equation (4.1)], we write

$$\text{L soln} = \frac{\text{mol NaOH}}{\text{molarity}}$$

↑ want to calculate
↑ need to find
↑ given

From the equation for the neutralization reaction just shown, we see that 1 mole of H<sub>2</sub>SO<sub>4</sub> neutralizes 2 moles of NaOH. How many moles of H<sub>2</sub>SO<sub>4</sub> are contained in 20.0 mL of a 0.245 *M* H<sub>2</sub>SO<sub>4</sub> solution? How many moles of NaOH would this quantity of H<sub>2</sub>SO<sub>4</sub> neutralize?

**Solution** First we calculate the number of moles of H<sub>2</sub>SO<sub>4</sub> in a 20.0 mL solution:

$$\begin{aligned} \text{moles H}_2\text{SO}_4 &= \frac{0.245 \text{ mol H}_2\text{SO}_4}{1000 \text{ mL soln}} \times 20.0 \text{ mL soln} \\ &= 4.90 \times 10^{-3} \text{ mol H}_2\text{SO}_4 \end{aligned}$$

From the stoichiometry we see that 1 mol H<sub>2</sub>SO<sub>4</sub>  $\approx$  2 mol NaOH. Therefore, the number of moles of NaOH reacted must be  $2 \times 4.90 \times 10^{-3}$  mole, or  $9.80 \times 10^{-3}$  mole. From the definition of molarity [see Equation (4.1)], we have

$$\text{liters of soln} = \frac{\text{moles of solute}}{\text{molarity}}$$

or

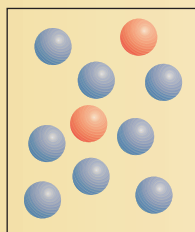
$$\begin{aligned} \text{volume of NaOH} &= \frac{9.80 \times 10^{-3} \text{ mol NaOH}}{0.610 \text{ mol/L soln}} \\ &= 0.0161 \text{ L or } 16.1 \text{ mL} \end{aligned}$$

Similar problem: 4.91(b), (c).

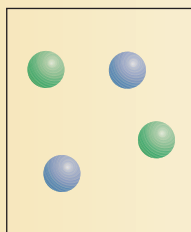
**Practice Exercise** How many milliliters of a 1.28 *M* H<sub>2</sub>SO<sub>4</sub> solution are needed to neutralize 60.2 mL of a 0.427 *M* KOH solution?

### Review of Concepts

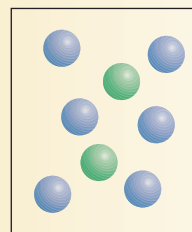
A NaOH solution is initially mixed with an acid solution shown in (a). Which of the diagrams shown in (b)–(d) corresponds to one of the following acids: HCl, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>? Color codes: Blue spheres (OH<sup>−</sup> ions); red spheres (acid molecules); green spheres (anions of the acids). Assume all the acid-base neutralization reactions go to completion.



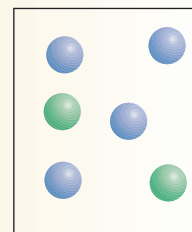
(a)



(b)



(c)



(d)



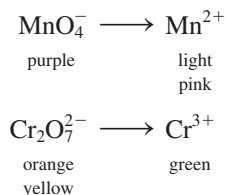
**Figure 4.22** Left to right: Solutions containing the  $\text{MnO}_4^-$ ,  $\text{Mn}^{2+}$ ,  $\text{Cr}_2\text{O}_7^{2-}$ , and  $\text{Cr}^{3+}$  ions.

## 4.8 Redox Titrations

As mentioned earlier, redox reactions involve the transfer of electrons, and acid-base reactions involve the transfer of protons. Just as an acid can be titrated against a base, we can titrate an oxidizing agent against a reducing agent, using a similar procedure. We can, for example, carefully add a solution containing an oxidizing agent to a solution containing a reducing agent. The *equivalence point* is reached when the reducing agent is completely oxidized by the oxidizing agent.

Like acid-base titrations, redox titrations normally require an indicator that clearly changes color. In the presence of large amounts of reducing agent, the color of the indicator is characteristic of its reduced form. The indicator assumes the color of its oxidized form when it is present in an oxidizing medium. At or near the equivalence point, a sharp change in the indicator's color will occur as it changes from one form to the other, so the equivalence point can be readily identified.

Two common oxidizing agents are potassium permanganate ( $\text{KMnO}_4$ ) and potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ). As Figure 4.22 shows, the colors of the permanganate and dichromate anions are distinctly different from those of the reduced species:



Thus, these oxidizing agents can themselves be used as an *internal* indicator in a redox titration because they have distinctly different colors in the oxidized and reduced forms.

Redox titrations require the same type of calculations (based on the mole method) as acid-base neutralizations. The difference is that the equations and the stoichiometry tend to be more complex for redox reactions. The following is an example of a redox titration.

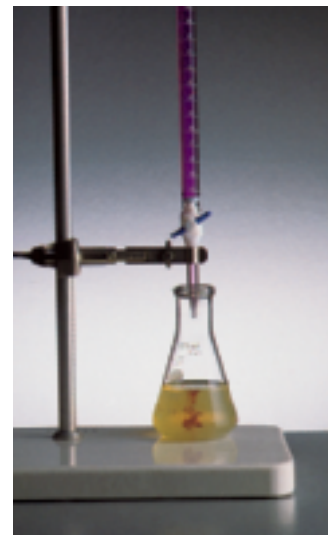
### Example 4.13

A 16.42-mL volume of 0.1327 *M*  $\text{KMnO}_4$  solution is needed to oxidize 25.00 mL of a  $\text{FeSO}_4$  solution in an acidic medium. What is the concentration of the  $\text{FeSO}_4$  solution in molarity? The net ionic equation is



(Continued)

There are not as many redox indicators as there are acid-base indicators.

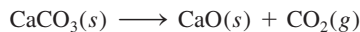


Addition of a  $\text{KMnO}_4$  solution from a buret to a  $\text{FeSO}_4$  solution.

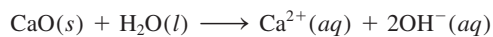
## Metal from the Sea

**M**agnesium is a valuable, lightweight metal used as a structural material as well as in alloys, in batteries, and in chemical synthesis. Although magnesium is plentiful in Earth's crust, it is cheaper to "mine" the metal from seawater. Magnesium forms the second most abundant cation in the sea (after sodium); there are about 1.3 g of magnesium in a kilogram of seawater. The process for obtaining magnesium from seawater employs all three types of reactions discussed in this chapter: precipitation, acid-base, and redox reactions.

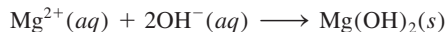
In the first stage in the recovery of magnesium, limestone ( $\text{CaCO}_3$ ) is heated at high temperatures to produce quicklime, or calcium oxide ( $\text{CaO}$ ):



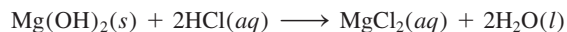
When calcium oxide is treated with seawater, it forms calcium hydroxide [ $\text{Ca}(\text{OH})_2$ ], which is slightly soluble and ionizes to give  $\text{Ca}^{2+}$  and  $\text{OH}^-$  ions:



The surplus hydroxide ions cause the much less soluble magnesium hydroxide to precipitate:



The solid magnesium hydroxide is filtered and reacted with hydrochloric acid to form magnesium chloride ( $\text{MgCl}_2$ ):

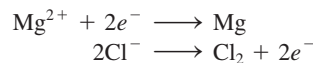


After the water is evaporated, the solid magnesium chloride is melted in a steel cell. The molten magnesium chloride contains

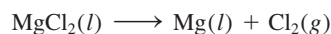


Magnesium hydroxide was precipitated from processed seawater in settling ponds at the Dow Chemical Company once operated in Freeport, Texas.

both  $\text{Mg}^{2+}$  and  $\text{Cl}^-$  ions. In a process called *electrolysis*, an electric current is passed through the cell to reduce the  $\text{Mg}^{2+}$  ions and oxidize the  $\text{Cl}^-$  ions. The half-reactions are



The overall reaction is



This is how magnesium metal is produced. The chlorine gas generated can be converted to hydrochloric acid and recycled through the process.

**Strategy** We want to calculate the molarity of the  $\text{FeSO}_4$  solution. From the definition of molarity

$$\text{molarity of FeSO}_4 = \frac{\text{mol FeSO}_4}{\text{L soln}}$$

↑ want to calculate
↑ need to find
↑ given

(Continued)

The volume of the  $\text{FeSO}_4$  solution is given in the problem. Therefore, we need to find the number of moles of  $\text{FeSO}_4$  to solve for the molarity. From the net ionic equation, what is the stoichiometric equivalence between  $\text{Fe}^{2+}$  and  $\text{MnO}_4^-$ ? How many moles of  $\text{KMnO}_4$  are contained in 16.42 mL of 0.1327 M  $\text{KMnO}_4$  solution?

**Solution** The number of moles of  $\text{KMnO}_4$  in 16.42 mL of the solution is

$$\begin{aligned}\text{moles of KMnO}_4 &= \frac{0.1327 \text{ mol KMnO}_4}{1000 \text{ mL soln}} \times 16.42 \text{ mL} \\ &= 2.179 \times 10^{-3} \text{ mol KMnO}_4\end{aligned}$$

From the net ionic equation we see that  $5 \text{ mol Fe}^{2+} \approx 1 \text{ mol MnO}_4^-$ . Therefore, the number of moles of  $\text{FeSO}_4$  oxidized is

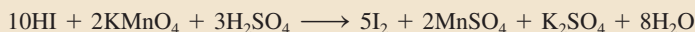
$$\begin{aligned}\text{moles FeSO}_4 &= 2.179 \times 10^{-3} \text{ mol KMnO}_4 \times \frac{5 \text{ mol FeSO}_4}{1 \text{ mol KMnO}_4} \\ &= 1.090 \times 10^{-2} \text{ mol FeSO}_4\end{aligned}$$

The concentration of the  $\text{FeSO}_4$  solution in moles of  $\text{FeSO}_4$  per liter of solution is

$$\begin{aligned}\text{molarity of FeSO}_4 &= \frac{\text{mol FeSO}_4}{\text{L soln}} \\ &= \frac{1.090 \times 10^{-2} \text{ mol FeSO}_4}{25.00 \text{ mL soln}} \times \frac{1000 \text{ mL soln}}{1 \text{ L soln}} \\ &= 0.4360 \text{ M}\end{aligned}$$

Similar problems: 4.95, 4.96.

