

WHAT'S AHEAD

4.1 GENERAL PROPERTIES OF AQUEOUS SOLUTIONS

We begin by examining whether substances dissolved in water exist as ions, molecules, or a mixture of the two.

4.2 PRECIPITATION REACTIONS

We identify reactions in which soluble reactants yield an insoluble product.

4.3 ACIDS, BASES, AND NEUTRALIZATION REACTIONS

We explore reactions in which protons, H^+ ions, are transferred from one reactant to another.

4.4 OXIDATION-REDUCTION REACTIONS

We examine reactions in which electrons are transferred from one reactant to another.



CAVERNS SUCH AS THIS FORM when underground rivers erode limestone bedrock through to the surface. These caverns, called cenotes, are but one of many ways in which chemical reactions that occur in water shape our planet and impact our lives.

4.5 CONCENTRATIONS OF SOLUTIONS

We learn how the amount of a compound dissolved in a given volume of a solution can be expressed as a *concentration*. Concentration can be defined in a number of ways, the most commonly used being moles of compound per liter of solution (*molarity*).

4.6 SOLUTION STOICHIOMETRY AND CHEMICAL ANALYSIS

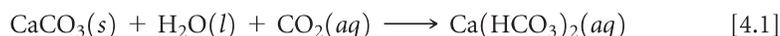
We see how the concepts of stoichiometry and concentration can be used to calculate amounts or concentrations of substances in solution through a process called *titration*.

REACTIONS IN AQUEOUS SOLUTION

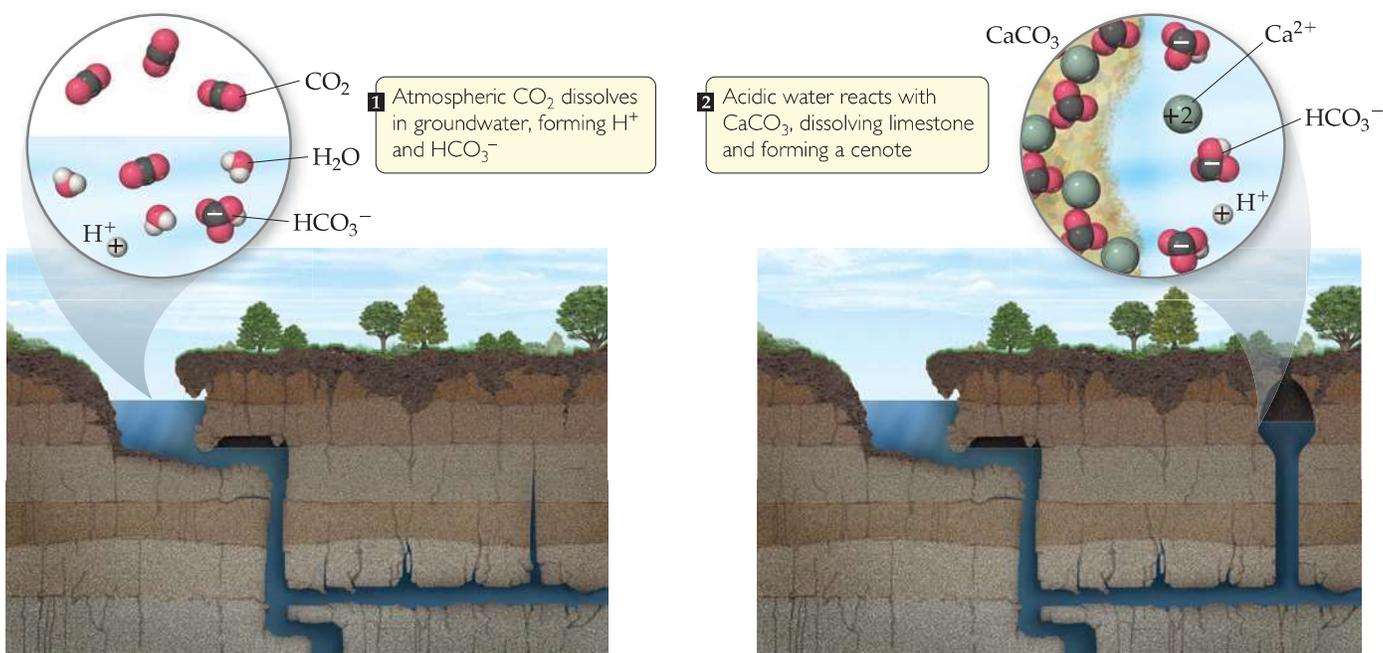
WATER COVERS NEARLY TWO-THIRDS of our planet, and this simple substance has been the key to much of Earth's evolutionary history. Life almost certainly originated in water, and the need for water by all forms of life has helped determine diverse biological structures.

Given the importance of water for life, it should come as no surprise that development of civilizations has been closely tied to reliable sources of fresh water. During the first millennium, Mayan civilization was one of the most advanced on Earth. Mayan city-states covered much of the Yucatan peninsula in what is now easternmost Mexico. The northern half of the peninsula is a flat shelf of land composed largely of carbonate rocks, such as limestone. Because there are no rivers and very few lakes, the Mayans depended on sinkholes called *cenotes*, for their fresh water (► **FIGURE 4.1**).

Chemical reactions that occur in water are responsible for creation of cenotes. When carbon dioxide, CO_2 , dissolves in water, the resulting solution is slightly acidic and reacts with CaCO_3 in the limestone:



A solution in which water is the dissolving medium is called an **aqueous solution**. In this chapter we examine chemical reactions that take place in aqueous solutions. In addition, we extend the concepts of stoichiometry learned in Chapter 3 by considering how solution concentrations are expressed and used.



▲ **FIGURE 4.1** Cenote formation.

4.1 GENERAL PROPERTIES OF AQUEOUS SOLUTIONS

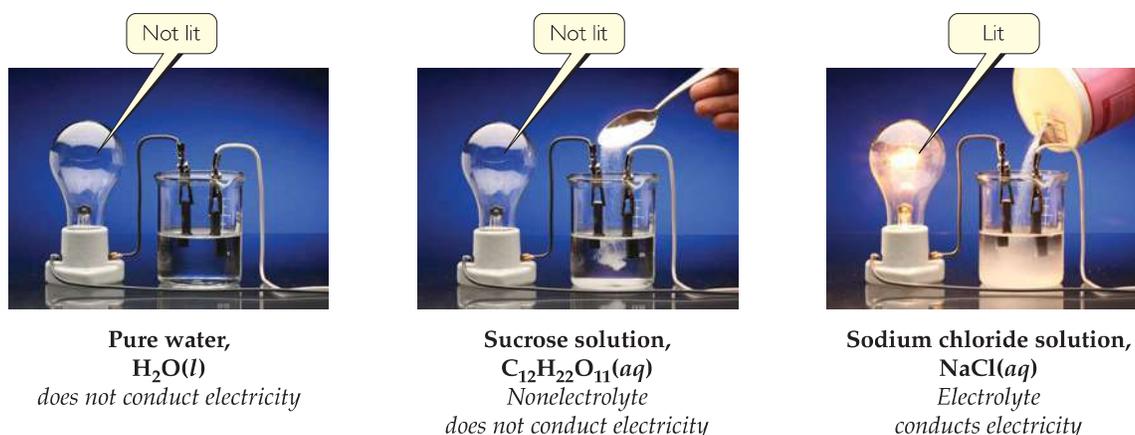
A *solution* is a homogeneous mixture of two or more substances. ∞ (Section 1.2) The substance present in the greatest quantity is usually called the **solvent**, and the other substances are called **solutes**; they are said to be *dissolved in* the solvent. When a small amount of sodium chloride (NaCl) is dissolved in a large quantity of water, for example, water is the solvent and sodium chloride is the solute.

Electrolytic Properties

At a young age we learn not to bring electrical devices into the bathtub so as not to electrocute ourselves. That's a useful lesson because most of the water you encounter in daily life is electrically conducting. Pure water, however, is a very poor conductor of electricity. The conductivity of bathwater originates from the substances dissolved in the water, not from the water itself.

Not all substances that dissolve in water make the resulting solution conducting. Imagine preparing two aqueous solutions—one by dissolving a teaspoon of table salt (sodium chloride) in a cup of water and the other by dissolving a teaspoon of table sugar (sucrose) in a cup of water (► **FIGURE 4.2**). Both solutions are clear and colorless, but they possess very different electrical conductivities: the salt solution is a good conductor of electricity, whereas the sugar solution is not.

In order for the bulb in the device of Figure 4.2 to light up, there must be a current (that is, a *flow* of electrically charged particles) between two electrodes immersed in the solution. The conductivity of pure water is not sufficient to complete the electrical circuit and light the bulb. The situation changes when ions are present in solution because the ions carry electrical charge from one electrode to the other, completing the circuit. Thus, the conductivity of NaCl solutions indicates the presence of ions. The lack of conductivity of sucrose solutions indicates the absence of ions. When NaCl dissolves in water, the solution contains Na^+ and Cl^- ions, each surrounded by water molecules. When sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) dissolves in water, the solution contains only neutral sucrose molecules surrounded by water molecules.



◀ **FIGURE 4.2**
 Electrical
 conductivities of
 water and two
 aqueous solutions.

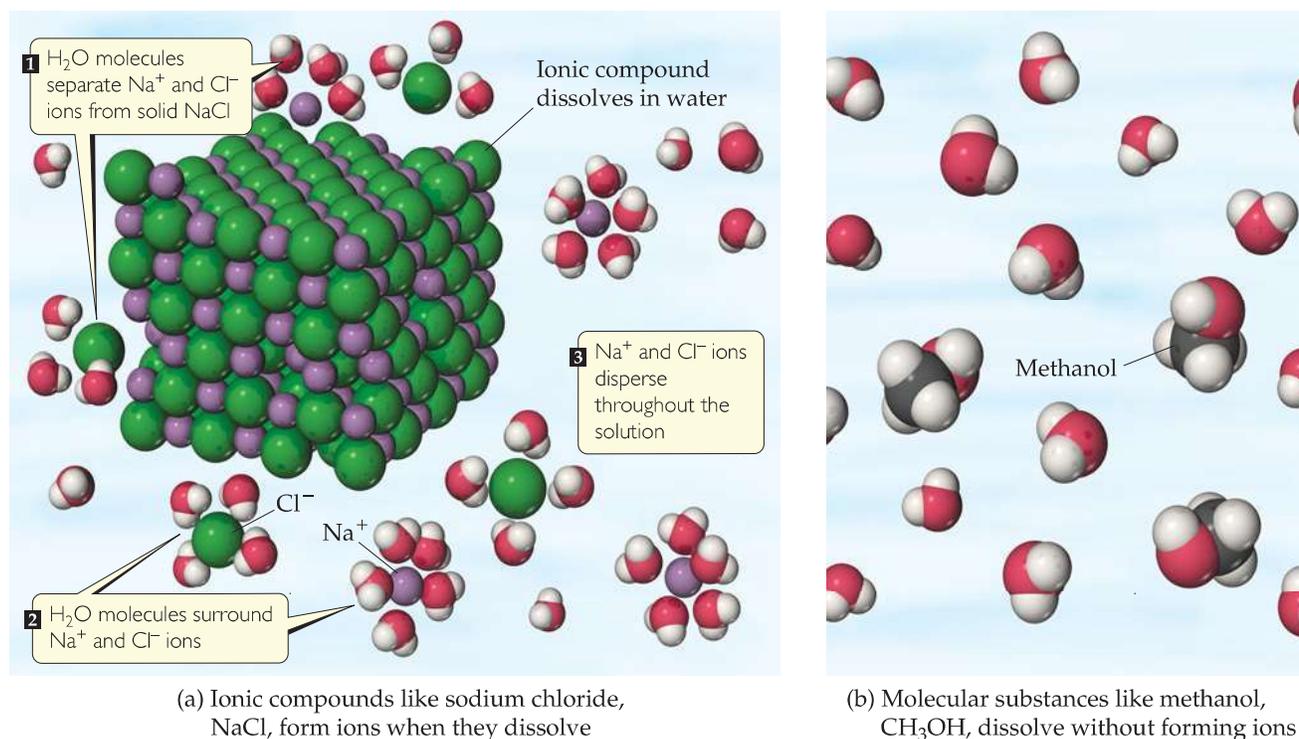
A substance (such as NaCl) whose aqueous solutions contain ions is called an **electrolyte**. A substance (such as $\text{C}_{12}\text{H}_{22}\text{O}_{11}$) that does not form ions in solution is called a **nonelectrolyte**. The different classifications of NaCl and $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ arise largely because NaCl is ionic, whereas $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ is molecular.

Ionic Compounds in Water

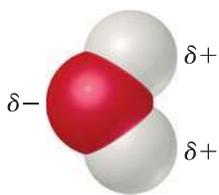
Recall from Figure 2.21 that solid NaCl consists of an orderly arrangement of Na^+ and Cl^- ions. When NaCl dissolves in water, each ion separates from the solid structure and disperses throughout the solution [▼ FIGURE 4.3(a)]. The ionic solid *dissociates* into its component ions as it dissolves.

GO FIGURE

Which solution, $\text{NaCl}(aq)$ or $\text{CH}_3\text{OH}(aq)$, conducts electricity?