**Practice Exercise** How many milliliters of a 0.206 M HI solution are needed to reduce 22.5 mL of a 0.374 M  $\text{KMnO}_4$  solution according to the following equation:



The Chemistry in Action essay on p. 156 describes an industrial process that involves the types of reactions discussed in this chapter.

## Key Equations

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}} \quad (4.1)$$

Calculating molarity

$$M = \frac{n}{V} \quad (4.2)$$

Calculating molarity

$$M_i V_i = M_f V_f \quad (4.3)$$

Dilution of solution

## Summary of Facts & Concepts

1. Aqueous solutions are electrically conducting if the solutes are electrolytes. If the solutes are nonelectrolytes, the solutions do not conduct electricity.
2. Three major categories of chemical reactions that take place in aqueous solution are precipitation reactions, acid-base reactions, and oxidation-reduction reactions.
3. From general rules about solubilities of ionic compounds, we can predict whether a precipitate will form in a reaction.
4. Arrhenius acids ionize in water to give  $\text{H}^+$  ions, and Arrhenius bases ionize in water to give  $\text{OH}^-$  ions. Brønsted acids donate protons, and Brønsted bases accept protons.

- The reaction of an acid and a base is called neutralization.
- In redox reactions, oxidation and reduction always occur simultaneously. Oxidation is characterized by the loss of electrons, reduction by the gain of electrons.
- Oxidation numbers help us keep track of charge distribution and are assigned to all atoms in a compound or ion according to specific rules. Oxidation can be defined as an increase in oxidation number; reduction can be defined as a decrease in oxidation number.
- Many redox reactions can be subclassified as combination, decomposition, combustion, displacement, or disproportionation reactions.
- The concentration of a solution is the amount of solute present in a given amount of solution. Molarity expresses concentration as the number of moles of solute in 1 L of solution.
- Adding a solvent to a solution, a process known as dilution, decreases the concentration (molarity) of the solution without changing the total number of moles of solute present in the solution.
- Gravimetric analysis is a technique for determining the identity of a compound and/or the concentration of a solution by measuring mass. Gravimetric experiments often involve precipitation reactions.
- In acid-base titration, a solution of known concentration (say, a base) is added gradually to a solution of unknown concentration (say, an acid) with the goal of determining the unknown concentration. The point at which the reaction in the titration is complete, as shown by the change in the indicator's color, is called the equivalence point.
- Redox titrations are similar to acid-base titrations. The point at which the oxidation-reduction reaction is complete is called the equivalence point.

## Key Words

Activity series, p. 140	Disproportionation reaction, p. 142	Monoprotic acid, p. 128	Reducing agent, p. 134
Aqueous solution, p. 119	Electrolyte, p. 119	Net ionic equation, p. 124	Reduction reaction, p. 133
Brønsted acid, p. 127	Equivalence point, p. 152	Neutralization reaction, p. 130	Reversible reaction, p. 121
Brønsted base, p. 127	Gravimetric analysis, p. 149	Nonelectrolyte, p. 119	Salt, p. 130
Combination reaction, p. 137	Half-reaction, p. 133	Oxidation number, p. 135	Solubility, p. 122
Combustion reaction, p. 139	Hydration, p. 120	Oxidation reaction, p. 133	Solute, p. 119
Concentration of a solution, p. 145	Hydronium ion, p. 128	Oxidation-reduction reaction, p. 132	Solution, p. 119
Decomposition reaction, p. 139	Indicator, p. 152	Oxidation state, p. 135	Solvent, p. 119
Dilution, p. 147	Ionic equation, p. 124	Oxidizing agent, p. 134	Spectator ion, p. 124
Diprotic acid, p. 128	Metathesis reaction, p. 121	Precipitate, p. 121	Standard solution, p. 151
Displacement reaction, p. 139	Molar concentration, p. 145	Precipitation reaction, p. 121	Titration, p. 151
	Molarity ( <i>M</i> ), p. 145	Quantitative analysis, p. 149	Triprotic acid, p. 128
	Molecular equation, p. 123	Redox reaction, p. 132	

## Questions & Problems

### Properties of Aqueous Solutions

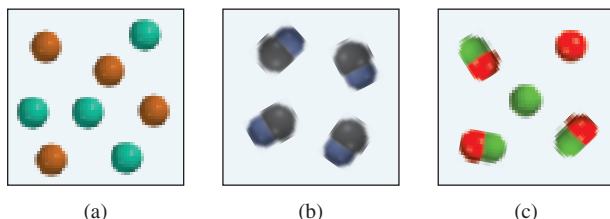
#### Review Questions

- Define solute, solvent, and solution by describing the process of dissolving a solid in a liquid.
- What is the difference between a nonelectrolyte and an electrolyte? Between a weak electrolyte and a strong electrolyte?
- Describe hydration. What properties of water enable its molecules to interact with ions in solution?
- What is the difference between the following symbols in chemical equations:  $\longrightarrow$  and  $\rightleftharpoons$ ?
- Water is an extremely weak electrolyte and therefore cannot conduct electricity. Why are we often cautioned not to operate electrical appliances when our hands are wet?

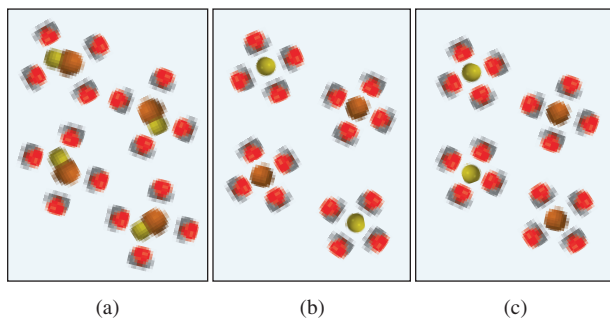
- 4.6 Sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) is a strong electrolyte. What species are present in  $\text{Na}_2\text{SO}_4(aq)$ ?

### Problems

- 4.7 The aqueous solutions of three compounds are shown in the diagram. Identify each compound as a nonelectrolyte, a weak electrolyte, and a strong electrolyte.



- 4.8 Which of the following diagrams best represents the hydration of  $\text{NaCl}$  when dissolved in water? The  $\text{Cl}^-$  ion is larger in size than the  $\text{Na}^+$  ion.



- 4.9 Identify each of the following substances as a strong electrolyte, weak electrolyte, or nonelectrolyte: (a)  $\text{H}_2\text{O}$ , (b)  $\text{KCl}$ , (c)  $\text{HNO}_3$ , (d)  $\text{CH}_3\text{COOH}$ , (e)  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ .
- 4.10 Identify each of the following substances as a strong electrolyte, weak electrolyte, or nonelectrolyte: (a)  $\text{Ba}(\text{NO}_3)_2$ , (b)  $\text{Ne}$ , (c)  $\text{NH}_3$ , (d)  $\text{NaOH}$ .
- 4.11 The passage of electricity through an electrolyte solution is caused by the movement of (a) electrons only, (b) cations only, (c) anions only, (d) both cations and anions.
- 4.12 Predict and explain which of the following systems are electrically conducting: (a) solid  $\text{NaCl}$ , (b) molten  $\text{NaCl}$ , (c) an aqueous solution of  $\text{NaCl}$ .
- 4.13 You are given a water-soluble compound X. Describe how you would determine whether it is an electrolyte or a nonelectrolyte. If it is an electrolyte,

how would you determine whether it is strong or weak?

- 4.14 Explain why a solution of  $\text{HCl}$  in benzene does not conduct electricity but in water it does.

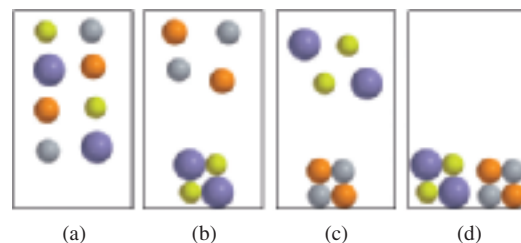
### Precipitation Reactions

#### Review Questions

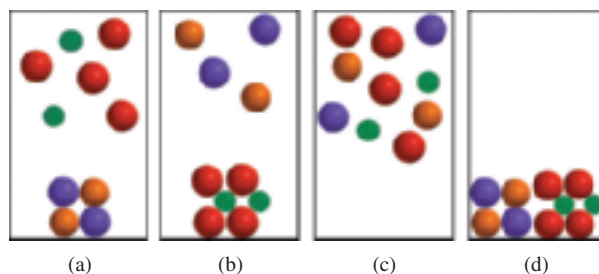
- 4.15 What is the difference between an ionic equation and a molecular equation?
- 4.16 What is the advantage of writing net ionic equations?

#### Problems

- 4.17 Two aqueous solutions of  $\text{AgNO}_3$  and  $\text{NaCl}$  are mixed. Which of the following diagrams best represents the mixture? For simplicity, water molecules are not shown. (Color codes are:  $\text{Ag}^+$  = gray,  $\text{Cl}^-$  = orange,  $\text{Na}^+$  = green,  $\text{NO}_3^-$  = blue.)



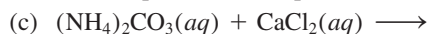
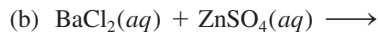
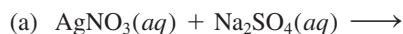
- 4.18 Two aqueous solutions of  $\text{KOH}$  and  $\text{MgCl}_2$  are mixed. Which of the following diagrams best represents the mixture? For simplicity, water molecules are not shown. (Color codes are:  $\text{K}^+$  = purple,  $\text{OH}^-$  = red,  $\text{Mg}^{2+}$  = green,  $\text{Cl}^-$  = orange.)