▲ **FIGURE 4.3** **Dissolution in water.** (a) When an ionic compound, such as sodium chloride, NaCl, dissolves in water, H_2O molecules separate, surround, and uniformly disperse the ions into the liquid. (b) Molecular substances that dissolve in water, such as methanol, CH_3OH , usually do so without forming ions. We can think of this as a simple mixing of two molecular species. In both (a) and (b) the water molecules have been moved apart so that the solute particles can be seen clearly.



Water is a very effective solvent for ionic compounds. Although H_2O is an electrically neutral molecule, the O atom is rich in electrons and has a partial negative charge, denoted by δ^- . Each H atom has a partial positive charge, denoted by δ^+ . Cations are attracted by the negative end of H_2O , and anions are attracted by the positive end.

As an ionic compound dissolves, the ions become surrounded by H_2O molecules, as shown in Figure 4.3(a). The ions are said to be *solvated*. In chemical equations, we denote solvated ions by writing them as $\text{Na}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$, where *aq* is an abbreviation for “aqueous.” ∞ (Section 3.1) **Solvation** helps stabilize the ions in solution and prevents cations and anions from recombining. Furthermore, because the ions and their shells of surrounding water molecules are free to move about, the ions become dispersed uniformly throughout the solution.

We can usually predict the nature of the ions in a solution of an ionic compound from the chemical name of the substance. Sodium sulfate (Na_2SO_4), for example, dissociates into sodium ions (Na^+) and sulfate ions (SO_4^{2-}). You must remember the formulas and charges of common ions (Tables 2.4 and 2.5) to understand the forms in which ionic compounds exist in aqueous solution.

GIVE IT SOME THOUGHT

What dissolved species are present in a solution of

- KCN,
- NaClO_4 ?

Molecular Compounds in Water

When a molecular compound dissolves in water, the solution usually consists of intact molecules dispersed throughout the solution. Consequently, most molecular compounds are nonelectrolytes. As we have seen, table sugar (sucrose) is a nonelectrolyte. As another example, a solution of methanol (CH_3OH) in water consists entirely of CH_3OH molecules dispersed in the water [Figure 4.3(b)].

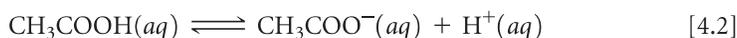
A few molecular substances have aqueous solutions that contain ions. Acids are the most important of these solutions. For example, when $\text{HCl}(\text{g})$ dissolves in water to form hydrochloric acid, $\text{HCl}(\text{aq})$, it *ionizes*; that is, it dissociates into $\text{H}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$ ions.

Strong and Weak Electrolytes

Electrolytes differ in the extent to which they conduct electricity. **Strong electrolytes** are those solutes that exist in solution completely or nearly completely as ions. Essentially all water-soluble ionic compounds (such as NaCl) and a few molecular compounds (such as HCl) are strong electrolytes. **Weak electrolytes** are those solutes that exist in solution mostly in the form of neutral molecules with only a small fraction in the form of ions. For example, in a solution of acetic acid (CH_3COOH) most of the solute is present as $\text{CH}_3\text{COOH}(\text{aq})$ molecules. Only a small fraction (about 1%) of the CH_3COOH has dissociated into $\text{H}^+(\text{aq})$ and $\text{CH}_3\text{COO}^-(\text{aq})$ ions.*

We must be careful not to confuse the extent to which an electrolyte dissolves (its solubility) with whether it is strong or weak. For example, CH_3COOH is extremely soluble in water but is a weak electrolyte. $\text{Ca}(\text{OH})_2$, on the other hand, is not very soluble in water, but the amount that does dissolve dissociates almost completely. Thus, $\text{Ca}(\text{OH})_2$ is a strong electrolyte.

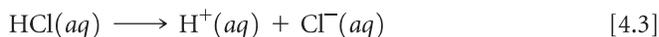
When a weak electrolyte, such as acetic acid, ionizes in solution, we write the reaction in the form



The half-arrows pointing in opposite directions mean that the reaction is significant in both directions. At any given moment some CH_3COOH molecules are ionizing to

*The chemical formula of acetic acid is sometimes written $\text{HC}_2\text{H}_3\text{O}_2$ so that the formula looks like that of other common acids such as HCl . The formula CH_3COOH conforms to the molecular structure of acetic acid, with the acidic H on the O atom at the end of the formula.

form H^+ and CH_3COO^- ions but H^+ and CH_3COO^- ions are recombining to form CH_3COOH . The balance between these opposing processes determines the relative numbers of ions and neutral molecules. This balance produces a state of **chemical equilibrium** in which the relative numbers of each type of ion or molecule in the reaction are constant over time. Chemists use half-arrows pointing in opposite directions to represent the ionization of weak electrolytes and a single arrow to represent the ionization of strong electrolytes. Because HCl is a strong electrolyte, we write the equation for the ionization of HCl as



The absence of a left-pointing arrow indicates that the H^+ and Cl^- ions have no tendency to recombine to form HCl molecules.

In the following sections we will look at how a compound's composition lets us predict whether it is a strong electrolyte, weak electrolyte, or nonelectrolyte. For the moment, you need only to remember that *water-soluble ionic compounds are strong electrolytes*. Ionic compounds can usually be identified by the presence of both metals and nonmetals [for example, NaCl , FeSO_4 , and $\text{Al}(\text{NO}_3)_3$]. Ionic compounds containing the ammonium ion, NH_4^+ [for example, NH_4Br and $(\text{NH}_4)_2\text{CO}_3$], are exceptions to this rule of thumb.

GIVE IT SOME THOUGHT

Which solute will cause the lightbulb in Figure 4.2 to glow most brightly, CH_3OH , NaOH , or CH_3COOH ?

SAMPLE EXERCISE 4.1 Relating Relative Numbers of Anions and Cations to Chemical Formulas

The accompanying diagram represents an aqueous solution of either MgCl_2 , KCl , or K_2SO_4 . Which solution does the drawing best represent?

SOLUTION

Analyze We are asked to associate the charged spheres in the diagram with ions present in a solution of an ionic substance.

Plan We examine each ionic substance given to determine the relative numbers and charges of its ions. We then correlate these ionic species with the ones shown in the diagram.

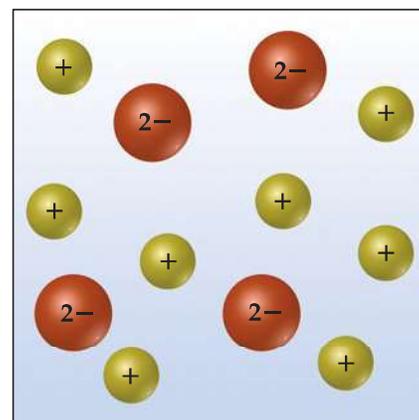
Solve The diagram shows twice as many cations as anions, consistent with the formulation K_2SO_4 .

Check Notice that the net charge in the diagram is zero, as it must be if it is to represent an ionic substance.

PRACTICE EXERCISE

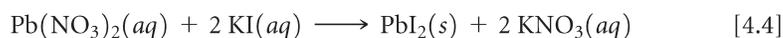
If you were to draw diagrams representing aqueous solutions of (a) NiSO_4 , (b) $\text{Ca}(\text{NO}_3)_2$, (c) Na_3PO_4 , (d) $\text{Al}_2(\text{SO}_4)_3$, how many anions would you show if each diagram contained six cations?

Answers: (a) 6, (b) 12, (c) 2, (d) 9



4.2 | PRECIPITATION REACTIONS

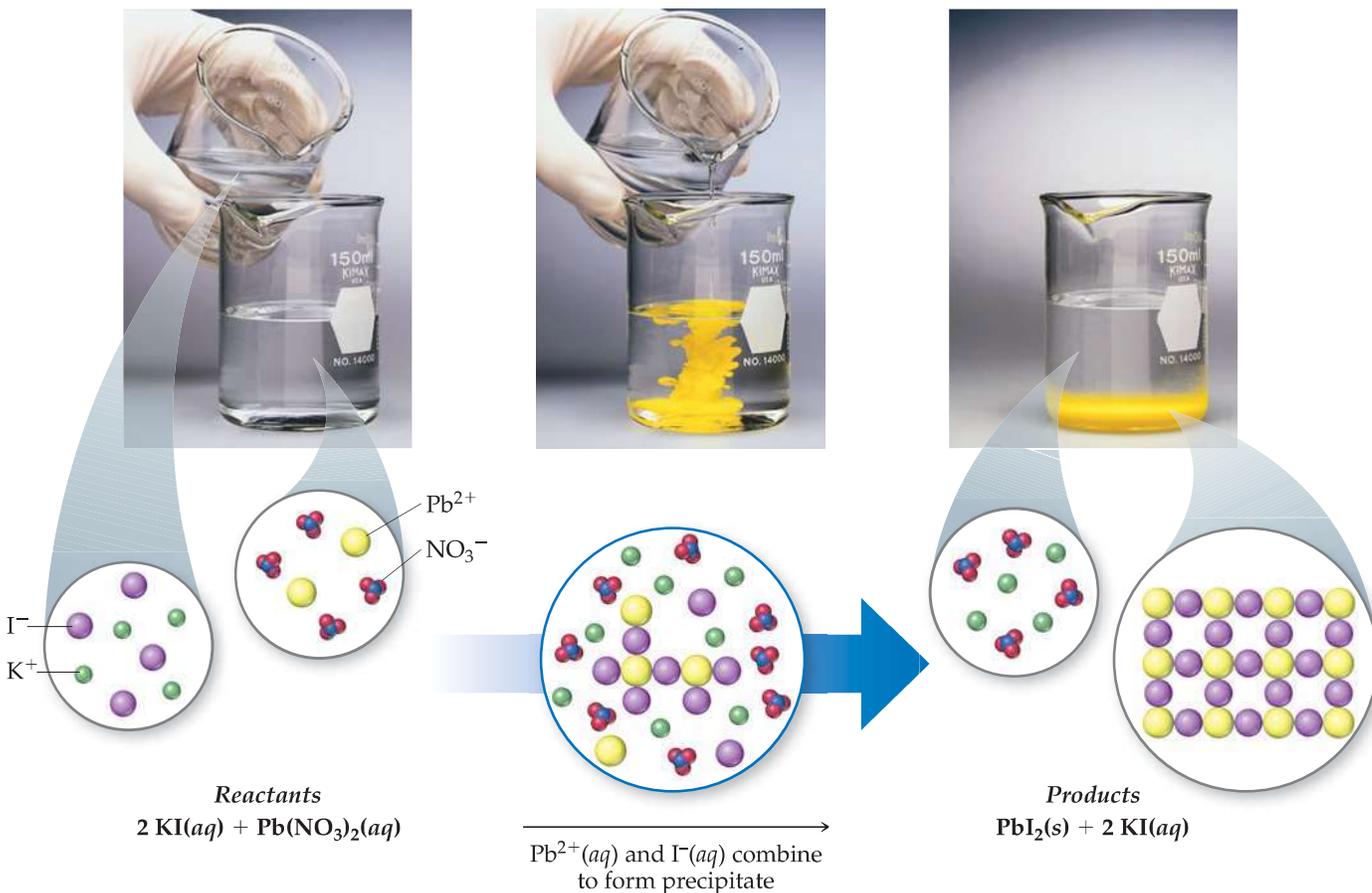
▶ FIGURE 4.4 shows two clear solutions being mixed. One solution contains potassium iodide, KI , dissolved in water and the other contains lead nitrate, $\text{Pb}(\text{NO}_3)_2$, dissolved in water. The reaction between these two solutes produces a water-insoluble yellow solid. Reactions that result in the formation of an insoluble product are called **precipitation reactions**. A **precipitate** is an insoluble solid formed by a reaction in solution. In Figure 4.4 the precipitate is lead iodide (PbI_2), a compound that has a very low solubility in water:



The other product of this reaction, potassium nitrate (KNO_3), remains in solution.

GO FIGURE

Which ions remain in solution after PbI_2 precipitation is complete?



▲ FIGURE 4.4 A precipitation reaction.

Precipitation reactions occur when pairs of oppositely charged ions attract each other so strongly that they form an insoluble ionic solid. To predict whether certain combinations of ions form insoluble compounds, we must consider some guidelines concerning the solubilities of common ionic compounds.

Solubility Guidelines for Ionic Compounds

The **solubility** of a substance at a given temperature is the amount of the substance that can be dissolved in a given quantity of solvent at the given temperature. In our discussions, any substance with a solubility less than 0.01 mol/L will be referred to as *insoluble*. In those cases the attraction between the oppositely charged ions in the solid is too great for the water molecules to separate the ions to any significant extent; the substance remains largely undissolved.