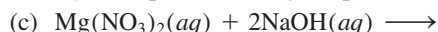
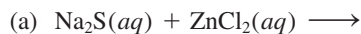
- 4.19 Characterize the following compounds as soluble or insoluble in water: (a)  $\text{Ca}_3(\text{PO}_4)_2$ , (b)  $\text{Mn}(\text{OH})_2$ , (c)  $\text{AgClO}_3$ , (d)  $\text{K}_2\text{S}$ .
- 4.20 Characterize the following compounds as soluble or insoluble in water: (a)  $\text{CaCO}_3$ , (b)  $\text{ZnSO}_4$ , (c)  $\text{Hg}(\text{NO}_3)_2$ , (d)  $\text{HgSO}_4$ , (e)  $\text{NH}_4\text{ClO}_4$ .



4.21 Write ionic and net ionic equations for the following reactions:



4.22 Write ionic and net ionic equations for the following reactions:



4.23 Which of the following processes will likely result in a precipitation reaction? (a) Mixing a  $\text{NaNO}_3$  solution with a  $\text{CuSO}_4$  solution. (b) Mixing a  $\text{BaCl}_2$  solution with a  $\text{K}_2\text{SO}_4$  solution. Write a net ionic equation for the precipitation reaction.

4.24 With reference to Table 4.2, suggest one method by which you might separate (a)  $\text{K}^+$  from  $\text{Ag}^+$ , (b)  $\text{Ba}^{2+}$  from  $\text{Pb}^{2+}$ , (c)  $\text{NH}_4^+$  from  $\text{Ca}^{2+}$ , (d)  $\text{Ba}^{2+}$  from  $\text{Cu}^{2+}$ . All cations are assumed to be in aqueous solution, and the common anion is the nitrate ion.

## Acid-Base Reactions

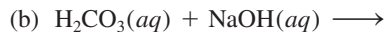
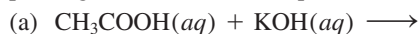
### Review Questions

- 4.25 List the general properties of acids and bases.
- 4.26 Give Arrhenius's and Brønsted's definitions of an acid and a base. Why are Brønsted's definitions more useful in describing acid-base properties?
- 4.27 Give an example of a monoprotic acid, a diprotic acid, and a triprotic acid.
- 4.28 What are the characteristics of an acid-base neutralization reaction?
- 4.29 What factors qualify a compound as a salt? Specify which of the following compounds are salts:  $\text{CH}_4$ ,  $\text{NaF}$ ,  $\text{NaOH}$ ,  $\text{CaO}$ ,  $\text{BaSO}_4$ ,  $\text{HNO}_3$ ,  $\text{NH}_3$ ,  $\text{KBr}$ ?
- 4.30 Identify the following as a weak or strong acid or base: (a)  $\text{NH}_3$ , (b)  $\text{H}_3\text{PO}_4$ , (c)  $\text{LiOH}$ , (d)  $\text{HCOOH}$  (formic acid), (e)  $\text{H}_2\text{SO}_4$ , (f)  $\text{HF}$ , (g)  $\text{Ba}(\text{OH})_2$ .

### Problems

- 4.31 Identify each of the following species as a Brønsted acid, base, or both: (a)  $\text{HI}$ , (b)  $\text{CH}_3\text{COO}^-$ , (c)  $\text{H}_2\text{PO}_4^-$ , (d)  $\text{HSO}_4^-$ .
- 4.32 Identify each of the following species as a Brønsted acid, base, or both:  $\text{PO}_4^{3-}$ , (b)  $\text{ClO}_2^-$ , (c)  $\text{NH}_4^+$ , (d)  $\text{HCO}_3^-$ .
- 4.33 Balance the following equations and write the corresponding ionic and net ionic equations (if appropriate):
- (a)  $\text{HBr}(aq) + \text{NH}_3(aq) \longrightarrow$
- (b)  $\text{Ba}(\text{OH})_2(aq) + \text{H}_3\text{PO}_4(aq) \longrightarrow$
- (c)  $\text{HClO}_4(aq) + \text{Mg}(\text{OH})_2(s) \longrightarrow$

4.34 Balance the following equations and write the corresponding ionic and net ionic equations (if appropriate):



## Oxidation-Reduction Reactions

### Review Questions

- 4.35 Give an example of a combination redox reaction, a decomposition redox reaction, and a displacement redox reaction.
- 4.36 All combustion reactions are redox reactions. True or false? Explain.
- 4.37 What is an oxidation number? How is it used to identify redox reactions? Explain why, except for ionic compounds, oxidation number does not have any physical significance.
- 4.38 (a) Without referring to Figure 4.11, give the oxidation numbers of the alkali and alkaline earth metals in their compounds. (b) Give the highest oxidation numbers that the Groups 3A–7A elements can have.
- 4.39 How is the activity series organized? How is it used in the study of redox reactions?
- 4.40 Use the following reaction to define redox reaction, half-reaction, oxidizing agent, reducing agent:
- $$4\text{Na}(s) + \text{O}_2(g) \longrightarrow 2\text{Na}_2\text{O}(s)$$
- 4.41 Is it possible to have a reaction in which oxidation occurs and reduction does not? Explain.
- 4.42 What is the requirement for an element to undergo disproportionation reactions? Name five common elements that are likely to take part in such reactions.

### Problems

- 4.43 For the complete redox reactions given here, (i) break down each reaction into its half-reactions; (ii) identify the oxidizing agent; (iii) identify the reducing agent.
- (a)  $2\text{Sr} + \text{O}_2 \longrightarrow 2\text{SrO}$
- (b)  $2\text{Li} + \text{H}_2 \longrightarrow 2\text{LiH}$
- (c)  $2\text{Cs} + \text{Br}_2 \longrightarrow 2\text{CsBr}$
- (d)  $3\text{Mg} + \text{N}_2 \longrightarrow \text{Mg}_3\text{N}_2$
- 4.44 For the complete redox reactions given here, write the half-reactions and identify the oxidizing and reducing agents.
- (a)  $4\text{Fe} + 3\text{O}_2 \longrightarrow 2\text{Fe}_2\text{O}_3$
- (b)  $\text{Cl}_2 + 2\text{NaBr} \longrightarrow 2\text{NaCl} + \text{Br}_2$
- (c)  $\text{Si} + 2\text{F}_2 \longrightarrow \text{SiF}_4$
- (d)  $\text{H}_2 + \text{Cl}_2 \longrightarrow 2\text{HCl}$

- 4.45 Arrange the following species in order of increasing oxidation number of the sulfur atom: (a)  $\text{H}_2\text{S}$ , (b)  $\text{S}_8$ , (c)  $\text{H}_2\text{SO}_4$ , (d)  $\text{S}^{2-}$ , (e)  $\text{HS}^-$ , (f)  $\text{SO}_2$ , (g)  $\text{SO}_3$ .
- 4.46 Phosphorus forms many oxoacids. Indicate the oxidation number of phosphorus in each of the following acids: (a)  $\text{HPO}_3$ , (b)  $\text{H}_3\text{PO}_2$ , (c)  $\text{H}_3\text{PO}_3$ , (d)  $\text{H}_3\text{PO}_4$ , (e)  $\text{H}_4\text{P}_2\text{O}_7$ , (f)  $\text{H}_5\text{P}_3\text{O}_{10}$ .
- 4.47 Give the oxidation number of the underlined atoms in the following molecules and ions: (a)  $\underline{\text{C}}\text{IF}$ , (b)  $\text{I}\underline{\text{F}}_7$ , (c)  $\underline{\text{C}}\text{H}_4$ , (d)  $\underline{\text{C}}_2\text{H}_2$ , (e)  $\underline{\text{C}}_2\text{H}_4$ , (f)  $\text{K}_2\underline{\text{C}}\text{rO}_4$ , (g)  $\text{K}_2\underline{\text{C}}\text{r}_2\text{O}_7$ , (h)  $\text{K}\underline{\text{Mn}}\text{O}_4$ , (i)  $\text{Na}\underline{\text{H}}\text{CO}_3$ , (j)  $\underline{\text{Li}}_2$ , (k)  $\text{Na}\underline{\text{I}}\text{O}_3$ , (l)  $\underline{\text{K}}\text{O}_2$ , (m)  $\underline{\text{P}}\text{F}_6^-$ , (n)  $\text{K}\underline{\text{Au}}\text{Cl}_4$ .
- 4.48 Give the oxidation number for the following species:  $\text{H}_2$ ,  $\text{Se}_8$ ,  $\text{P}_4$ ,  $\text{O}$ ,  $\text{U}$ ,  $\text{As}_4$ ,  $\text{B}_{12}$ .
- 4.49 Give oxidation numbers for the underlined atoms in the following molecules and ions: (a)  $\underline{\text{C}}\text{s}_2\text{O}$ , (b)  $\text{Ca}\underline{\text{I}}_2$ , (c)  $\underline{\text{Al}}_3\text{O}_3$ , (d)  $\text{H}_3\underline{\text{As}}\text{O}_3$ , (e)  $\underline{\text{Ti}}\text{O}_2$ , (f)  $\underline{\text{Mo}}\text{O}_4^{2-}$ , (g)  $\underline{\text{Pt}}\text{Cl}_4^{2-}$ , (h)  $\underline{\text{Pt}}\text{Cl}_6^{2-}$ , (i)  $\underline{\text{Sn}}\text{F}_2$ , (j)  $\underline{\text{Cl}}\text{F}_3$ , (k)  $\underline{\text{Sb}}\text{F}_6^-$ .
- 4.50 Give the oxidation numbers of the underlined atoms in the following molecules and ions: (a)  $\text{Mg}_3\underline{\text{N}}_2$ , (b)  $\text{Cs}\underline{\text{O}}_2$ , (c)  $\text{Ca}\underline{\text{C}}_2$ , (d)  $\underline{\text{C}}\text{O}_3^{2-}$ , (e)  $\underline{\text{C}}_2\text{O}_4^{2-}$ , (f)  $\text{Zn}\underline{\text{O}}_2^{2-}$ , (g)  $\text{Na}\underline{\text{B}}\text{H}_4$ , (h)  $\underline{\text{W}}\text{O}_4^{2-}$ .
- 4.51 Nitric acid is a strong oxidizing agent. State which of the following species is *least* likely to be produced when nitric acid reacts with a strong reducing agent such as zinc metal, and explain why:  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_4$ ,  $\text{N}_2\text{O}_5$ ,  $\text{NH}_4^+$ .
- 4.52 Which of the following metals can react with water? (a)  $\text{Au}$ , (b)  $\text{Li}$ , (c)  $\text{Hg}$ , (d)  $\text{Ca}$ , (e)  $\text{Pt}$ .
- 4.53 On the basis of oxidation number considerations, one of the following oxides would not react with molecular oxygen:  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{P}_4\text{O}_6$ . Which one is it? Why?
- 4.54 Predict the outcome of the reactions represented by the following equations by using the activity series, and balance the equations.
- (a)  $\text{Cu}(s) + \text{HCl}(aq) \longrightarrow$   
 (b)  $\text{I}_2(s) + \text{NaBr}(aq) \longrightarrow$   
 (c)  $\text{Mg}(s) + \text{CuSO}_4(aq) \longrightarrow$   
 (d)  $\text{Cl}_2(g) + \text{KBr}(aq) \longrightarrow$
- 4.55 Classify the following redox reactions:
- (a)  $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$   
 (b)  $\text{Mg} + 2\text{AgNO}_3 \longrightarrow \text{Mg}(\text{NO}_3)_2 + 2\text{Ag}$   
 (c)  $\text{NH}_4\text{NO}_2 \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$   
 (d)  $\text{H}_2 + \text{Br}_2 \longrightarrow 2\text{HBr}$
- 4.56 Classify the following redox reactions:
- (a)  $\text{P}_4 + 10\text{Cl}_2 \longrightarrow 4\text{PCl}_5$   
 (b)  $2\text{NO} \longrightarrow \text{N}_2 + \text{O}_2$   
 (c)  $\text{Cl}_2 + 2\text{KI} \longrightarrow 2\text{KCl} + \text{I}_2$   
 (d)  $3\text{HNO}_2 \longrightarrow \text{HNO}_3 + \text{H}_2\text{O} + 2\text{NO}$
- 4.57 Which of the following are redox processes?  
 (a)  $\text{CO}_2 \longrightarrow \text{CO}_3^{2-}$   
 (b)  $\text{VO}_3 \longrightarrow \text{VO}_2$   
 (c)  $\text{SO}_3 \longrightarrow \text{SO}_4^{2-}$   
 (d)  $\text{NO}_2^- \longrightarrow \text{NO}_3^-$   
 (e)  $\text{Cr}^{3+} \longrightarrow \text{CrO}_4^{2-}$
- 4.58 Of the following, which is most likely to be the strongest oxidizing agent?  $\text{O}_2$ ,  $\text{O}_2^+$ ,  $\text{O}_2^-$ ,  $\text{O}_2^{2-}$ .