Unfortunately, there are no rules based on simple physical properties such as ionic charge to guide us in predicting whether a particular ionic compound will be soluble. Experimental observations, however, have led to guidelines for predicting solubility for ionic compounds. For example, experiments show that all common ionic compounds that contain the nitrate anion, NO_3^- , are soluble in water. ► **TABLE 4.1** summarizes the solubility guidelines for common ionic compounds. The table is organized according to the anion in the compound, but it also reveals many important facts about cations. Note that *all common ionic compounds of the alkali metal ions (group 1A of the periodic table) and of the ammonium ion (NH_4^+) are soluble in water.*

TABLE 4.1 • Solubility Guidelines for Common Ionic Compounds in Water

Soluble Ionic Compounds		Important Exceptions
Compounds containing	NO_3^-	None
	CH_3COO^-	None
	Cl^-	Compounds of Ag^+ , Hg_2^{2+} , and Pb^{2+}
	Br^-	Compounds of Ag^+ , Hg_2^{2+} , and Pb^{2+}
	I^-	Compounds of Ag^+ , Hg_2^{2+} , and Pb^{2+}
	SO_4^{2-}	Compounds of Sr^{2+} , Ba^{2+} , Hg_2^{2+} , and Pb^{2+}
Insoluble Ionic Compounds		Important Exceptions
Compounds containing	S^{2-}	Compounds of NH_4^+ , the alkali metal cations, Ca^{2+} , Sr^{2+} , and Ba^{2+}
	CO_3^{2-}	Compounds of NH_4^+ and the alkali metal cations
	PO_4^{3-}	Compounds of NH_4^+ and the alkali metal cations
	OH^-	Compounds of NH_4^+ , the alkali metal cations, Ca^{2+} , Sr^{2+} , and Ba^{2+}

SAMPLE EXERCISE 4.2 Using Solubility Rules

Classify these ionic compounds as soluble or insoluble in water: (a) sodium carbonate, Na_2CO_3 , (b) lead sulfate, PbSO_4 .

SOLUTION

Analyze We are given the names and formulas of two ionic compounds and asked to predict whether they are soluble or insoluble in water.

Plan We can use Table 4.1 to answer the question. Thus, we need to focus on the anion in each compound because the table is organized by anions.

Solve

(a) According to Table 4.1, most carbonates are insoluble. But carbonates of the alkali metal cations (such as sodium ion) are an exception to this rule and are soluble. Thus, Na_2CO_3 is soluble in water.

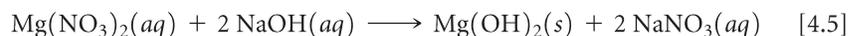
(b) Table 4.1 indicates that although most sulfates are water soluble, the sulfate of Pb^{2+} is an exception. Thus, PbSO_4 is insoluble in water.

PRACTICE EXERCISE

Classify the following compounds as soluble or insoluble in water: (a) cobalt(II) hydroxide, (b) barium nitrate, (c) ammonium phosphate.

Answers: (a) insoluble, (b) soluble, (c) soluble

To predict whether a precipitate forms when we mix aqueous solutions of two strong electrolytes, we must (1) note the ions present in the reactants, (2) consider the possible cation-anion combinations, and (3) use Table 4.1 to determine if any of these combinations is insoluble. For example, will a precipitate form when solutions of $\text{Mg}(\text{NO}_3)_2$ and NaOH are mixed? Both substances are soluble ionic compounds and strong electrolytes. Mixing the solutions first produces a solution containing Mg^{2+} , NO_3^- , Na^+ , and OH^- ions. Will either cation interact with either anion to form an insoluble compound? Knowing from Table 4.1 that $\text{Mg}(\text{NO}_3)_2$ and NaOH are both soluble in water, our only possibilities are Mg^{2+} with OH^- and Na^+ with NO_3^- . From Table 4.1 we see that hydroxides are generally insoluble. Because Mg^{2+} is not an exception, $\text{Mg}(\text{OH})_2$ is insoluble and thus forms a precipitate. NaNO_3 , however, is soluble, so Na^+ and NO_3^- remain in solution. The balanced equation for the precipitation reaction is

**Exchange (Metathesis) Reactions**

Notice in Equation 4.5 that the reactant cations exchange anions— Mg^{2+} ends up with OH^- , and Na^+ ends up with NO_3^- . The chemical formulas of the products are based on the charges of the ions—two OH^- ions are needed to give a neutral compound with Mg^{2+} ,

and one NO_3^- ion is needed to give a neutral compound with Na^+ . ∞ (Section 2.7) The equation can be balanced only after the chemical formulas of the products have been determined.

Reactions in which cations and anions appear to exchange partners conform to the general equation



Such reactions are called either **exchange reactions** or **metathesis reactions** (meh-TATH-eh-sis, Greek for “to transpose”). Precipitation reactions conform to this pattern, as do many neutralization reactions between acids and bases, as we will see in Section 4.3.

To complete and balance the equation for a metathesis reaction, we follow these steps:

1. Use the chemical formulas of the reactants to determine which ions are present.
2. Write the chemical formulas of the products by combining the cation from one reactant with the anion of the other, using the ionic charges to determine the subscripts in the chemical formulas.
3. Check the water solubilities of the products. For a precipitation reaction to occur, at least one product must be insoluble in water.
4. Balance the equation.

SAMPLE EXERCISE 4.3 Predicting a Metathesis Reaction

(a) Predict the identity of the precipitate that forms when aqueous solutions of BaCl_2 and K_2SO_4 are mixed. (b) Write the balanced chemical equation for the reaction.

SOLUTION

Analyze We are given two ionic reactants and asked to predict the insoluble product that they form.

Plan We need to write the ions present in the reactants and exchange the anions between the two cations. Once we have written the chemical formulas for these products, we can use Table 4.1 to determine which is insoluble in water. Knowing the products also allows us to write the equation for the reaction.

Solve

(a) The reactants contain Ba^{2+} , Cl^- , K^+ , and SO_4^{2-} ions. Exchanging the anions gives us BaSO_4 and KCl . According to Table 4.1, most compounds of SO_4^{2-} are soluble but those of Ba^{2+} are not. Thus, BaSO_4 is insoluble and will precipitate from solution. KCl is soluble.

(b) From part (a) we know the chemical formulas of the products, BaSO_4 and KCl . The balanced equation is



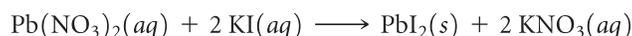
PRACTICE EXERCISE

(a) What compound precipitates when aqueous solutions of $\text{Fe}_2(\text{SO}_4)_3$ and LiOH are mixed? (b) Write a balanced equation for the reaction. (c) Will a precipitate form when solutions of $\text{Ba}(\text{NO}_3)_2$ and KOH are mixed?

Answers: (a) $\text{Fe}(\text{OH})_3$, (b) $\text{Fe}_2(\text{SO}_4)_3(aq) + 6 \text{LiOH}(aq) \longrightarrow 2 \text{Fe}(\text{OH})_3(s) + 3 \text{Li}_2\text{SO}_4(aq)$, (c) no (both possible products, $\text{Ba}(\text{OH})_2$ and KNO_3 , are water soluble)

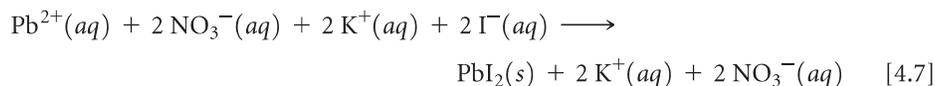
Ionic Equations

In writing equations for reactions in aqueous solution, it is often useful to indicate whether the dissolved substances are present predominantly as ions or as molecules. Let's reconsider the precipitation reaction between $\text{Pb}(\text{NO}_3)_2$ and 2 KI :



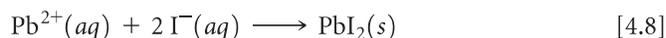
An equation written in this fashion, showing the complete chemical formulas of reactants and products, is called a **molecular equation** because it shows chemical formulas

without indicating ionic character. Because $\text{Pb}(\text{NO}_3)_2$, KI , and KNO_3 are all water-soluble ionic compounds and therefore strong electrolytes, we can write the equation in a form that indicates which species exist as ions in the solution:



An equation written in this form, with all soluble strong electrolytes shown as ions, is called a **complete ionic equation**.

Notice that $\text{K}^{+}(\text{aq})$ and $\text{NO}_3^{-}(\text{aq})$ appear on both sides of Equation 4.7. Ions that appear in identical forms on both sides of a complete ionic equation, called **spectator ions**, play no direct role in the reaction. When spectator ions are omitted from the equation (they cancel out like algebraic quantities), we are left with the **net ionic equation**, which is one that includes only the ions and molecules directly involved in the reaction:



Because charge is conserved in reactions, the sum of the ionic charges must be the same on both sides of a balanced net ionic equation. In this case the $2+$ charge of the cation and the two $1-$ charges of the anions add to zero, the charge of the electrically neutral product. *If every ion in a complete ionic equation is a spectator, no reaction occurs.*

GIVE IT SOME THOUGHT

Which ions, if any, are spectator ions in the reaction $\text{AgNO}_3(\text{aq}) + \text{NaCl}(\text{aq}) \longrightarrow \text{AgCl}(\text{s}) + \text{NaNO}_3(\text{aq})$?

Net ionic equations illustrate the similarities between various reactions involving electrolytes. For example, Equation 4.8 expresses the essential feature of the precipitation reaction between any strong electrolyte containing $\text{Pb}^{2+}(\text{aq})$ and any strong electrolyte containing $\text{I}^{-}(\text{aq})$: The ions combine to form a precipitate of PbI_2 . Thus, a net ionic equation demonstrates that more than one set of reactants can lead to the same net reaction. For example, aqueous solutions of KI and MgI_2 share many chemical similarities because both contain I^{-} ions. Either solution when mixed with a $\text{Pb}(\text{NO}_3)_2$ solution produces $\text{PbI}_2(\text{s})$. The complete ionic equation, on the other hand, identifies the actual reactants that participate in a reaction.

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

1. Write a balanced molecular equation for the reaction.
2. Rewrite the equation to show the ions that form in solution when each soluble strong electrolyte dissociates into its ions. *Only strong electrolytes dissolved in aqueous solution are written in ionic form.*
3. Identify and cancel spectator ions.

SAMPLE EXERCISE 4.4 Writing a Net Ionic Equation

Write the net ionic equation for the precipitation reaction that occurs when aqueous solutions of calcium chloride and sodium carbonate are mixed.

SOLUTION

Analyze Our task is to write a net ionic equation for a precipitation reaction, given the names of the reactants present in solution.

Plan We write the chemical formulas of the reactants and products and then determine which product is insoluble. We then write and balance the molecular equation. Next, we write each soluble strong electrolyte as separated ions to obtain the complete ionic equation. Finally, we eliminate the spectator ions to obtain the net ionic equation.

Solve Calcium chloride is composed of calcium ions, Ca^{2+} , and chloride ions, Cl^{-} ; hence, an aqueous solution of the substance is $\text{CaCl}_2(\text{aq})$. Sodium carbonate is composed of Na^{+} ions and CO_3^{2-} ions; hence, an aqueous solution of the compound is $\text{Na}_2\text{CO}_3(\text{aq})$. In the molecular

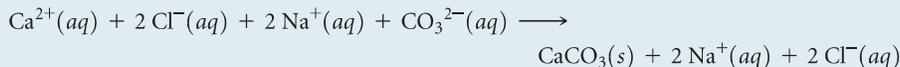


▲ **FIGURE 4.5** Vinegar and lemon juice are common household acids. Ammonia and baking soda (sodium bicarbonate) are common household bases.

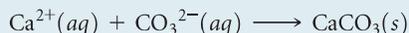
equations for precipitation reactions, the anions and cations appear to exchange partners. Thus, we put Ca^{2+} and CO_3^{2-} together to give CaCO_3 and Na^+ and Cl^- together to give NaCl . According to the solubility guidelines in Table 4.1, CaCO_3 is insoluble and NaCl is soluble. The balanced molecular equation is



In a complete ionic equation, *only* dissolved strong electrolytes (such as soluble ionic compounds) are written as separate ions. As the (aq) designations remind us, CaCl_2 , Na_2CO_3 , and NaCl are all dissolved in the solution. Furthermore, they are all strong electrolytes. CaCO_3 is an ionic compound, but it is not soluble. We do not write the formula of any insoluble compound as its component ions. Thus, the complete ionic equation is



Cl^- and Na^+ are spectator ions. Canceling them gives the following net ionic equation:



Check We can check our result by confirming that both the elements and the electric charge are balanced. Each side has one Ca, one C, and three O, and the net charge on each side equals 0.

Comment If none of the ions in an ionic equation is removed from solution or changed in some way, all ions are spectator ions and a reaction does not occur.

PRACTICE EXERCISE

Write the net ionic equation for the precipitation reaction that occurs when aqueous solutions of silver nitrate and potassium phosphate are mixed.

Answer: $3 \text{Ag}^+(aq) + \text{PO}_4^{3-}(aq) \longrightarrow \text{Ag}_3\text{PO}_4(s)$

4.3 ACIDS, BASES, AND NEUTRALIZATION REACTIONS

Many acids and bases are industrial and household substances (◀ **FIGURE 4.5**), and some are important components of biological fluids. Hydrochloric acid, for example, is an important industrial chemical and the main constituent of gastric juice in your stomach. Acids and bases are also common electrolytes.

Acids

As noted in Section 2.8, **acids** are substances that ionize in aqueous solution to form hydrogen ions $\text{H}^+(aq)$. Because a hydrogen atom consists of a proton and an electron, H^+ is simply a proton. Thus, acids are often called *proton donors*. Molecular models of three common acids are shown in ◀ **FIGURE 4.6**.

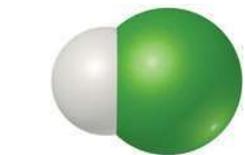
Protons in aqueous solution are solvated by water molecules, just as other cations are [Figure 4.3(a)]. In writing chemical equations involving protons in water, therefore, we write $\text{H}^+(aq)$.

Molecules of different acids ionize to form different numbers of H^+ ions. Both HCl and HNO_3 are *monoprotic* acids, yielding one H^+ per molecule of acid. Sulfuric acid, H_2SO_4 , is a *diprotic* acid, one that yields two H^+ per molecule of acid. The ionization of H_2SO_4 and other diprotic acids occurs in two steps:

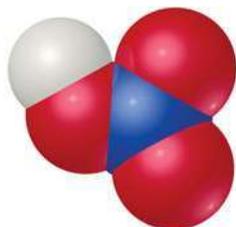


Although H_2SO_4 is a strong electrolyte, only the first ionization (Equation 4.9) is complete. Thus, aqueous solutions of sulfuric acid contain a mixture of $\text{H}^+(aq)$, $\text{HSO}_4^-(aq)$, and $\text{SO}_4^{2-}(aq)$.

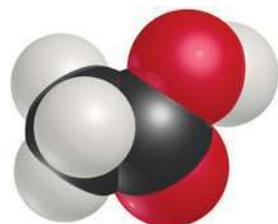
The molecule CH_3COOH (acetic acid) that we have mentioned frequently is the primary component in vinegar. Acetic acid has four hydrogens, as Figure 4.6 shows, but only one of them, the H in the COOH group, is ionized in water. The three other hydrogens are bound to carbon and do not break their $\text{C}-\text{H}$ bonds in water.



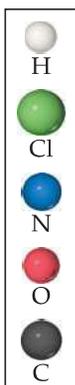
Hydrochloric acid, HCl



Nitric acid, HNO_3



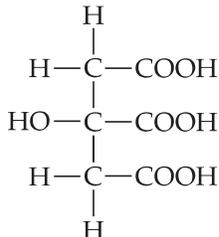
Acetic acid, CH_3COOH



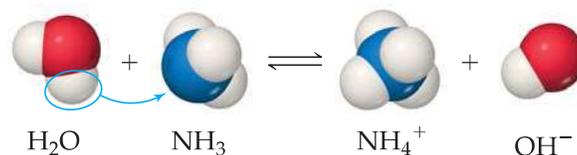
▲ **FIGURE 4.6** Molecular models of three common acids.

GIVE IT SOME THOUGHT

The structural formula of citric acid, a main component of citrus fruits, is



How many $\text{H}^+(\text{aq})$ can be generated by each citric acid molecule dissolved in water?

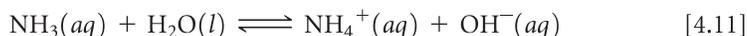


▲ FIGURE 4.7 Hydrogen ion transfer. An H_2O molecule acts as a proton donor (acid), and NH_3 acts as a proton acceptor (base). Only a fraction of the NH_3 molecules react with H_2O . Consequently, NH_3 is a weak electrolyte.

Bases

Bases are substances that accept (react with) H^+ ions. Bases produce hydroxide ions (OH^-) when they dissolve in water. Ionic hydroxide compounds, such as NaOH , KOH , and $\text{Ca}(\text{OH})_2$, are among the most common bases. When dissolved in water, they dissociate into ions, introducing OH^- ions into the solution.

Compounds that do not contain OH^- ions can also be bases. For example, ammonia (NH_3) is a common base. When added to water, it accepts an H^+ ion from a water molecule and thereby produces an OH^- ion (► **FIGURE 4.7**):



Ammonia is a weak electrolyte because only about 1% of the NH_3 forms NH_4^+ and OH^- ions.

Strong and Weak Acids and Bases

Acids and bases that are strong electrolytes (completely ionized in solution) are **strong acids** and **strong bases**. Those that are weak electrolytes (partly ionized) are **weak acids** and **weak bases**. When reactivity depends only on $\text{H}^+(\text{aq})$ concentration, strong acids are more reactive than weak acids. The reactivity of an acid, however, can depend on the anion as well as on $\text{H}^+(\text{aq})$ concentration. For example, hydrofluoric acid (HF) is a weak acid (only partly ionized in aqueous solution), but it is very reactive and vigorously attacks many substances, including glass. This reactivity is due to the combined action of $\text{H}^+(\text{aq})$ and $\text{F}^-(\text{aq})$.

▼ **TABLE 4.2** lists the strong acids and bases we are most likely to encounter. You need to commit this information to memory in order to correctly identify strong electrolytes and write net ionic equations. The brevity of this list tells us that most acids are weak. (For H_2SO_4 , as we noted earlier, only the first proton completely ionizes.) The only common strong bases are the common soluble metal hydroxides. Most other metal hydroxides are insoluble in water. The most common weak base is NH_3 , which reacts with water to form OH^- ions (Equation 4.11).

TABLE 4.2 • Common Strong Acids and Bases

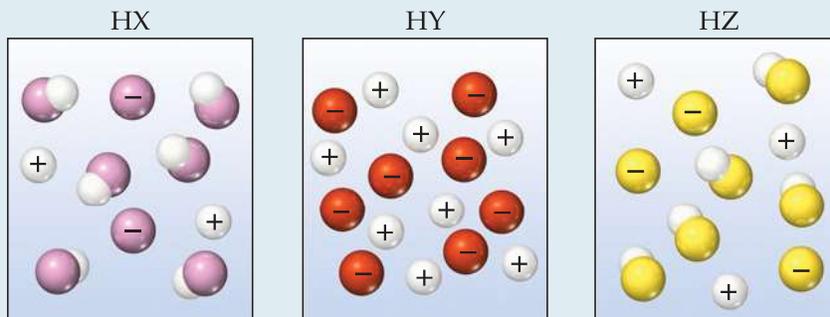
Strong Acids	Strong Bases
Hydrochloric, HCl	Group 1A metal hydroxides [LiOH , NaOH , KOH , RbOH , CsOH]
Hydrobromic, HBr	Heavy group 2A metal hydroxides [$\text{Ca}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$]
Hydroiodic, HI	
Chloric, HClO_3	
Perchloric, HClO_4	
Nitric, HNO_3	
Sulfuric, H_2SO_4	

GIVE IT SOME THOUGHT

Why isn't $\text{Al}(\text{OH})_3$ classified as a strong base?

SAMPLE EXERCISE 4.5 Comparing Acid Strengths

The following diagrams represent aqueous solutions of acids HX, HY, and HZ, with water molecules omitted for clarity. Rank the acids from strongest to weakest.



SOLUTION

Analyze We are asked to rank three acids from strongest to weakest, based on schematic drawings of their solutions.

Plan We can determine the relative numbers of uncharged molecular species in the diagrams. The strongest acid is the one with the most H^+ ions and fewest undissociated molecules in solution. The weakest acid is the one with the largest number of undissociated molecules.

Solve The order is $\text{HY} > \text{HZ} > \text{HX}$. HY is a strong acid because it is totally ionized (no HY molecules in solution), whereas both HX and HZ are weak acids, whose solutions consist of a mixture of molecules and ions. Because HZ contains more H^+ ions and fewer molecules than HX, it is a stronger acid.

PRACTICE EXERCISE

Imagine a diagram showing 10 Na^+ ions and 10 OH^- ions. If this solution were mixed with the one pictured above for HY, what species would be present in a diagram that represents the combined solutions after any possible reaction?

Answer: The diagram would show 10 Na^+ ions, 2 OH^- ions, 8 Y^- ions, and 8 H_2O molecules.

Identifying Strong and Weak Electrolytes

If we remember the common strong acids and bases (Table 4.2) and also remember that NH_3 is a weak base, we can make reasonable predictions about the electrolytic strength of a great number of *water-soluble* substances. ▼ TABLE 4.3 summarizes our observations about electrolytes. To classify a soluble substance as strong electrolyte, weak electrolyte, or nonelectrolyte, we work our way down and across this table. We first ask whether the substance is ionic or molecular. If it is ionic, it is a strong electrolyte. The second column of Table 4.3 tells us that all ionic compounds are strong electrolytes. If the substance is molecular, we ask whether it is an acid or a base. (It is an acid if it either has H first in the chemical formula or contains a COOH group.) If it is an acid, we use Table 4.2 to determine whether it is a strong or weak electrolyte: All strong acids are strong electrolytes, and all weak acids are weak electrolytes. If an acid is not listed in Table 4.2, it is probably a weak acid and therefore a weak electrolyte.

TABLE 4.3 • Summary of the Electrolytic Behavior of Common Soluble Ionic and Molecular Compounds

	Strong Electrolyte	Weak Electrolyte	Nonelectrolyte
Ionic	All	None	None
Molecular	Strong acids (see Table 4.2)	Weak acids, weak bases	All other compounds

If our substance is a base, we use Table 4.2 to determine whether it is a strong base. NH_3 is the only molecular base that we consider in this chapter, and Table 4.3 tells us it is a weak electrolyte. Finally, any molecular substance that we encounter in this chapter that is not an acid or NH_3 is probably a nonelectrolyte.

SAMPLE EXERCISE 4.6 Identifying Strong, Weak, and Nonelectrolytes

Classify these dissolved substances as strong, weak, or nonelectrolyte: CaCl_2 , HNO_3 , $\text{C}_2\text{H}_5\text{OH}$ (ethanol), HCOOH (formic acid), KOH .

SOLUTION

Analyze We are given several chemical formulas and asked to classify each substance as a strong electrolyte, weak electrolyte, or nonelectrolyte.

Plan The approach we take is outlined in Table 4.3. We can predict whether a substance is ionic or molecular based on its composition. As we saw in Section 2.7, most ionic compounds we encounter in this text are composed of a metal and a nonmetal, whereas most molecular compounds are composed only of nonmetals.

Solve Two compounds fit the criteria for ionic compounds: CaCl_2 and KOH . Because Table 4.3 tells us that all ionic compounds are strong electrolytes, that is how we classify these two substances. The three remaining compounds are molecular. Two, HNO_3 and HCOOH , are acids. Nitric acid, HNO_3 , is a common strong acid, as shown in Table 4.2, and therefore is a strong electrolyte. Because most acids are weak acids, our best guess would be that HCOOH is a weak acid (weak electrolyte). This is correct. The remaining molecular compound, $\text{C}_2\text{H}_5\text{OH}$, is neither an acid nor a base, so it is a nonelectrolyte.

Comment Although $\text{C}_2\text{H}_5\text{OH}$ has an OH group, it is not a metal hydroxide and so not a base. Rather, it is a member of a class of organic compounds that have C—OH bonds, which are known as alcohols. ∞ (Section 2.9) Organic compounds containing the COOH group are called carboxylic acids (Chapter 16). Molecules that have this group are weak acids.

PRACTICE EXERCISE

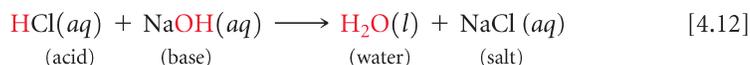
Consider solutions in which 0.1 mol of each of the following compounds is dissolved in 1 L of water: $\text{Ca}(\text{NO}_3)_2$ (calcium nitrate), $\text{C}_6\text{H}_{12}\text{O}_6$ (glucose), NaCH_3COO (sodium acetate), and CH_3COOH (acetic acid). Rank the solutions in order of increasing electrical conductivity, based on the fact that the greater the number of ions in solution, the greater the conductivity.

Answers: $\text{C}_6\text{H}_{12}\text{O}_6$ (nonelectrolyte) < CH_3COOH (weak electrolyte, existing mainly in the form of molecules with few ions) < NaCH_3COO (strong electrolyte that provides two ions, Na^+ and CH_3COO^-) < $\text{Ca}(\text{NO}_3)_2$ (strong electrolyte that provides three ions, Ca^{2+} and 2 NO_3^-)

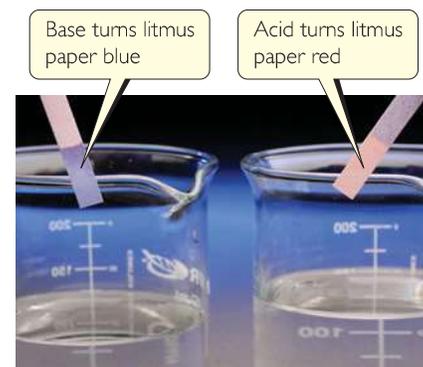
Neutralization Reactions and Salts

The properties of acidic solutions are quite different from those of basic solutions. Acids have a sour taste, whereas bases have a bitter taste.* Acids change the colors of certain dyes in a way that differs from the way bases affect the same dyes. This is the principle behind the indicator known as litmus paper (► FIGURE 4.8). In addition, acidic and basic solutions differ in chemical properties in several other important ways that we explore in this chapter and in later chapters.

When a solution of an acid and a solution of a base are mixed, a **neutralization reaction** occurs. The products of the reaction have none of the characteristic properties of either the acidic solution or the basic solution. For example, when hydrochloric acid is mixed with a solution of sodium hydroxide, the reaction is



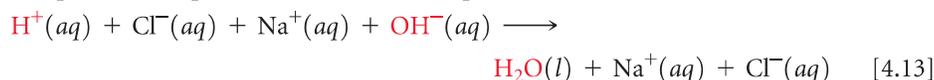
*Tasting chemical solutions is not a good practice. However, we have all had acids such as ascorbic acid (vitamin C), acetylsalicylic acid (aspirin), and citric acid (in citrus fruits) in our mouths, and we are familiar with their characteristic sour taste. Soaps, which are basic, have the characteristic bitter taste of bases.