## Concentration of Solutions

### Review Questions

- 4.59 Write the equation for calculating molarity. Why is molarity a convenient concentration unit in chemistry?
- 4.60 Describe the steps involved in preparing a solution of known molar concentration using a volumetric flask.

### Problems

- 4.61 Calculate the mass of  $\text{KI}$  in grams required to prepare  $5.00 \times 10^2$  mL of a  $2.80$  M solution.
- 4.62 Describe how you would prepare 250 mL of a  $0.707$  M  $\text{NaNO}_3$  solution.
- 4.63 How many moles of  $\text{MgCl}_2$  are present in 60.0 mL of  $0.100$  M  $\text{MgCl}_2$  solution?
- 4.64 How many grams of  $\text{KOH}$  are present in 35.0 mL of a  $5.50$  M solution?
- 4.65 Calculate the molarity of each of the following solutions: (a) 29.0 g of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) in 545 mL of solution, (b) 15.4 g of sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) in 74.0 mL of solution, (c) 9.00 g of sodium chloride ( $\text{NaCl}$ ) in 86.4 mL of solution.
- 4.66 Calculate the molarity of each of the following solutions: (a) 6.57 g of methanol ( $\text{CH}_3\text{OH}$ ) in  $1.50 \times 10^2$  mL of solution, (b) 10.4 g of calcium chloride ( $\text{CaCl}_2$ ) in  $2.20 \times 10^2$  mL of solution, (c) 7.82 g of naphthalene ( $\text{C}_{10}\text{H}_8$ ) in 85.2 mL of benzene solution.
- 4.67 Calculate the volume in mL of a solution required to provide the following: (a) 2.14 g of sodium chloride from a  $0.270$  M solution, (b) 4.30 g of ethanol from a  $1.50$  M solution, (c) 0.85 g of acetic acid ( $\text{CH}_3\text{COOH}$ ) from a  $0.30$  M solution.
- 4.68 Determine how many grams of each of the following solutes would be needed to make  $2.50 \times 10^2$  mL of a  $0.100$  M solution: (a) cesium iodide ( $\text{CsI}$ ), (b) sulfuric acid ( $\text{H}_2\text{SO}_4$ ), (c) sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), (d) potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), (e) potassium permanganate ( $\text{KMnO}_4$ ).
- 4.69 What volume of  $0.416$  M  $\text{Mg}(\text{NO}_3)_2$  should be added to 255 mL of  $0.102$  M  $\text{KNO}_3$  to produce a solution with a concentration of  $0.278$  M  $\text{NO}_3^-$  ions? Assume volumes are additive.

- 4.70** Barium hydroxide, often used to titrate weak organic acids, is obtained as the octahydrate,  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ . What mass of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  would be required to make 500.0 mL of a solution that is 0.1500 *M* in hydroxide ions?

## Dilution of Solutions

### Review Questions

- 4.71 Describe the basic steps involved in diluting a solution of known concentration.
- 4.72 Write the equation that enables us to calculate the concentration of a diluted solution. Give units for all the terms.

### Problems

- 4.73 Describe how to prepare 1.00 L of 0.646 *M* HCl solution, starting with a 2.00 *M* HCl solution.
- 4.74** Water is added to 25.0 mL of a 0.866 *M*  $\text{KNO}_3$  solution until the volume of the solution is exactly 500 mL. What is the concentration of the final solution?
- 4.75 How would you prepare 60.0 mL of 0.200 *M*  $\text{HNO}_3$  from a stock solution of 4.00 *M*  $\text{HNO}_3$ ?
- 4.76** You have 505 mL of a 0.125 *M* HCl solution and you want to dilute it to exactly 0.100 *M*. How much water should you add? Assume volumes are additive.
- 4.77 A 35.2-mL, 1.66 *M*  $\text{KMnO}_4$  solution is mixed with 16.7 mL of 0.892 *M*  $\text{KMnO}_4$  solution. Calculate the concentration of the final solution.
- 4.78** A 46.2-mL, 0.568 *M* calcium nitrate [ $\text{Ca}(\text{NO}_3)_2$ ] solution is mixed with 80.5 mL of 1.396 *M* calcium nitrate solution. Calculate the concentration of the final solution.

## Gravimetric Analysis

### Review Questions

- 4.79 Describe the basic steps involved in gravimetric analysis. How does this procedure help us determine the identity of a compound or the purity of a compound if its formula is known?
- 4.80 Distilled water must be used in the gravimetric analysis of chlorides. Why?

### Problems

- 4.81 If 30.0 mL of 0.150 *M*  $\text{CaCl}_2$  is added to 15.0 mL of 0.100 *M*  $\text{AgNO}_3$ , what is the mass in grams of AgCl precipitate?
- 4.82** A sample of 0.6760 g of an unknown compound containing barium ions ( $\text{Ba}^{2+}$ ) is dissolved in water and treated with an excess of  $\text{Na}_2\text{SO}_4$ . If the mass of the  $\text{BaSO}_4$  precipitate formed is 0.4105 g, what is the percent by mass of Ba in the original unknown compound?
- 4.83 How many grams of NaCl are required to precipitate most of the  $\text{Ag}^+$  ions from  $2.50 \times 10^2$  mL of

0.0113 *M*  $\text{AgNO}_3$  solution? Write the net ionic equation for the reaction.

- 4.84** The concentration of sulfate in water can be determined by adding a solution of barium chloride to precipitate the sulfate ion. Write the net ionic equation for this reaction. Treating a 145-mL sample of water with excess  $\text{BaCl}_2(aq)$  precipitated 0.330 g of  $\text{BaSO}_4$ . Determine the concentration of sulfate in the original water sample.

## Acid-Base Titrations

### Review Questions

- 4.85 Describe the basic steps involved in an acid-base titration. Why is this technique of great practical value?
- 4.86 How does an acid-base indicator work?
- 4.87 A student carried out two titrations using a NaOH solution of unknown concentration in the buret. In one titration she weighed out 0.2458 g of KHP (see p. 152) and transferred it to an Erlenmeyer flask. She then added 20.00 mL of distilled water to dissolve the acid. In the other titration she weighed out 0.2507 g of KHP but added 40.00 mL of distilled water to dissolve the acid. Assuming no experimental error, would she obtain the same result for the concentration of the NaOH solution?
- 4.88 Would the volume of a 0.10 *M* NaOH solution needed to titrate 25.0 mL of a 0.10 *M*  $\text{HNO}_2$  (a weak acid) solution be different from that needed to titrate 25.0 mL of a 0.10 *M* HCl (a strong acid) solution?

### Problems

- 4.89 A quantity of 18.68 mL of a KOH solution is needed to neutralize 0.4218 g of KHP. What is the concentration (in molarity) of the KOH solution?
- 4.90** Calculate the concentration (in molarity) of a NaOH solution if 25.0 mL of the solution are needed to neutralize 17.4 mL of a 0.312 *M* HCl solution.
- 4.91 Calculate the volume in mL of a 1.420 *M* NaOH solution required to titrate the following solutions:
- 25.00 mL of a 2.430 *M* HCl solution
  - 25.00 mL of a 4.500 *M*  $\text{H}_2\text{SO}_4$  solution
  - 25.00 mL of a 1.500 *M*  $\text{H}_3\text{PO}_4$  solution
- 4.92** What volume of a 0.500 *M* HCl solution is needed to neutralize each of the following:
- 10.0 mL of a 0.300 *M* NaOH solution
  - 10.0 mL of a 0.200 *M*  $\text{Ba}(\text{OH})_2$  solution

## Redox Titrations

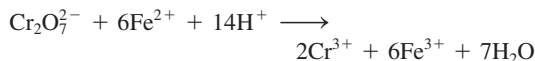
### Review Questions

- 4.93 What are the similarities and differences between acid-base titrations and redox titrations?