▲ FIGURE 4.8 Litmus paper. Litmus paper is coated with dyes that change color in response to exposure to either acids or bases.

Water and table salt, NaCl, are the products of the reaction. By analogy to this reaction, the term **salt** has come to mean any ionic compound whose cation comes from a base (for example, Na^+ from NaOH) and whose anion comes from an acid (for example, Cl^- from HCl). In general, a *neutralization reaction between an acid and a metal hydroxide produces water and a salt*.

Because HCl, NaOH, and NaCl are all water-soluble strong electrolytes, the complete ionic equation associated with Equation 4.12 is



Therefore, the net ionic equation is



Equation 4.14 summarizes the main feature of the neutralization reaction between any strong acid and any strong base: $\text{H}^+(aq)$ and $\text{OH}^-(aq)$ ions combine to form H_2O .

▼ **FIGURE 4.9** shows the neutralization reaction between hydrochloric acid and the water-insoluble base $\text{Mg}(\text{OH})_2$:

Molecular equation:



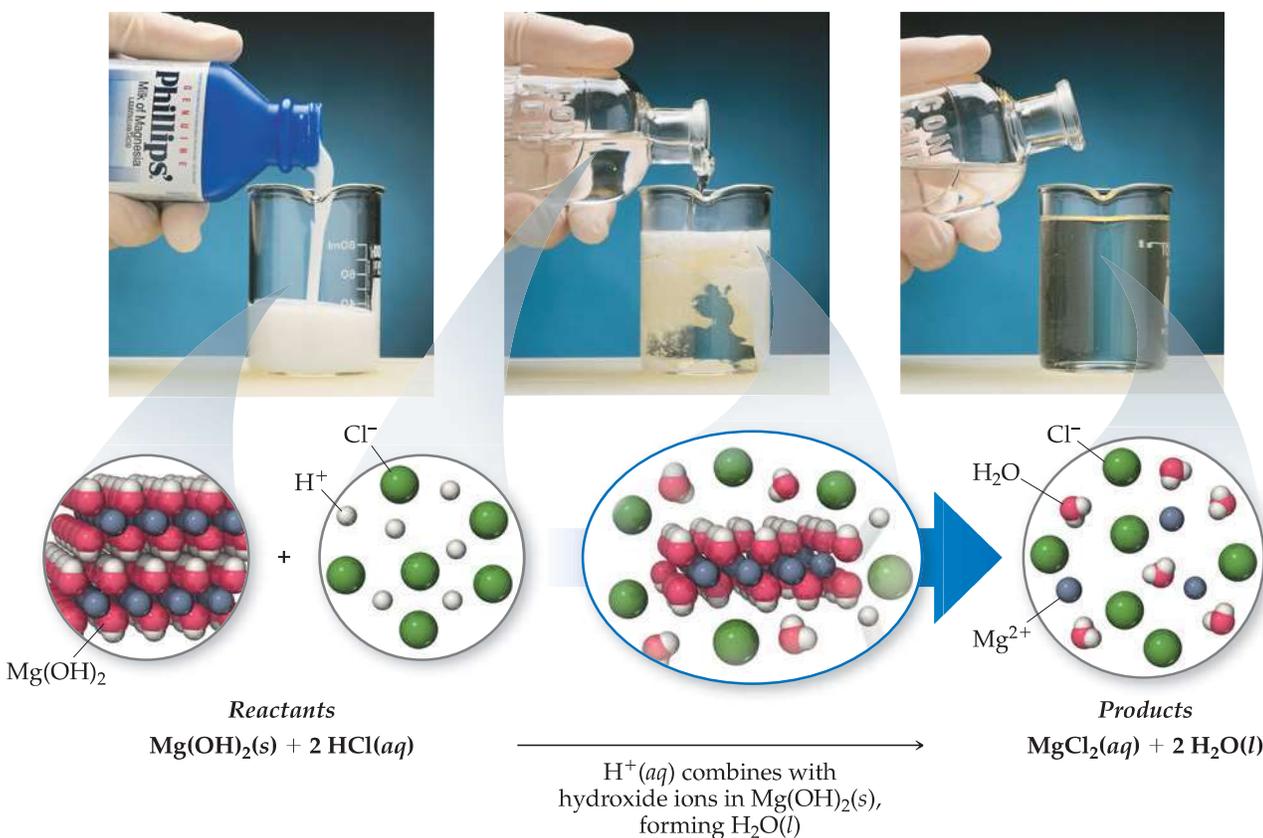
Net ionic equation:



Notice that the OH^- ions (this time in a solid reactant) and H^+ ions combine to form H_2O . Because the ions exchange partners, neutralization reactions between acids and metal hydroxides are metathesis reactions.

GO FIGURE

Adding just a few drops of hydrochloric acid would not be sufficient to dissolve all the $\text{Mg}(\text{OH})_2(s)$. Why not?



▲ **FIGURE 4.9** Neutralization reaction between $\text{Mg}(\text{OH})_2(s)$ and hydrochloric acid. Milk of magnesia is a suspension of water-insoluble magnesium hydroxide, $\text{Mg}(\text{OH})_2(s)$, in water. When sufficient hydrochloric acid, $\text{HCl}(aq)$, is added a reaction ensues that leads to an aqueous solution containing $\text{Mg}^{2+}(aq)$ and $\text{Cl}^-(aq)$ ions.

SAMPLE EXERCISE 4.7 Writing Chemical Equations for a Neutralization Reaction

For the reaction between aqueous solutions of acetic acid (CH_3COOH) and barium hydroxide, $\text{Ba}(\text{OH})_2$, write (a) the balanced molecular equation, (b) the complete ionic equation, (c) the net ionic equation.

SOLUTION

Analyze We are given the chemical formulas for an acid and a base and asked to write a balanced molecular equation, a complete ionic equation, and a net ionic equation for their neutralization reaction.

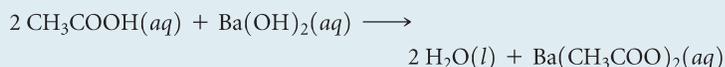
Plan As Equation 4.12 and the italicized statement that follows it indicate, neutralization reactions form two products, H_2O and a salt. We examine the cation of the base and the anion of the acid to determine the composition of the salt.

Solve

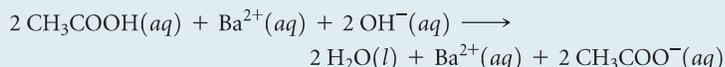
(a) The salt contains the cation of the base (Ba^{2+}) and the anion of the acid (CH_3COO^-). Thus, the salt formula is $\text{Ba}(\text{CH}_3\text{COO})_2$. According to Table 4.1, this compound is soluble in water. The unbalanced molecular equation for the neutralization reaction is



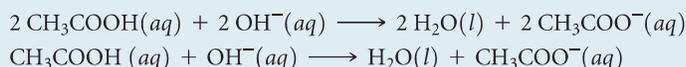
To balance this equation, we must provide two molecules of CH_3COOH to furnish the two CH_3COO^- ions and to supply the two H^+ ions needed to combine with the two OH^- ions of the base. The balanced molecular equation is



(b) To write the complete ionic equation, we identify the strong electrolytes and break them into ions. In this case $\text{Ba}(\text{OH})_2$ and $\text{Ba}(\text{CH}_3\text{COO})_2$ are both water-soluble ionic compounds and hence strong electrolytes. Thus, the complete ionic equation is



(c) Eliminating the spectator ion, Ba^{2+} , and simplifying coefficients gives the net ionic equation:



Check We can determine whether the molecular equation is balanced by counting the number of atoms of each kind on both sides of the arrow (10 H, 6 O, 4 C, and 1 Ba on each side). However, it is often easier to check equations by counting groups: There are

2 CH_3COO groups, as well as 1 Ba, and 4 additional H atoms and 2 additional O atoms on each side of the equation. The net ionic equation checks out because the numbers of each kind of element and the net charge are the same on both sides of the equation.

PRACTICE EXERCISE

For the reaction of phosphorous acid (H_3PO_3) and potassium hydroxide (KOH), write (a) the balanced molecular equation and (b) the net ionic equation.

Answers: (a) $\text{H}_3\text{PO}_3(aq) + 3 \text{KOH}(aq) \longrightarrow 3 \text{H}_2\text{O}(l) + \text{K}_3\text{PO}_3(aq)$,

(b) $\text{H}_3\text{PO}_3(aq) + 3 \text{OH}^-(aq) \longrightarrow 3 \text{H}_2\text{O}(l) + \text{PO}_3^{3-}(aq)$. (H_3PO_3 is a weak acid and therefore a weak electrolyte, whereas KOH, a strong base, and K_3PO_3 , an ionic compound, are strong electrolytes.)

Neutralization Reactions with Gas Formation

Many bases besides OH^- react with H^+ to form molecular compounds. Two of these that you might encounter in the laboratory are the sulfide ion and the carbonate ion. Both of these anions react with acids to form gases that have low solubilities in water. Hydrogen sulfide (H_2S), the substance that gives rotten eggs their foul odor, forms when an acid such as $\text{HCl}(aq)$ reacts with a metal sulfide such as Na_2S :

Molecular equation:



Net ionic equation:



Carbonates and bicarbonates react with acids to form $\text{CO}_2(g)$. Reaction of CO_3^{2-} or HCO_3^- with an acid first gives carbonic acid (H_2CO_3). For example, when hydrochloric acid is added to sodium bicarbonate, the reaction is



Carbonic acid is unstable. If present in solution in sufficient concentrations, it decomposes to H_2O and CO_2 , which escapes from the solution as a gas:



The overall reaction is summarized by the equations

Molecular equation:



Net ionic equation:



Both $\text{NaHCO}_3(\text{s})$ and $\text{Na}_2\text{CO}_3(\text{s})$ are used as neutralizers in acid spills, either salt is added until the fizzing caused by $\text{CO}_2(\text{g})$ formation stops. Sometimes sodium bicarbonate is used as an antacid to soothe an upset stomach. In that case the HCO_3^- reacts with stomach acid to form $\text{CO}_2(\text{g})$.

GIVE IT SOME THOUGHT

By analogy to examples given in the text, predict what gas forms when $\text{Na}_2\text{SO}_3(\text{s})$ reacts with $\text{HCl}(\text{aq})$.

CHEMISTRY PUT TO WORK

Antacids

Your stomach secretes acids to help digest foods. These acids, which include hydrochloric acid, contain about 0.1 mol of H^+ per liter of solution. The stomach and digestive tract are normally protected from the corrosive effects of stomach acid by a mucosal lining. Holes can develop in this lining, however, allowing the acid to attack the underlying tissue, causing painful damage. These holes, known as ulcers, can be caused by the secretion of excess acids or by a weakness in the digestive lining. Studies indicate, however, that many ulcers are caused by bacterial infection. Between 10 and 20% of Americans suffer from ulcers at some point in their lives. Many



▲ FIGURE 4.10 Antacids. These products all serve as acid-neutralizing agents in the stomach.

others experience occasional indigestion or heartburn due to digestive acids entering the esophagus.

We can address the problem of excess stomach acid in two ways: (1) removing the excess acid or (2) decreasing the production of acid. Substances that remove excess acid are called *antacids*, whereas those that decrease acid production are called *acid inhibitors*. **◀ FIGURE 4.10** shows several common over-the-counter antacids, which usually contain hydroxide, carbonate, or bicarbonate ions (**▼ TABLE 4.4**). Antiulcer drugs, such as Tagamet® and Zantac®, are acid inhibitors. They act on acid-producing cells in the lining of the stomach. Formulations that control acid in this way are now available as over-the-counter drugs.

RELATED EXERCISE: 4.95

TABLE 4.4 • Some Common Antacids

Commercial Name	Acid-Neutralizing Agents
Alka-Seltzer®	NaHCO_3
Amphojel®	$\text{Al}(\text{OH})_3$
Di-Gel®	$\text{Mg}(\text{OH})_2$ and CaCO_3
Milk of Magnesia	$\text{Mg}(\text{OH})_2$
Maalox®	$\text{Mg}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$
Mylanta®	$\text{Mg}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$
Rolaid®	$\text{NaAl}(\text{OH})_2\text{CO}_3$
Tums®	CaCO_3

4.4 | OXIDATION-REDUCTION REACTIONS

In precipitation reactions, cations and anions come together to form an insoluble ionic compound. In neutralization reactions, H^+ ions and OH^- ions come together to form H_2O molecules. Now let's consider a third kind of reaction, one in which electrons are transferred from one reactant to another. Such reactions are called either **oxidation-reduction reactions** or **redox reactions**. In this chapter we concentrate on redox reactions where one of the reactants is a metal in its elemental form.

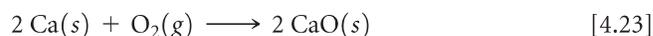
Oxidation and Reduction

One of the most familiar redox reactions is *corrosion* of a metal (▼ FIGURE 4.11). In some instances corrosion is limited to the surface of the metal, with the green coating that forms on copper roofs and statues being one such case. In other instances the corrosion goes deeper, eventually compromising the structural integrity of the metal. Iron rusting is an important example.

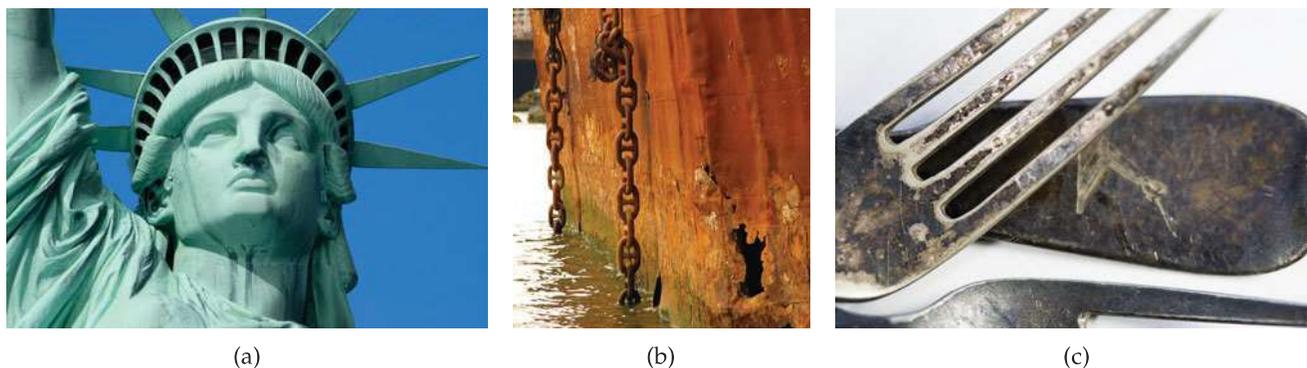
Corrosion is the conversion of a metal into a metal compound by a reaction between the metal and some substance in its environment. When a metal corrodes, each metal atom loses electrons and so forms a cation, which can combine with an anion to form an ionic compound. The green coating on the Statue of Liberty contains Cu^{2+} combined with carbonate and hydroxide anions, rust contains Fe^{3+} combined with oxide and hydroxide anions, and silver tarnish contains Ag^+ combined with sulfide anions.

When an atom, ion, or molecule becomes more positively charged (that is, when it loses electrons), we say that it has been oxidized. *Loss of electrons by a substance is called oxidation*. The term *oxidation* is used because the first reactions of this sort to be studied were reactions with oxygen. Many metals react directly with O_2 in air to form metal oxides. In these reactions the metal loses electrons to oxygen, forming an ionic compound of the metal ion and oxide ion. The familiar example of rusting involves the reaction between iron metal and oxygen in the presence of water. In this process Fe is *oxidized* (loses electrons) to form Fe^{3+} .

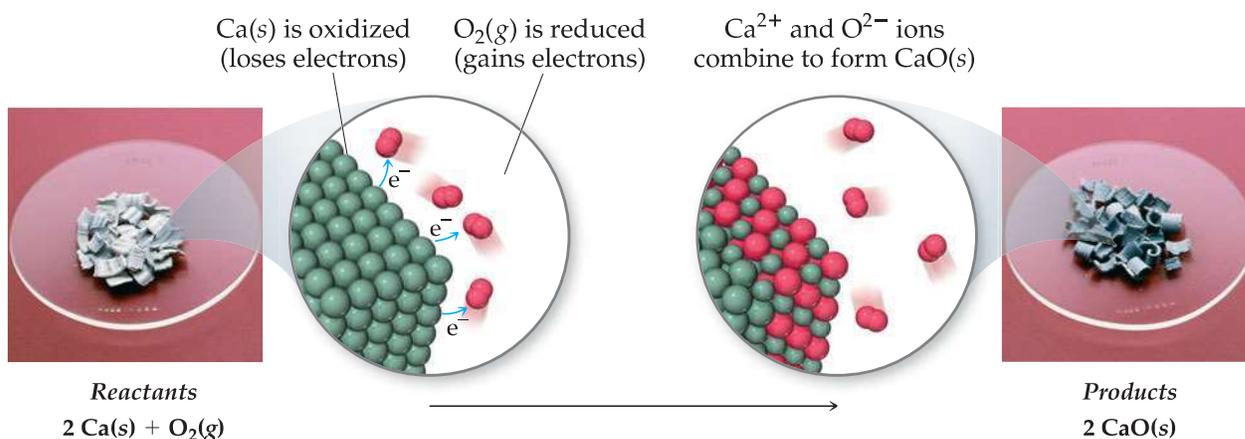
The reaction between iron and oxygen tends to be relatively slow, but other metals, such as the alkali and alkaline earth metals, react quickly upon exposure to air. ► FIGURE 4.12 shows how the bright metallic surface of calcium tarnishes as CaO forms in the reaction



In this reaction Ca is oxidized to Ca^{2+} and neutral O_2 is transformed to O^{2-} ions. When an atom, ion, or molecule becomes more negatively charged (gains electrons), we say that it is *reduced*. *The gain of electrons by a substance is called reduction*. When one reactant loses electrons (that is, when it is *oxidized*), another reactant must gain them. In other words, oxidation of one substance must be accompanied by reduction of some other substance.



▲ FIGURE 4.11 Familiar corrosion products. (a) A green coating forms when copper is oxidized. (b) Rust forms when iron corrodes. (c) A black tarnish forms as silver corrodes.



▲ **FIGURE 4.12** Oxidation of calcium metal by molecular oxygen. The oxidation involves transfer of electrons from the calcium metal to the O_2 , leading to formation of CaO .

Oxidation Numbers

Before we can identify an oxidation-reduction reaction, we must have a bookkeeping system—a way of keeping track of electrons gained by the substance being reduced and electrons lost by the substance being oxidized. The concept of oxidation numbers (also called *oxidation states*) was devised as a way of doing this. Each atom in a neutral substance or ion is assigned an **oxidation number**. For monatomic ions the oxidation number is the same as the charge. For neutral molecules and polyatomic ions, the oxidation number of a given atom is a hypothetical charge. This charge is assigned by artificially dividing up the electrons among the atoms in the molecule or ion. We use the following rules for assigning oxidation numbers:

1. For an atom in its **elemental form**, the oxidation number is always zero. Thus, each H atom in the H_2 molecule has an oxidation number of 0 and each P atom in the P_4 molecule has an oxidation number of 0.
2. For any **monatomic ion** the oxidation number equals the ionic charge. Thus, K^+ has an oxidation number of +1, S^{2-} has an oxidation number of -2 , and so forth. In ionic compounds the alkali metal ions (group 1A) always have a $1+$ charge and therefore an oxidation number of +1. The alkaline earth metals (group 2A) are always $+2$, and aluminum (group 3A) is always $+3$ in ionic compounds. (In writing oxidation numbers we will write the sign before the number to distinguish them from the actual electronic charges, which we write with the number first.)
3. **Nonmetals** usually have negative oxidation numbers, although they can sometimes be positive:
 - (a) The oxidation number of **oxygen** is usually -2 in both ionic and molecular compounds. The major exception is in compounds called peroxides, which contain the O_2^{2-} ion, giving each oxygen an oxidation number of -1 .
 - (b) The oxidation number of **hydrogen** is usually $+1$ when bonded to nonmetals and -1 when bonded to metals.
 - (c) The oxidation number of **fluorine** is -1 in all compounds. The other **halogens** have an oxidation number of -1 in most binary compounds. When combined with oxygen, as in oxyanions, however, they have positive oxidation states.
4. **The sum of the oxidation numbers** of all atoms in a neutral compound is zero. The sum of the oxidation numbers in a polyatomic ion equals the charge of the ion. For example, in the hydronium ion H_3O^+ the oxidation number of each hydrogen is $+1$ and that of oxygen is -2 . Thus, the sum of the oxidation numbers is $3(+1) + (-2) = +1$, which equals the net charge of the ion. This rule is useful in obtaining the oxidation number of one atom in a compound or ion if you know the oxidation numbers of the other atoms, as illustrated in Sample Exercise 4.8.

It's important to remember that in every oxidation-reduction reaction, the oxidation numbers of at least two atoms must change. The oxidation number increases for any atom that is oxidized and decreases for any atom that is reduced.

GIVE IT SOME THOUGHT

What is the oxidation number of nitrogen (a) in aluminum nitride, AlN, and (b) in nitric acid, HNO₃?

SAMPLE EXERCISE 4.8 Determining Oxidation Numbers

Determine the oxidation number of sulfur in (a) H₂S, (b) S₈, (c) SCl₂, (d) Na₂SO₃, (e) SO₄²⁻.

SOLUTION

Analyze We are asked to determine the oxidation number of sulfur in two molecular species, in the elemental form, and in two substances containing ions.

Plan In each species the sum of oxidation numbers of all the atoms must equal the charge on the species. We will use the rules outlined previously to assign oxidation numbers.

Solve

(a) When bonded to a nonmetal, hydrogen has an oxidation number of +1 (rule 3b). Because the H₂S molecule is neutral, the sum of the oxidation numbers must equal zero (rule 4). Letting x equal the oxidation number of S, we have $2(+1) + x = 0$. Thus, S has an oxidation number of -2 .

(b) Because this is an elemental form of sulfur, the oxidation number of S is 0 (rule 1).

(c) Because this is a binary compound, we expect chlorine to have an oxidation number of -1 (rule 3c). The sum of the oxidation numbers must equal zero (rule 4). Letting x equal the oxidation number of S, we have $x + 2(-1) = 0$. Consequently, the oxidation number of S must be $+2$.

(d) Sodium, an alkali metal, always has an oxidation number of $+1$ in its compounds (rule 2). Oxygen has a common oxidation state of -2 (rule 3a). Letting x equal the oxidation number of S, we have $2(+1) + x + 3(-2) = 0$. Therefore, the oxidation number of S in this compound is $+4$.

(e) The oxidation state of O is -2 (rule 3a). The sum of the oxidation numbers equals -2 , the net charge of the SO₄²⁻ ion (rule 4). Thus, we have $x + 4(-2) = -2$. From this relation we conclude that the oxidation number of S in this ion is $+6$.

Comment These examples illustrate that the oxidation number of a given element depends on the compound in which it occurs. The oxidation numbers of sulfur, as seen in these examples, range from -2 to $+6$.

PRACTICE EXERCISE

What is the oxidation state of the boldfaced element in (a) P₂O₅, (b) Na**H**, (c) Cr₂O₇²⁻, (d) Sn**Br**₄, (e) Ba**O**₂?

Answers: (a) $+5$, (b) -1 , (c) $+6$, (d) $+4$, (e) -1

Oxidation of Metals by Acids and Salts

The reaction between a metal and either an acid or a metal salt conforms to the general pattern



Examples: $Zn(s) + 2HBr(aq) \longrightarrow ZnBr_2(aq) + H_2(g)$



These reactions are called **displacement reactions** because the ion in solution is *displaced* (replaced) through oxidation of an element.

SAMPLE EXERCISE 4.9 Writing Equations for Oxidation-Reduction Reactions

Write the balanced molecular and net ionic equations for the reaction of aluminum with hydrobromic acid.

SOLUTION

Analyze We must write two equations—molecular and net ionic—for the redox reaction between a metal and an acid.

Plan Metals react with acids to form salts and H₂ gas. To write the balanced equations, we must write the chemical formulas for the two reactants and then determine the formula of the salt, which is composed of the cation formed by the metal and the anion of the acid.

Solve The reactants are Al and HBr. The cation formed by Al is Al³⁺, and the anion from hydrobromic acid is Br⁻. Thus, the salt formed in the reaction is AlBr₃. Writing the reactants and products and then balancing the equation gives the molecular equation:



Both HBr and AlBr₃ are soluble strong electrolytes. Thus, the complete ionic equation is



Because Br⁻ is a spectator ion, the net ionic equation is



Comment The substance oxidized is the aluminum metal because its oxidation state changes from 0 in the metal to +3 in the cation, thereby increasing in oxidation number. The H⁺ is reduced because its oxidation state changes from +1 in the acid to 0 in H₂.

PRACTICE EXERCISE

(a) Write the balanced molecular and net ionic equations for the reaction between magnesium and cobalt(II) sulfate. (b) What is oxidized and what is reduced in the reaction?

Answers: (a) $\text{Mg}(s) + \text{CoSO}_4(aq) \longrightarrow \text{MgSO}_4(aq) + \text{Co}(s)$;
 $\text{Mg}(s) + \text{Co}^{2+}(aq) \longrightarrow \text{Mg}^{2+}(aq) + \text{Co}(s)$, (b) Mg is oxidized and Co²⁺ is reduced.

The Activity Series

Can we predict whether a certain metal will be oxidized either by an acid or by a particular salt? This question is of practical importance as well as chemical interest. According to Equation 4.27, for example, it would be unwise to store a solution of nickel nitrate in an iron container because the solution would dissolve the container. When a metal is oxidized, it forms various compounds. Extensive oxidation can lead to the failure of metal machinery parts or the deterioration of metal structures.

Different metals vary in the ease with which they are oxidized. Zn is oxidized by aqueous solutions of Cu²⁺, for example, but Ag is not. Zn, therefore, loses electrons more readily than Ag; that is, Zn is easier to oxidize than Ag.

A list of metals arranged in order of decreasing ease of oxidation, such as ► **TABLE 4.5**, is called an **activity series**. The metals at the top of the table, such as the alkali metals and the alkaline earth metals, are most easily oxidized; that is, they react most readily to form compounds. They are called the *active metals*. The metals at the bottom of the activity series, such as the transition elements from groups 8B and 1B, are very stable and form compounds less readily. These metals, which are used to make coins and jewelry, are called *noble metals* because of their low reactivity.