- 4.94 Explain why potassium permanganate ( $\text{KMnO}_4$ ) and potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) can serve as internal indicators in redox titrations.

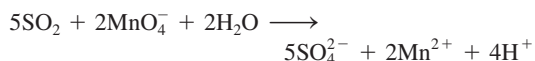
### Problems

- 4.95 Iron(II) can be oxidized by an acidic  $\text{K}_2\text{Cr}_2\text{O}_7$  solution according to the net ionic equation:



If it takes 26.0 mL of 0.0250  $M$   $\text{K}_2\text{Cr}_2\text{O}_7$  to titrate 25.0 mL of a solution containing  $\text{Fe}^{2+}$ , what is the molar concentration of  $\text{Fe}^{2+}$ ?

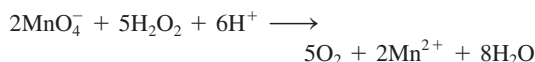
- 4.96 The  $\text{SO}_2$  present in air is mainly responsible for the acid rain phenomenon. Its concentration can be determined by titrating against a standard permanganate solution as follows:



Calculate the number of grams of  $\text{SO}_2$  in a sample of air if 7.37 mL of 0.00800  $M$   $\text{KMnO}_4$  solution are required for the titration.

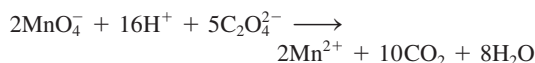
- 4.97 A sample of iron ore (containing only  $\text{Fe}^{2+}$  ions) weighing 0.2792 g was dissolved in dilute acid solution, and all the Fe(II) was converted to Fe(III) ions. The solution required 23.30 mL of 0.0194  $M$   $\text{K}_2\text{Cr}_2\text{O}_7$  for titration. Calculate the percent by mass of iron in the ore. (*Hint*: See Problem 4.95 for the balanced equation.)

- 4.98 The concentration of a hydrogen peroxide solution can be conveniently determined by titration against a standardized potassium permanganate solution in an acidic medium according to the following equation:



If 36.44 mL of a 0.01652  $M$   $\text{KMnO}_4$  solution are required to oxidize 25.00 mL of a  $\text{H}_2\text{O}_2$  solution, calculate the molarity of the  $\text{H}_2\text{O}_2$  solution.

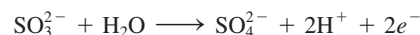
- 4.99 Oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) is present in many plants and vegetables. If 24.0 mL of 0.0100  $M$   $\text{KMnO}_4$  solution is needed to titrate 1.00 g of a sample of  $\text{H}_2\text{C}_2\text{O}_4$  to the equivalence point, what is the percent by mass of  $\text{H}_2\text{C}_2\text{O}_4$  in the sample? The net ionic equation is



- 4.100 A 15.0-mL sample of an oxalic acid solution requires 25.2 mL of 0.149  $M$   $\text{NaOH}$  for neutralization. Calculate the volume of a 0.122  $M$   $\text{KMnO}_4$  solution needed to react with a second 15.0-mL sample of the

oxalic acid solution. (*Hint*: Oxalic acid is a diprotic acid. See Problem 4.99 for redox equation.)

- 4.101 Iodate ion,  $\text{IO}_3^-$ , oxidizes  $\text{SO}_3^{2-}$  in acidic solution. The half-reaction for the oxidation is

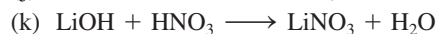
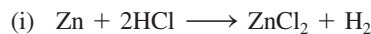
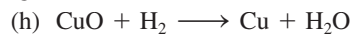
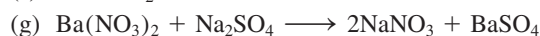
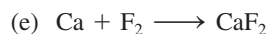
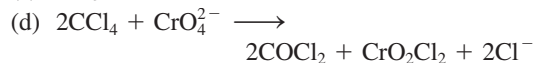
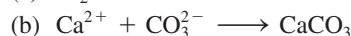
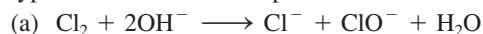


A 100.0-mL sample of solution containing 1.390 g of  $\text{KIO}_3$  reacts with 32.5 mL of 0.500  $M$   $\text{Na}_2\text{SO}_3$ . What is the final oxidation state of the iodine after the reaction has occurred?

- 4.102 Calcium oxalate ( $\text{CaC}_2\text{O}_4$ ), the main component of kidney stones, is insoluble in water. For this reason it can be used to determine the amount of  $\text{Ca}^{2+}$  ions in fluids such as blood. The calcium oxalate isolated from blood is dissolved in acid and titrated against a standardized  $\text{KMnO}_4$  solution, as shown in Problem 4.99. In one test it is found that the calcium oxalate isolated from a 10.0-mL sample of blood requires 24.2 mL of  $9.56 \times 10^{-4} M$   $\text{KMnO}_4$  for titration. Calculate the number of milligrams of calcium per milliliter of blood.

### Additional Problems

- 4.103 Classify the following reactions according to the types discussed in the chapter:



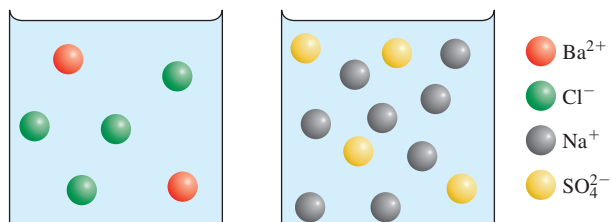
- 4.104 Oxygen ( $\text{O}_2$ ) and carbon dioxide ( $\text{CO}_2$ ) are colorless and odorless gases. Suggest two chemical tests that would enable you to distinguish between these two gases.

- 4.105 Which of the following aqueous solutions would you expect to be the best conductor of electricity at 25°C? Explain your answer.

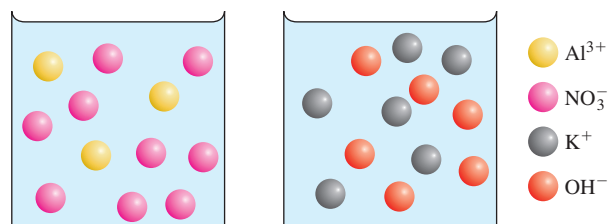


- 4.106 A  $5.00 \times 10^2$ -mL sample of 2.00  $M$   $\text{HCl}$  solution is treated with 4.47 g of magnesium. Calculate the concentration of the acid solution after all the metal has reacted. Assume that the volume remains unchanged.

- 4.107 Shown here are two aqueous solutions containing various ions. The volume of each solution is 200 mL. (a) Calculate the mass of the precipitate (in g) after the solutions are mixed. (b) What are the concentrations (in  $M$ ) of the ions in the final solution? Treat each sphere as 0.100 mol. Assume the volumes are additive.



- 4.108 Shown here are two aqueous solutions containing various ions. The volume of each solution is 200 mL. (a) Calculate the mass of the precipitate (in g) after the solutions are mixed. (b) What are the concentrations (in  $M$ ) of the ions in the final solution? Treat each sphere as 0.100 mol. Assume the volumes are additive.



- 4.109 Calculate the volume of a 0.156  $M$   $\text{CuSO}_4$  solution that would react with 7.89 g of zinc.
- 4.110 Sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) is available in very pure form and can be used to standardize acid solutions. What is the molarity of a  $\text{HCl}$  solution if 28.3 mL of the solution are required to react with 0.256 g of  $\text{Na}_2\text{CO}_3$ ?
- 4.111 A 3.664-g sample of a monoprotic acid was dissolved in water. It took 20.27 mL of a 0.1578  $M$   $\text{NaOH}$  solution to neutralize the acid. Calculate the molar mass of the acid.
- 4.112 Acetic acid ( $\text{CH}_3\text{COOH}$ ) is an important ingredient of vinegar. A sample of 50.0 mL of a commercial vinegar is titrated against a 1.00  $M$   $\text{NaOH}$  solution. What is the concentration (in  $M$ ) of acetic acid present in the vinegar if 5.75 mL of the base are needed for the titration?
- 4.113 A 15.00-mL solution of potassium nitrate ( $\text{KNO}_3$ ) was diluted to 125.0 mL, and 25.00 mL of this solution were then diluted to  $1.000 \times 10^3$  mL. The concentration of the final solution is 0.00383  $M$ . Calculate the concentration of the original solution.

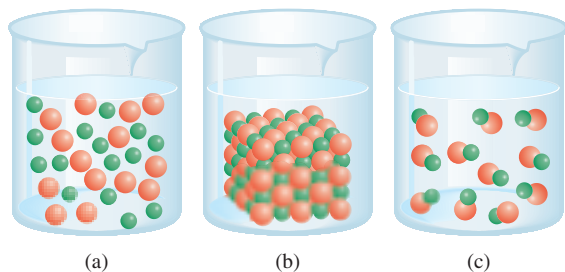
- 4.114 When 2.50 g of a zinc strip were placed in a  $\text{AgNO}_3$  solution, silver metal formed on the surface of the strip. After some time had passed, the strip was removed from the solution, dried, and weighed. If the mass of the strip was 3.37 g, calculate the mass of  $\text{Ag}$  and  $\text{Zn}$  metals present.
- 4.115 Calculate the mass of the precipitate formed when 2.27 L of 0.0820  $M$   $\text{Ba}(\text{OH})_2$  are mixed with 3.06 L of 0.0664  $M$   $\text{Na}_2\text{SO}_4$ .
- 4.116 Calculate the concentration of the acid (or base) remaining in solution when 10.7 mL of 0.211  $M$   $\text{HNO}_3$  are added to 16.3 mL of 0.258  $M$   $\text{NaOH}$ .
- 4.117 (a) Describe a preparation for magnesium hydroxide [ $\text{Mg}(\text{OH})_2$ ] and predict its solubility. (b) Milk of magnesia contains mostly  $\text{Mg}(\text{OH})_2$  and is effective in treating acid (mostly hydrochloric acid) indigestion. Calculate the volume of a 0.035  $M$   $\text{HCl}$  solution (a typical acid concentration in an upset stomach) needed to react with two spoonfuls (approximately 10 mL) of milk of magnesia [at 0.080 g  $\text{Mg}(\text{OH})_2/\text{mL}$ ].
- 4.118 A 1.00-g sample of a metal  $X$  (that is known to form  $X^{2+}$  ions) was added to 0.100 L of 0.500  $M$   $\text{H}_2\text{SO}_4$ . After all the metal had reacted, the remaining acid required 0.0334 L of 0.500  $M$   $\text{NaOH}$  solution for neutralization. Calculate the molar mass of the metal and identify the element.
- 4.119 Carbon dioxide in air can be removed by an aqueous metal hydroxide solution such as  $\text{LiOH}$  and  $\text{Ba}(\text{OH})_2$ . (a) Write equations for the reactions. (Carbon dioxide reacts with water to form carbonic acid.) (b) Calculate the mass of  $\text{CO}_2$  that can be removed by  $5.00 \times 10^2$  mL of a 0.800  $M$   $\text{LiOH}$  and a 0.800  $M$   $\text{Ba}(\text{OH})_2$  solution. (c) Which solution would you choose for use in a space capsule and which for use in a submarine?
- 4.120 The molecular formula of malonic acid is  $\text{C}_3\text{H}_4\text{O}_4$ . If a solution containing 0.762 g of the acid requires 12.44 mL of 1.174  $M$   $\text{NaOH}$  for neutralization, how many ionizable  $\text{H}$  atoms are present in the molecule?
- 4.121 A quantitative definition of solubility is the maximum number of grams of a solute that will dissolve in a given volume of water at a particular temperature. Describe an experiment that would enable you to determine the solubility of a soluble compound.
- 4.122 A 60.0-mL 0.513  $M$  glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) solution is mixed with 120.0 mL of 2.33  $M$  glucose solution. What is the concentration of the final solution? Assume the volumes are additive.
- 4.123 An ionic compound  $X$  is only slightly soluble in water. What test would you employ to show that the compound does indeed dissolve in water to a certain extent?



- 4.124** A student is given an unknown that is either iron(II) sulfate or iron(III) sulfate. Suggest a chemical procedure for determining its identity. (Both iron compounds are water soluble.)
- 4.125 You are given a colorless liquid. Describe three chemical tests you would perform on the liquid to show that it is water.
- 4.126** Using the apparatus shown in Figure 4.1, a student found that a sulfuric acid solution caused the lightbulb to glow brightly. However, after the addition of a certain amount of a barium hydroxide  $[\text{Ba}(\text{OH})_2]$  solution, the light began to dim even though  $\text{Ba}(\text{OH})_2$  is also a strong electrolyte. Explain.
- 4.127 The molar mass of a certain metal carbonate,  $\text{MCO}_3$ , can be determined by adding an excess of  $\text{HCl}$  acid to react with all the carbonate and then “back titrating” the remaining acid with a  $\text{NaOH}$  solution. (a) Write an equation for these reactions. (b) In a certain experiment, 20.00 mL of 0.0800  $M$   $\text{HCl}$  were added to a 0.1022-g sample of  $\text{MCO}_3$ . The excess  $\text{HCl}$  required 5.64 mL of 0.1000  $M$   $\text{NaOH}$  for neutralization. Calculate the molar mass of the carbonate and identify  $M$ .
- 4.128** A 5.012-g sample of an iron chloride hydrate was dried in an oven. The mass of the anhydrous compound was 3.195 g. The compound was then dissolved in water and reacted with an excess of  $\text{AgNO}_3$ . The  $\text{AgCl}$  precipitate formed weighed 7.225 g. What is the formula of the original compound?
- 4.129 You are given a soluble compound of unknown molecular formula. (a) Describe three tests that would show that the compound is an acid. (b) Once you have established that the compound is an acid, describe how you would determine its molar mass using a  $\text{NaOH}$  solution of known concentration. (Assume the acid is monoprotic.) (c) How would you find out whether the acid is weak or strong? You are provided with a sample of  $\text{NaCl}$  and an apparatus like that shown in Figure 4.1 for comparison.
- 4.130** You are given two colorless solutions, one containing  $\text{NaCl}$  and the other sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ). Suggest a chemical and a physical test that would allow you to distinguish between these two solutions.
- 4.131 The concentration of lead ions ( $\text{Pb}^{2+}$ ) in a sample of polluted water that also contains nitrate ions ( $\text{NO}_3^-$ ) is determined by adding solid sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) to exactly 500 mL of the water. (a) Write the molecular and net ionic equations for the reaction. (b) Calculate the molar concentration of  $\text{Pb}^{2+}$  if 0.00450 g of  $\text{Na}_2\text{SO}_4$  was needed for the complete precipitation of  $\text{Pb}^{2+}$  ions as  $\text{PbSO}_4$ .
- 4.132** Hydrochloric acid is not an oxidizing agent in the sense that sulfuric acid and nitric acid are. Explain why the chloride ion is not a strong oxidizing agent like  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ .
- 4.133 Explain how you would prepare potassium iodide ( $\text{KI}$ ) by means of (a) an acid-base reaction and (b) a reaction between an acid and a carbonate compound.
- 4.134** Sodium reacts with water to yield hydrogen gas. Why is this reaction not used in the laboratory preparation of hydrogen?
- 4.135 Describe how you would prepare the following compounds: (a)  $\text{Mg}(\text{OH})_2$ , (b)  $\text{AgI}$ , (c)  $\text{Ba}_3(\text{PO}_4)_2$ .
- 4.136** Someone spilled concentrated sulfuric acid on the floor of a chemistry laboratory. To neutralize the acid, would it be preferable to pour concentrated sodium hydroxide solution or spray solid sodium bicarbonate over the acid? Explain your choice and the chemical basis for the action.
- 4.137 Describe in each case how you would separate the cations or anions in an aqueous solution of: (a)  $\text{NaNO}_3$  and  $\text{Ba}(\text{NO}_3)_2$ , (b)  $\text{Mg}(\text{NO}_3)_2$  and  $\text{KNO}_3$ , (c)  $\text{KBr}$  and  $\text{KNO}_3$ , (d)  $\text{K}_3\text{PO}_4$  and  $\text{KNO}_3$ , (e)  $\text{Na}_2\text{CO}_3$  and  $\text{NaNO}_3$ .
- 4.138** The following are common household compounds: table salt ( $\text{NaCl}$ ), table sugar (sucrose), vinegar (contains acetic acid), baking soda ( $\text{NaHCO}_3$ ), washing soda ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ), boric acid ( $\text{H}_3\text{BO}_3$ , used in eyewash), epsom salt ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), sodium hydroxide (used in drain openers), ammonia, milk of magnesia [ $\text{Mg}(\text{OH})_2$ ], and calcium carbonate. Based on what you have learned in this chapter, describe test(s) that would enable you to identify each of these compounds.
- 4.139 Sulfites (compounds containing the  $\text{SO}_3^{2-}$  ions) are used as preservatives in dried fruit and vegetables and in wine making. In an experiment to test the presence of sulfite in fruit, a student first soaked several dried apricots in water overnight and then filtered the solution to remove all solid particles. She then treated the solution with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) to oxidize the sulfite ions to sulfate ions. Finally, the sulfate ions were precipitated by treating the solution with a few drops of a barium chloride ( $\text{BaCl}_2$ ) solution. Write a balanced equation for each of the preceding steps.
- 4.140** A 0.8870-g sample of a mixture of  $\text{NaCl}$  and  $\text{KCl}$  is dissolved in water, and the solution is then treated with an excess of  $\text{AgNO}_3$  to yield 1.913 g of  $\text{AgCl}$ . Calculate the percent by mass of each compound in the mixture.
- 4.141 Based on oxidation number consideration, explain why carbon monoxide ( $\text{CO}$ ) is flammable but carbon dioxide ( $\text{CO}_2$ ) is not.
- 4.142** Which of the diagrams shown here corresponds to the reaction between  $\text{AgOH}(s)$  and  $\text{HNO}_3(aq)$ ?

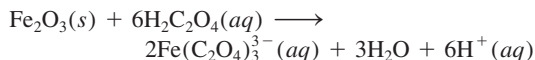


Write a balanced equation for the reaction. The green spheres represent the  $\text{Ag}^+$  ions and the red spheres represent the  $\text{NO}_3^-$  ions.



4.143 Chlorine forms a number of oxides with the following oxidation numbers: +1, +3, +4, +6, and +7. Write a formula for each of these compounds.

4.144 A useful application of oxalic acid is the removal of rust ( $\text{Fe}_2\text{O}_3$ ) from, say, bathtub rings according to the reaction



Calculate the number of grams of rust that can be removed by  $5.00 \times 10^2$  mL of a  $0.100 M$  solution of oxalic acid.

4.145 Acetylsalicylic acid ( $\text{C}_9\text{H}_8\text{O}_4$ ) is a monoprotic acid commonly known as “aspirin.” A typical aspirin tablet, however, contains only a small amount of the acid. In an experiment to determine its composition, an aspirin tablet was crushed and dissolved in water. It took 12.25 mL of  $0.1466 M$  NaOH to neutralize the solution. Calculate the number of grains of aspirin in the tablet. (One grain = 0.0648 g.)

4.146 A 0.9157-g mixture of  $\text{CaBr}_2$  and NaBr is dissolved in water, and  $\text{AgNO}_3$  is added to the solution to form AgBr precipitate. If the mass of the precipitate is 1.6930 g, what is the percent by mass of NaBr in the original mixture?

4.147 Hydrogen halides (HF, HCl, HBr, HI) are highly reactive compounds that have many industrial and laboratory uses. (a) In the laboratory, HF and HCl can be generated by reacting  $\text{CaF}_2$  and NaCl with concentrated sulfuric acid. Write appropriate equations for the reactions. (*Hint:* These are not redox reactions.) (b) Why is it that HBr and HI cannot be prepared similarly, that is, by reacting NaBr and NaI with concentrated sulfuric acid? (*Hint:*  $\text{H}_2\text{SO}_4$  is a stronger oxidizing agent than both  $\text{Br}_2$  and  $\text{I}_2$ .) (c) HBr can be prepared by reacting phosphorus tribromide ( $\text{PBr}_3$ ) with water. Write an equation for this reaction.

4.148 A 325-mL sample of solution contains 25.3 g of  $\text{CaCl}_2$ . (a) Calculate the molar concentration of  $\text{Cl}^-$  in this solution. (b) How many grams of  $\text{Cl}^-$  are in 0.100 L of this solution?