The activity series can be used to predict the outcome of reactions between metals and either metal salts or acids. *Any metal on the list can be oxidized by the ions of elements below it.* For example, copper is above silver in the series. Thus, copper metal is oxidized by silver ions:

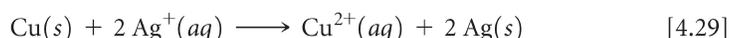


TABLE 4.5 • Activity Series of Metals in Aqueous Solution

Metal	Oxidation Reaction
Lithium	$\text{Li}(s) \longrightarrow \text{Li}^+(aq) + e^-$
Potassium	$\text{K}(s) \longrightarrow \text{K}^+(aq) + e^-$
Barium	$\text{Ba}(s) \longrightarrow \text{Ba}^{2+}(aq) + 2e^-$
Calcium	$\text{Ca}(s) \longrightarrow \text{Ca}^{2+}(aq) + 2e^-$
Sodium	$\text{Na}(s) \longrightarrow \text{Na}^+(aq) + e^-$
Magnesium	$\text{Mg}(s) \longrightarrow \text{Mg}^{2+}(aq) + 2e^-$
Aluminum	$\text{Al}(s) \longrightarrow \text{Al}^{3+}(aq) + 3e^-$
Manganese	$\text{Mn}(s) \longrightarrow \text{Mn}^{2+}(aq) + 2e^-$
Zinc	$\text{Zn}(s) \longrightarrow \text{Zn}^{2+}(aq) + 2e^-$
Chromium	$\text{Cr}(s) \longrightarrow \text{Cr}^{3+}(aq) + 3e^-$
Iron	$\text{Fe}(s) \longrightarrow \text{Fe}^{2+}(aq) + 2e^-$
Cobalt	$\text{Co}(s) \longrightarrow \text{Co}^{2+}(aq) + 2e^-$
Nickel	$\text{Ni}(s) \longrightarrow \text{Ni}^{2+}(aq) + 2e^-$
Tin	$\text{Sn}(s) \longrightarrow \text{Sn}^{2+}(aq) + 2e^-$
Lead	$\text{Pb}(s) \longrightarrow \text{Pb}^{2+}(aq) + 2e^-$
Hydrogen	$\text{H}_2(g) \longrightarrow 2\text{H}^+(aq) + 2e^-$
Copper	$\text{Cu}(s) \longrightarrow \text{Cu}^{2+}(aq) + 2e^-$
Silver	$\text{Ag}(s) \longrightarrow \text{Ag}^+(aq) + e^-$
Mercury	$\text{Hg}(l) \longrightarrow \text{Hg}^{2+}(aq) + 2e^-$
Platinum	$\text{Pt}(s) \longrightarrow \text{Pt}^{2+}(aq) + 2e^-$
Gold	$\text{Au}(s) \longrightarrow \text{Au}^{3+}(aq) + 3e^-$

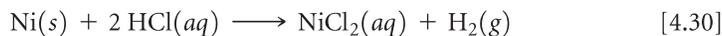


The oxidation of copper to copper ions is accompanied by the reduction of silver ions to silver metal. The silver metal is evident on the surface of the copper wire in ► **FIGURE 4.14**. The copper(II) nitrate produces a blue color in the solution, as can be seen most clearly in the photograph on the right of Figure 4.14.

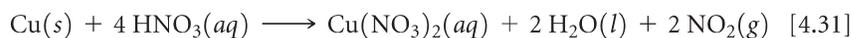
GIVE IT SOME THOUGHT

Does a reaction occur (a) when an aqueous solution of $\text{NiCl}_2(aq)$ is added to a test tube containing strips of metallic zinc, and (b) when $\text{NiCl}_2(aq)$ is added to a test tube containing $\text{Zn}(\text{NO}_3)_2(aq)$?

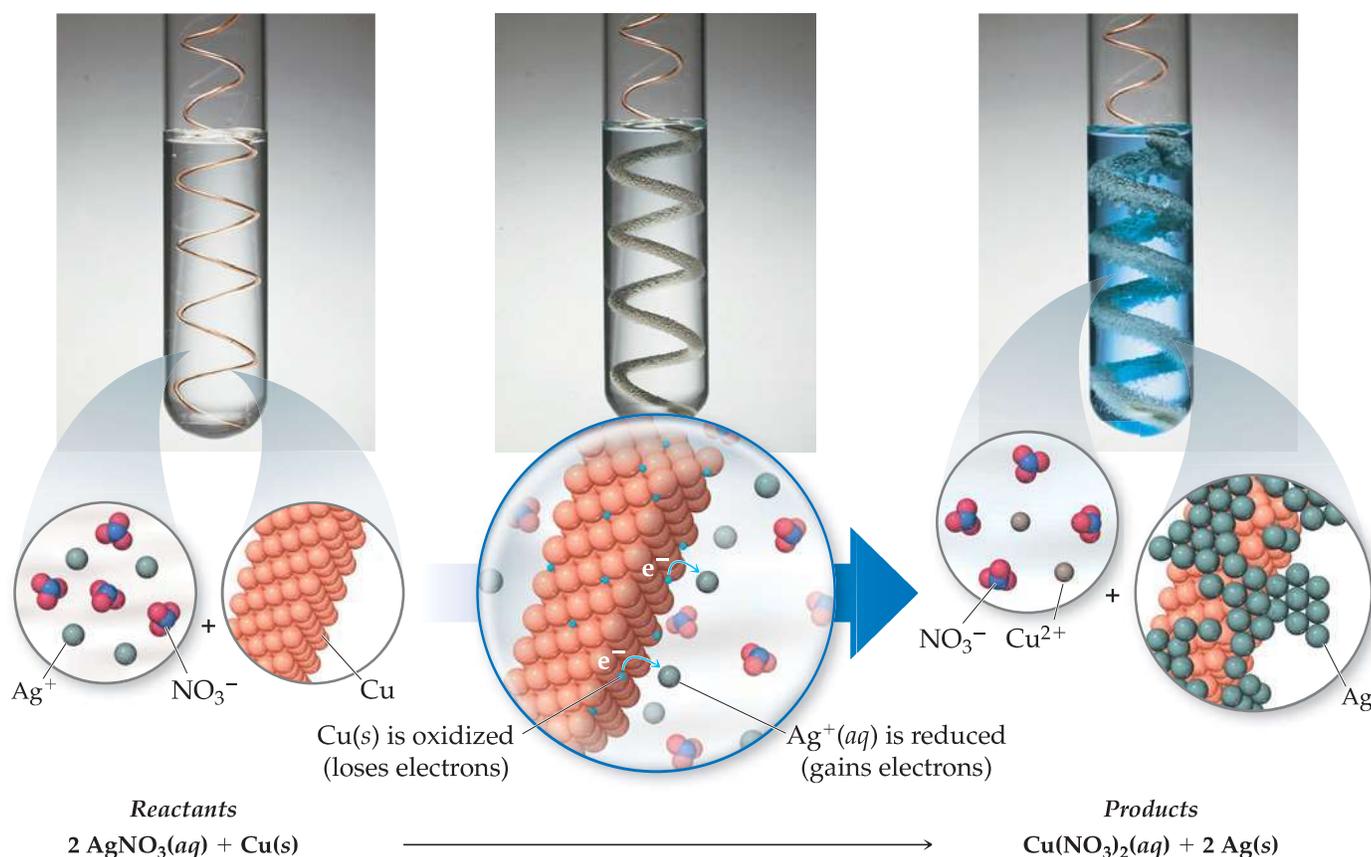
Only metals above hydrogen in the activity series are able to react with acids to form H_2 . For example, Ni reacts with $\text{HCl}(aq)$ to form H_2 :



Because elements below hydrogen in the activity series are not oxidized by H^+ , Cu does not react with $\text{HCl}(aq)$. Interestingly, copper does react with nitric acid, as shown in Figure 1.11, but the reaction is not oxidation of Cu by H^+ ions. Instead, the metal is oxidized to Cu^{2+} by the nitrate ion, accompanied by the formation of brown nitrogen dioxide, $\text{NO}_2(g)$:



As the copper is oxidized in this reaction, NO_3^- , where the oxidation number of nitrogen is +5, is reduced to NO_2 , where the oxidation number of nitrogen is +4. We will examine reactions of this type in Chapter 20.



▲ FIGURE 4.14 Reaction of copper metal with silver ion. When copper metal is placed in a solution of silver nitrate, a redox reaction forms silver metal and a blue solution of copper(II) nitrate.

SAMPLE EXERCISE 4.10 Determining When an Oxidation-Reduction Reaction Can Occur

Will an aqueous solution of iron(II) chloride oxidize magnesium metal? If so, write the balanced molecular and net ionic equations for the reaction.

SOLUTION

Analyze We are given two substances—an aqueous salt, FeCl_2 , and a metal, Mg —and asked if they react with each other.

Plan A reaction occurs if the reactant that is a metal in its elemental form (Mg) is located above the reactant that is a metal in its oxidized form (Fe^{2+}) in Table 4.5. If the reaction occurs, the Fe^{2+} ion in FeCl_2 is reduced to Fe , and the Mg is oxidized to Mg^{2+} .

Solve Because Mg is above Fe in the table, the reaction occurs. To write the formula for the salt produced in the reaction, we must remember the charges on common ions. Magnesium is always present in compounds as Mg^{2+} ; the chloride ion is Cl^- . The magnesium salt formed in the reaction is MgCl_2 , meaning the balanced molecular equation is



Both FeCl_2 and MgCl_2 are soluble strong electrolytes and can be written in ionic form, which shows us that Cl^- is a spectator ion in the reaction. The net ionic equation is



The net ionic equation shows that Mg is oxidized and Fe^{2+} is reduced in this reaction.

Check Note that the net ionic equation is balanced with respect to both charge and mass.

PRACTICE EXERCISE

Which of the following metals will be oxidized by $\text{Pb}(\text{NO}_3)_2$: Zn , Cu , Fe ?

Answer: Zn and Fe

A CLOSER LOOK

THE AURA OF GOLD

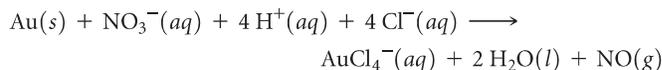
Throughout history, people have cherished gold, fought for it, and even died for it.

The physical and chemical properties of gold make it special. First, its intrinsic beauty and rarity make it precious. Second, it is soft and can be easily formed into jewelry, coins, and other objects. Third, it is one of the least active metals (Table 4.5). It is not oxidized in air and does not react with water (▼ FIGURE 4.15), with basic solutions, or with most acidic solutions.



▲ FIGURE 4.15 The chemical inertness of gold. Two, stamped, weighed, and priced (in the 1800's) gold bars recently recovered from a steamship that sank off the coast of Central America in 1857.

Many of the early studies on gold arose from *alchemy*, in which people attempted to turn cheap metals, such as lead, into gold. Alchemists discovered that gold can be dissolved in a 3:1 mixture of concentrated hydrochloric and nitric acids, known as aqua regia (“royal water”). The action of the nitric acid on gold is similar to that on copper (Equation 4.31) in that the nitrate ion, rather than H^+ , oxidizes the metal to Au^{3+} . The Cl^- ions interact with Au^{3+} to form highly stable $AuCl_4^-$ ions. The net ionic equation is



All the gold ever mined would fit in a cube 21 m on a side and weighing about 1.6×10^8 kg. More than 90% of this amount has been produced since the 1848 California gold rush. Annual worldwide production of gold is about 2.4×10^6 kg. By contrast 16,000 times more aluminum, over 3.97×10^{10} kg, are produced annually.

Roughly three-quarters of gold production goes to make jewelry, where it is often alloyed with other metals. Approximately 12% of gold production is used to meet a variety of industrial applications, most notably in electronic devices where its excellent conductivity and corrosion resistance make it a valuable component. A typical touch-tone telephone contains 33 gold-plated contacts. Gold is also used in computers and other microelectronic devices where fine gold wire is used to link components.

Because of its resistance to corrosion, gold is an ideal metal for dental crowns and caps, which accounts for about 3% of the annual use of the element. The pure metal is too soft to use in dentistry, so it is combined with other metals to form alloys.

RELATED EXERCISE: 4.91

STRATEGIES IN CHEMISTRY

ANALYZING CHEMICAL REACTIONS

In this chapter you have been introduced to a great number of chemical reactions. A major difficulty students face in trying to master material of this sort is gaining a “feel” for what happens when chemicals react. In fact, you might marvel at the ease with which your professor or teaching assistant can figure out the results of a chemical reaction. One of our goals in this textbook is to help you become more adept at predicting the outcomes of reactions. The key to gaining this “chemical intuition” is understanding how to categorize reactions.

Attempting to memorize individual reactions would be a futile task. It is far more fruitful to recognize patterns to determine the general category of a reaction, such as metathesis or oxidation-reduction. Thus, when you are faced with the challenge of predicting the outcome of a chemical reaction, ask yourself the following questions:

- What are the reactants?
- Are they electrolytes or nonelectrolytes?

- Are they acids and bases?
- If the reactants are electrolytes, will metathesis produce a precipitate? Water? A gas?
- If metathesis cannot occur, can the reactants engage in an oxidation-reduction reaction? This requires that there be both a reactant that can be oxidized and a reactant that can be reduced.