4.149 Phosphoric acid ( $\text{H}_3\text{PO}_4$ ) is an important industrial chemical used in fertilizers, in detergents, and in the food industry. It is produced by two different methods. In the *electric furnace method*, elemental phosphorus ( $\text{P}_4$ ) is burned in air to form  $\text{P}_4\text{O}_{10}$ , which is then reacted with water to give  $\text{H}_3\text{PO}_4$ . In the *wet process*, the mineral phosphate rock fluorapatite [ $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ] is reacted with sulfuric acid to give  $\text{H}_3\text{PO}_4$  (and HF and  $\text{CaSO}_4$ ). Write equations for these processes and classify each step as precipitation, acid-base, or redox reaction.

4.150 Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) is one of the most important nitrogen-containing fertilizers. Its purity can be analyzed by titrating a solution of  $\text{NH}_4\text{NO}_3$  with a standard NaOH solution. In one experiment a 0.2041-g sample of industrially prepared  $\text{NH}_4\text{NO}_3$  required 24.42 mL of  $0.1023 M$  NaOH for neutralization.

- (a) Write a net ionic equation for the reaction.  
(b) What is the percent purity of the sample?

4.151 Is the following reaction a redox reaction? Explain.



4.152 What is the oxidation number of O in HFO?

4.153 Use molecular models like those in Figures 4.7 and 4.8 to represent the following acid-base reactions:

- (a)  $\text{OH}^- + \text{H}_3\text{O}^+ \longrightarrow 2\text{H}_2\text{O}$   
(b)  $\text{NH}_4^+ + \text{NH}_2^- \longrightarrow 2\text{NH}_3$

Identify the Brønsted acid and base in each case.

4.154 The alcohol content in a 10.0-g sample of blood from a driver required 4.23 mL of  $0.07654 M$   $\text{K}_2\text{Cr}_2\text{O}_7$  for titration. Should the police prosecute the individual for drunken driving? (*Hint:* See Chemistry in Action essay on p. 144.)

4.155 On standing, a concentrated nitric acid gradually turns yellow in color. Explain. (*Hint:* Nitric acid slowly decomposes. Nitrogen dioxide is a colored gas.)

4.156 Describe the laboratory preparation for the following gases: (a) hydrogen, (b) oxygen, (c) carbon dioxide, and (d) nitrogen. Indicate the physical states of the reactants and products in each case. [*Hint:* Nitrogen can be obtained by heating ammonium nitrite ( $\text{NH}_4\text{NO}_2$ ).]

4.157 Referring to Figure 4.18, explain why one must first dissolve the solid completely before making up the solution to the correct volume.

4.158 Can the following decomposition reaction be characterized as an acid-base reaction? Explain.



4.159 Give a chemical explanation for each of the following:  
(a) When calcium metal is added to a sulfuric acid solution, hydrogen gas is generated. After a few

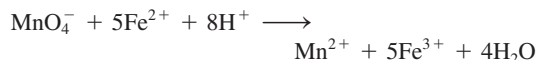
minutes, the reaction slows down and eventually stops even though none of the reactants is used up. Explain. (b) In the activity series, aluminum is above hydrogen, yet the metal appears to be unreactive toward steam and hydrochloric acid. Why? (c) Sodium and potassium lie above copper in the activity series. Explain why  $\text{Cu}^{2+}$  ions in a  $\text{CuSO}_4$  solution are not converted to metallic copper upon the addition of these metals. (d) A metal M reacts slowly with steam. There is no visible change when it is placed in a pale green iron(II) sulfate solution. Where should we place M in the activity series? (e) Before aluminum metal was obtained by electrolysis, it was produced by reducing its chloride ( $\text{AlCl}_3$ ) with an active metal. What metals would you use to produce aluminum in that way?

**4.160** The recommended procedure for preparing a very dilute solution is not to weigh out a very small mass or measure a very small volume of a stock solution. Instead, it is done by a series of dilutions. A sample of 0.8214 g of  $\text{KMnO}_4$  was dissolved in water and made up to the volume in a 500-mL volumetric flask. A 2.000-mL sample of this solution was transferred to a 1000-mL volumetric flask and diluted to the mark with water. Next, 10.00 mL of the diluted solution were transferred to a 250-mL flask and diluted to the mark with water. (a) Calculate the concentration (in molarity) of the final solution. (b) Calculate the mass of  $\text{KMnO}_4$  needed to directly prepare the final solution.

4.161 The following “cycle of copper” experiment is performed in some general chemistry laboratories. The series of reactions starts with copper and ends with metallic copper. The steps are as follows: (1) A piece of copper wire of known mass is allowed to react with concentrated nitric acid [the products are copper(II) nitrate, nitrogen dioxide, and water]. (2) The copper(II) nitrate is treated with a sodium hydroxide solution to form copper(II) hydroxide precipitate. (3) On heating, copper(II) hydroxide decomposes to yield copper(II) oxide. (4) The copper(II) oxide is reacted with concentrated sulfuric acid to yield copper(II) sulfate. (5) Copper(II) sulfate is treated with an excess of zinc metal to form metallic copper. (6) The remaining zinc metal is removed by treatment with hydrochloric acid, and metallic copper is filtered, dried, and weighed. (a) Write a balanced equation for each step and classify the reactions. (b) Assuming that a student started with 65.6 g of copper, calculate the theoretical yield at each step. (c) Considering the nature of the steps, comment on why it is possible to recover most of the copper used at the start.

**4.162** A quantity of 25.0 mL of a solution containing both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions is titrated with 23.0 mL of 0.0200 M  $\text{KMnO}_4$  (in dilute sulfuric acid). As a result, all of the  $\text{Fe}^{2+}$  ions are oxidized to  $\text{Fe}^{3+}$  ions. Next, the solution is treated with Zn metal to convert

all of the  $\text{Fe}^{3+}$  ions to  $\text{Fe}^{2+}$  ions. Finally, the solution containing only the  $\text{Fe}^{2+}$  ions requires 40.0 mL of the same  $\text{KMnO}_4$  solution for oxidation to  $\text{Fe}^{3+}$ . Calculate the molar concentrations of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in the original solution. The net ionic equation is



4.163 Use the periodic table framework shown to show the names and positions of two metals that can (a) displace hydrogen from cold water, (b) displace hydrogen from steam, and (c) displace hydrogen from acid. Also show two metals that can react neither with water nor acid.

The image shows a blank periodic table grid with 18 columns and 7 rows. The grid is intended for students to identify two metals that can displace hydrogen from cold water, steam, and acid, and two metals that do not react with water or acid.

**4.164** Referring to the Chemistry in Action essay on page 156, answer the following questions: (a) Identify the precipitation, acid-base, and redox processes. (b) Instead of calcium oxide, why don't we simply add sodium hydroxide to seawater to precipitate magnesium hydroxide? (c) Sometimes a mineral called dolomite (a mixture of  $\text{CaCO}_3$  and  $\text{MgCO}_3$ ) is substituted for limestone to bring about the precipitation of magnesium hydroxide. What is the advantage of using dolomite?

4.165 A 22.02-mL solution containing 1.615 g  $\text{Mg}(\text{NO}_3)_2$  is mixed with a 28.64-mL solution containing 1.073 g  $\text{NaOH}$ . Calculate the concentrations of the ions remaining in solution after the reaction is complete. Assume volumes are additive.

**4.166** Chemical tests of four metals A, B, C, and D show the following results.

(a) Only B and C react with 0.5 M  $\text{HCl}$  to give  $\text{H}_2$  gas.

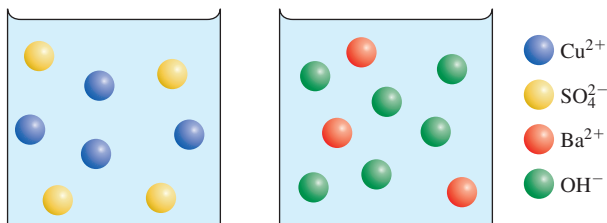
(b) When B is added to a solution containing the ions of the other metals, metallic A, C, and D are formed.

(c) A reacts with 6 M  $\text{HNO}_3$  but D does not.

Arrange the metals in the increasing order as reducing agents. Suggest four metals that fit these descriptions.

4.167 The antibiotic gramicidin A can transport  $\text{Na}^+$  ions into a certain cell at the rate of  $5.0 \times 10^7 \text{ Na}^+ \text{ ions s}^{-1}$ . Calculate the time in seconds to transport enough  $\text{Na}^+$  ions to increase its concentration by  $8.0 \times 10^{-3} \text{ M}$  in a cell whose intracellular volume is  $2.0 \times 10^{-10} \text{ mL}$ .

- 4.168** Shown here are two aqueous solutions containing various ions. The volume of each solution is 600 mL. (a) Write a net ionic equation for the reaction after the solutions are mixed. (b) Calculate the mass of the precipitates formed and the concentrations of the ions in the mixed solution. Treat each sphere as 0.0500 mol.



### Interpreting, Modeling & Estimating

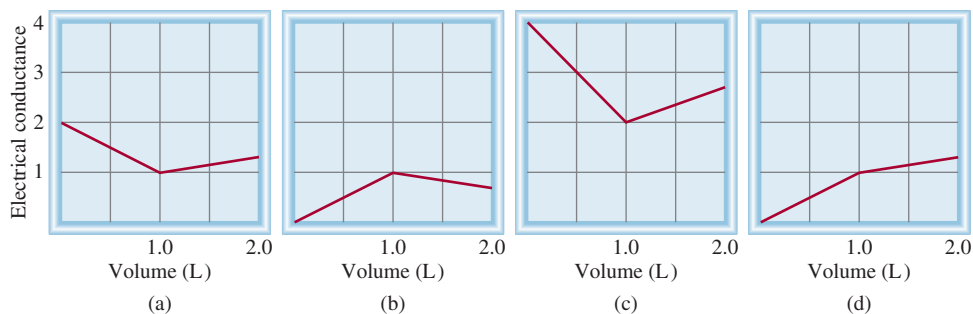
- 4.169 Many proteins contain metal ions for structural and/or redox functions. Which of the following metals fit into one or both categories: Ca, Cu, Fe, Mg, Mn, Ni, Zn?
- 4.170 The fastest way to introduce therapeutic agents into the bloodstream is by direct delivery into a vein (intravenous therapy, or IV therapy). A clinical researcher wishes to establish an initial concentration of  $6 \times 10^{-4}$  mmol/L in the bloodstream of an adult male participating in a trial study of a new drug. The drug serum is prepared in the hospital's pharmacy at a concentration of  $1.2 \times 10^{-3}$  mol/L. How much of the serum should be introduced intravenously in order to achieve the desired initial blood concentration of the drug?
- 4.171 Public water supplies are often "fluoridated" by the addition of compounds such as NaF,  $\text{H}_2\text{SiF}_6$ , and  $\text{Na}_2\text{SiF}_6$ . It is well established that fluoride helps prevent tooth decay; however, care must be taken not to exceed safe levels of fluoride, which can stain or etch tooth enamel (dental fluorosis). A safe and effective concentration of fluoride in drinking water is generally considered to be around 1 mg/L. How much fluoride would a person consume by drinking fluoridated water in 1 year? What would be the equivalent mass as sodium fluoride?
- 4.172 Potassium superoxide ( $\text{KO}_2$ ), a useful source of oxygen employed in breathing equipment, reacts with water to form potassium hydroxide, hydrogen peroxide, and oxygen. Furthermore, potassium superoxide also reacts with carbon dioxide to form potassium carbonate and oxygen. (a) Write equations for these two reactions and comment on the effectiveness of potassium superoxide in this application. (b) Focusing only on the reaction between  $\text{KO}_2$  and  $\text{CO}_2$ , estimate the amount of  $\text{KO}_2$  needed to sustain a worker in a polluted environment for 30 min. See Problem 1.69 for useful information.



- 4.173 Muriatic acid, a commercial-grade hydrochloric acid used for cleaning masonry surfaces, is typically around 10 percent HCl by mass and has a density of  $1.2 \text{ g/cm}^3$ . A 0.5-in layer of boiler scale has accumulated on a 6.0-ft section of hot water pipe with an internal diameter of 2.0 in (see the Chemistry in Action on p. 126). What is the minimum volume of muriatic acid in gallons that would be needed to remove the boiler scale?
- 4.174 Because acid-base and precipitation reactions discussed in this chapter all involve ionic species, their progress can be monitored by measuring the electrical conductance of the solution. Match the following reactions with the diagrams shown here. The electrical conductance is shown in arbitrary units.
- (1) A 1.0 M KOH solution is added to 1.0 L of 1.0 M  $\text{CH}_3\text{COOH}$ .
  - (2) A 1.0 M NaOH solution is added to 1.0 L of 1.0 M HCl.

- (3) A 1.0 M BaCl<sub>2</sub> solution is added to 1.0 L of 1.0 M K<sub>2</sub>SO<sub>4</sub>.  
 (4) A 1.0 M NaCl solution is added to 1.0 L of 1.0 M AgNO<sub>3</sub>.

- (5) A 1.0 M CH<sub>3</sub>COOH solution is added to 1.0 L of 1.0 M NH<sub>3</sub>.



## Answers to Practice Exercises

**4.1** (a) Insoluble, (b) insoluble, (c) soluble. **4.2**  $\text{Al}^{3+}(aq) + 3\text{OH}^{-}(aq) \longrightarrow \text{Al}(\text{OH})_3(s)$ . **4.3** (a) Brønsted base, (b) Brønsted acid. **4.4** Molecular equation:  $\text{H}_3\text{PO}_4(aq) + 3\text{NaOH}(aq) \longrightarrow \text{Na}_3\text{PO}_4(aq) + 3\text{H}_2\text{O}(l)$ ; ionic equation:  $\text{H}_3\text{PO}_4(aq) + 3\text{Na}^{+}(aq) + 3\text{OH}^{-}(aq) \longrightarrow 3\text{Na}^{+}(aq) + \text{PO}_4^{3-}(aq) + 3\text{H}_2\text{O}(l)$ ; net ionic equation:  $\text{H}_3\text{PO}_4(aq) + 3\text{OH}^{-}(aq) \longrightarrow \text{PO}_4^{3-}(aq) + 3\text{H}_2\text{O}(l)$ . **4.5** (a) P: +3, F: -1;

(b) Mn: +7, O: -2. **4.6** (a) Hydrogen displacement reaction, (b) combination reaction, (c) disproportionation reaction, (d) metal displacement reaction. **4.7** 0.452 M. **4.8** 494 mL. **4.9** Dilute 34.2 mL of the stock solution to 200 mL. **4.10** 92.02%. **4.11** 0.3822 g. **4.12** 10.1 mL. **4.13** 204 mL.

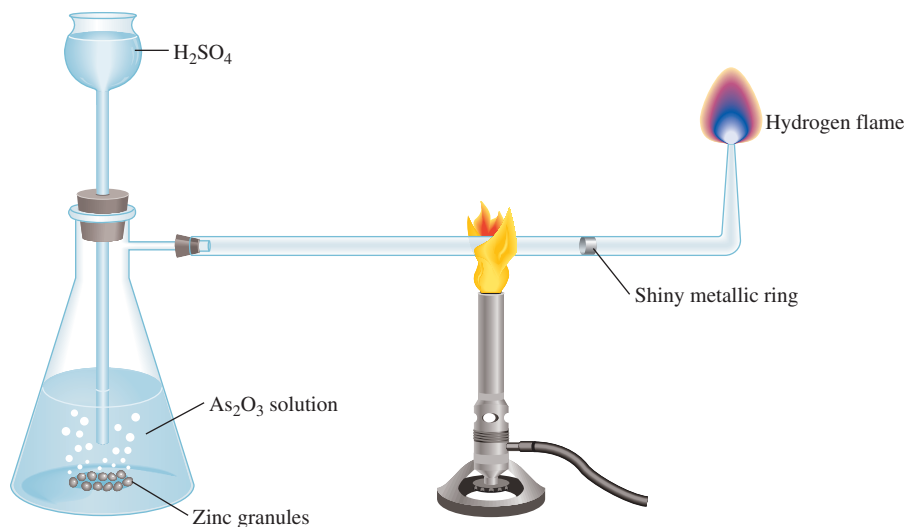
## Who Killed Napoleon?

After his defeat at Waterloo in 1815, Napoleon was exiled to St. Helena, a small island in the Atlantic Ocean, where he spent the last 6 years of his life. In the 1960s, samples of his hair were analyzed and found to contain a high level of arsenic, suggesting that he might have been poisoned. The prime suspects are the governor of St. Helena, with whom Napoleon did not get along, and the French royal family, who wanted to prevent his return to France.

Elemental arsenic is not that harmful. The commonly used poison is actually arsenic(III) oxide,  $\text{As}_2\text{O}_3$ , a white compound that dissolves in water, is tasteless, and if administered over a period of time, is hard to detect. It was once known as the “inheritance powder” because it could be added to grandfather’s wine to hasten his demise so that his grandson could inherit the estate!

In 1832 the English chemist James Marsh devised a procedure for detecting arsenic. This test, which now bears Marsh’s name, combines hydrogen formed by the reaction between zinc and sulfuric acid with a sample of the suspected poison. If  $\text{As}_2\text{O}_3$  is present, it reacts with hydrogen to form a toxic gas, arsine ( $\text{AsH}_3$ ). When arsine gas is heated, it decomposes to form arsenic, which is recognized by its metallic luster. The Marsh test is an effective deterrent to murder by  $\text{As}_2\text{O}_3$ , but it was invented too late to do Napoleon any good, if, in fact, he was a victim of deliberate arsenic poisoning.

*Apparatus for Marsh’s test. Sulfuric acid is added to zinc metal and a solution containing arsenic(III) oxide. The hydrogen produced reacts with  $\text{As}_2\text{O}_3$  to yield arsine ( $\text{AsH}_3$ ). On heating, arsine decomposes to elemental arsenic, which has a metallic appearance, and hydrogen gas.*





Doubts about the conspiracy theory of Napoleon's death developed in the early 1990s, when a sample of the wallpaper from his drawing room was found to contain copper arsenate ( $\text{CuHAsO}_4$ ), a green pigment that was commonly used at the time Napoleon lived. It has been suggested that the damp climate on St. Helena promoted the growth of molds on the wallpaper. To rid themselves of arsenic, the molds could have converted it to trimethyl arsine  $[(\text{CH}_3)_3\text{As}]$ , which is a volatile and highly poisonous compound. Prolonged exposure to these vapors would have ruined Napoleon's health and would also account for the presence of arsenic in his body, though it may not have been the primary cause of his death. This provocative theory is supported by the fact that Napoleon's regular guests suffered from gastrointestinal disturbances and other symptoms of arsenic poisoning and that their health all seemed to improve whenever they spent hours working outdoors in the garden, their main hobby on the island.

We will probably never know whether Napoleon died from arsenic poisoning, intentional or accidental, but this exercise in historical sleuthing provides a fascinating example of the use of chemical analysis. Not only is chemical analysis used in forensic science, but it also plays an essential part in endeavors ranging from pure research to practical applications, such as quality control of commercial products and medical diagnosis.

## Chemical Clues

1. The arsenic in Napoleon's hair was detected using a technique called *neutron activation*. When As-75 is bombarded with high-energy neutrons, it is converted to the radioactive As-76 isotope. The energy of the  $\gamma$  rays emitted by the radioactive isotope is characteristic of arsenic, and the intensity of the rays establishes how much arsenic is present in a sample. With this technique, as little as 5 ng ( $5 \times 10^{-9}$  g) of arsenic can be detected in 1 g of material. (a) Write symbols for the two isotopes of As, showing mass number and atomic number. (b) Name two advantages of analyzing the arsenic content by neutron activation instead of a chemical analysis.
2. Arsenic is not an essential element for the human body. (a) Based on its position in the periodic table, suggest a reason for its toxicity. (b) In addition to hair, where else might one look for the accumulation of the element if arsenic poisoning is suspected?
3. The Marsh test for arsenic involves the following steps: (a) The generation of hydrogen gas when sulfuric acid is added to zinc. (b) The reaction of hydrogen with As(III) oxide to produce arsine. (c) Conversion of arsine to arsenic by heating. Write equations representing these steps and identify the type of the reaction in each step.



A lock of Napoleon's hair.