By asking questions such as these, you should be able to predict what happens during the reaction. You might not always be entirely correct, but if you keep your wits about you, you will not be far off. As you gain experience, you will begin to look for reactants that might not be immediately obvious, such as water from the solution or oxygen from the atmosphere.

One of the greatest tools available to chemists is experimentation. If you perform an experiment in which two solutions are mixed, you can make observations that help you understand what is happening. For example, using Table 4.1 to predict whether a precipitate will form is not nearly as exciting as seeing the precipitate form, as in Figure 4.4. Careful observations in the laboratory portion of the course will make your lecture material easier to master.

4.5 CONCENTRATIONS OF SOLUTIONS

Scientists use the term **concentration** to designate the amount of solute dissolved in a given quantity of solvent or quantity of solution. The greater the amount of solute dissolved in a certain amount of solvent, the more concentrated the resulting solution. In chemistry we often need to express the concentrations of solutions quantitatively.

Molarity

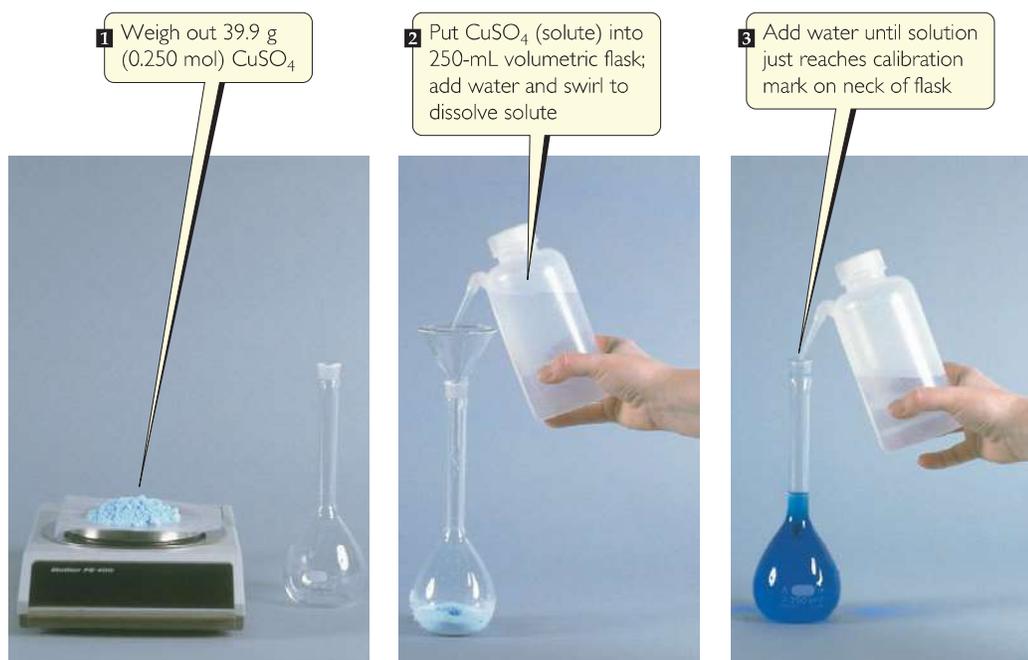
Molarity (symbol M) expresses the concentration of a solution as the number of moles of solute in a liter of solution (soln):

$$\text{Molarity} = \frac{\text{moles solute}}{\text{volume of solution in liters}} \quad [4.32]$$

A 1.00 molar solution (written 1.00 M) contains 1.00 mol of solute in every liter of solution. ▼ **FIGURE 4.16** shows the preparation of 250.0 mL of a 1.00 M solution of CuSO_4 . The molarity of the solution is $(0.250 \text{ mol CuSO}_4)/(0.250 \text{ L soln}) = 1.00 M$.

GIVE IT SOME THOUGHT

Which is more concentrated, a solution prepared by dissolving 21.0 g of NaF (0.500 mol) in enough water to make 500 mL of solution or a solution prepared by dissolving 10.5 g (0.250 mol) of NaF in enough water to make 100 mL of solution?



◀ **FIGURE 4.16** Preparing 0.250 L of a 1.00 M solution of CuSO_4 .

SAMPLE EXERCISE 4.11 Calculating Molarity

Calculate the molarity of a solution made by dissolving 23.4 g of sodium sulfate (Na_2SO_4) in enough water to form 125 mL of solution.

SOLUTION

Analyze We are given the number of grams of solute (23.4 g), its chemical formula (Na_2SO_4), and the volume of the solution (125 mL) and asked to calculate the molarity of the solution.

Plan We can calculate molarity using Equation 4.32. To do so, we must convert the number of grams of solute to moles and the volume of the solution from milliliters to liters.

Solve The number of moles of Na_2SO_4 is obtained by using its molar mass:

$$\text{Moles Na}_2\text{SO}_4 = (23.4 \text{ g Na}_2\text{SO}_4) \left(\frac{1 \text{ mol Na}_2\text{SO}_4}{142 \text{ g Na}_2\text{SO}_4} \right) = 0.165 \text{ mol Na}_2\text{SO}_4$$

Converting the volume of the solution to liters: Liters soln = $(125 \text{ mL}) \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) = 0.125 \text{ L}$

Thus, the molarity is $\text{Molarity} = \frac{0.165 \text{ mol Na}_2\text{SO}_4}{0.125 \text{ L soln}} = 1.32 \frac{\text{mol Na}_2\text{SO}_4}{\text{L soln}} = 1.32 \text{ M}$

Check Because the numerator is only slightly larger than the denominator, it is reasonable for the answer to be a little over 1 M. The units (mol/L) are appropriate for molarity, and three significant

figures are appropriate for the answer because each of the initial pieces of data had three significant figures.

PRACTICE EXERCISE

Calculate the molarity of a solution made by dissolving 5.00 g of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) in sufficient water to form exactly 100 mL of solution.

Answer: 0.278 M

Expressing the Concentration of an Electrolyte

When an ionic compound dissolves, the relative concentrations of the ions in the solution depend on the chemical formula of the compound. For example, a 1.0 M solution of NaCl is 1.0 M in Na^+ ions and 1.0 M in Cl^- ions, and a 1.0 M solution of Na_2SO_4 is 2.0 M in Na^+ ions and 1.0 M in SO_4^{2-} ions. Thus, the concentration of an electrolyte solution can be specified either in terms of the compound used to make the solution (1.0 M Na_2SO_4) or in terms of the ions in the solution (2.0 M Na^+ and 1.0 M SO_4^{2-}).

SAMPLE EXERCISE 4.12 Calculating Molar Concentrations of Ions

What is the molar concentration of each ion present in a 0.025 M aqueous solution of calcium nitrate?

SOLUTION:

Analyze We are given the concentration of the ionic compound used to make the solution and asked to determine the concentrations of the ions in the solution.

Plan We can use the subscripts in the chemical formula of the compound to determine the relative ion concentrations.

Solve Calcium nitrate is composed of calcium ions (Ca^{2+}) and nitrate ions (NO_3^-), so its chemical formula is $\text{Ca}(\text{NO}_3)_2$. Because there are two NO_3^- ions for each Ca^{2+} ion, each mole of $\text{Ca}(\text{NO}_3)_2$ that dissolves dissociates into 1 mol of Ca^{2+} and 2 mol of NO_3^- . Thus, a solution that is 0.025 M in $\text{Ca}(\text{NO}_3)_2$ is 0.025 M in Ca^{2+} and $2 \times 0.025 \text{ M} = 0.050 \text{ M}$ in NO_3^- :

$$\frac{\text{mol NO}_3^-}{\text{L}} = \left(\frac{0.025 \text{ mol Ca}(\text{NO}_3)_2}{\text{L}} \right) \left(\frac{2 \text{ mol NO}_3^-}{1 \text{ mol Ca}(\text{NO}_3)_2} \right) = 0.050 \text{ M}$$

Check The concentration of NO_3^- ions is twice that of Ca^{2+} ions, as the subscript 2 after the NO_3^- in the chemical formula $\text{Ca}(\text{NO}_3)_2$ suggests it should be.

PRACTICE EXERCISE

What is the molar concentration of K^+ ions in a 0.015 M solution of potassium carbonate?

Answer: 0.030 M

Interconverting Molarity, Moles, and Volume

If we know any two of the three quantities in Equation 4.32, we can calculate the third. For example, if we know the molarity of an HNO_3 solution to be 0.200 M, which means 0.200 mol of HNO_3 per liter of solution, we can calculate the number of moles of solute in a given volume, say 2.0 L. Molarity therefore is a conversion factor between volume of solution and moles of solute:

$$\text{Moles HNO}_3 = (2.0 \text{ L soln}) \left(\frac{0.200 \text{ mol HNO}_3}{1 \text{ L soln}} \right) = 0.40 \text{ mol HNO}_3$$

To illustrate the conversion of moles to volume, let's calculate the volume of 0.30 M HNO₃ solution required to supply 2.0 mol of HNO₃:

$$\text{Liters soln} = (2.0 \text{ mol HNO}_3) \left(\frac{1 \text{ L soln}}{0.30 \text{ mol HNO}_3} \right) = 6.7 \text{ L soln}$$

In this case we must use the reciprocal of molarity in the conversion: Liters = moles \times 1/M = ~~moles~~ \times liters/~~mole~~.

SAMPLE EXERCISE 4.13 Using Molarity to Calculate Grams of Solute

How many grams of Na₂SO₄ are required to make 0.350 L of 0.500 M Na₂SO₄?

SOLUTION

Analyze We are given the volume of the solution (0.350 L), its concentration (0.500 M), and the identity of the solute Na₂SO₄ and asked to calculate the number of grams of the solute in the solution.

Plan We can use the definition of molarity (Equation 4.32) to determine the number of moles of solute, and then convert moles to grams using the molar mass of the solute.

$$M_{\text{Na}_2\text{SO}_4} = \frac{\text{moles Na}_2\text{SO}_4}{\text{liters soln}}$$

Solve Calculating the moles of Na₂SO₄ using the molarity and volume of solution gives

$$\begin{aligned} M_{\text{Na}_2\text{SO}_4} &= \frac{\text{moles Na}_2\text{SO}_4}{\text{liters soln}} \\ \text{Moles Na}_2\text{SO}_4 &= \text{liters soln} \times M_{\text{Na}_2\text{SO}_4} \\ &= (0.350 \text{ L soln}) \left(\frac{0.500 \text{ mol Na}_2\text{SO}_4}{1 \text{ L soln}} \right) \\ &= 0.175 \text{ mol Na}_2\text{SO}_4 \end{aligned}$$

Because each mole of Na₂SO₄ has a mass of 142 g, the required number of grams of Na₂SO₄ is

$$\text{Grams Na}_2\text{SO}_4 = (0.175 \text{ mol Na}_2\text{SO}_4) \left(\frac{142 \text{ g Na}_2\text{SO}_4}{1 \text{ mol Na}_2\text{SO}_4} \right) = 24.9 \text{ g Na}_2\text{SO}_4$$

Check The magnitude of the answer, the units, and the number of significant figures are all appropriate.

PRACTICE EXERCISE

(a) How many grams of Na₂SO₄ are there in 15 mL of 0.50 M Na₂SO₄? (b) How many milliliters of 0.50 M Na₂SO₄ solution are needed to provide 0.038 mol of this salt?

Answers: (a) 1.1 g, (b) 76 mL

Dilution

Solutions used routinely in the laboratory are often purchased or prepared in concentrated form (called *stock solutions*). Solutions of lower concentrations can then be obtained by adding water, a process called **dilution**.*

Let's see how we can prepare a dilute solution from a concentrated one. Suppose we want to prepare 250.0 mL (that is, 0.2500 L) of 0.100 M CuSO₄ solution by diluting a 1.00 M CuSO₄ stock solution. The main point to remember is that when solvent is added to a solution, the number of moles of solute remains unchanged:

$$\text{Moles solute before dilution} = \text{moles solute after dilution} \quad [4.33]$$

*In diluting a concentrated acid or base, the acid or base should be added to water and then further diluted by adding more water. Adding water directly to concentrated acid or base can cause spattering because of the intense heat generated.

Because we know both the volume (250 mL) and the concentration (0.100 mol/L) of the dilute solution, we can calculate the number of moles of CuSO_4 it contains:

$$\begin{aligned}\text{Moles CuSO}_4 \text{ in dilute soln} &= (0.2500 \cancel{\text{ L soln}}) \left(\frac{0.100 \text{ mol CuSO}_4}{\cancel{\text{ L soln}}} \right) \\ &= 0.0250 \text{ mol CuSO}_4\end{aligned}$$

The volume of stock solution needed to provide 0.0250 mol CuSO_4 is therefore:

$$\text{Liters of conc soln} = (0.0250 \cancel{\text{ mol CuSO}_4}) \left(\frac{1 \text{ L soln}}{1.00 \cancel{\text{ mol CuSO}_4}} \right) = 0.0250 \text{ L}$$

▼ **FIGURE 4.17** shows the dilution carried out in the laboratory. Notice that the diluted solution is less intensely colored than the concentrated one.

▲ GIVE IT SOME THOUGHT

How is the molarity of a 0.50 M KBr solution changed when water is added to double its volume?

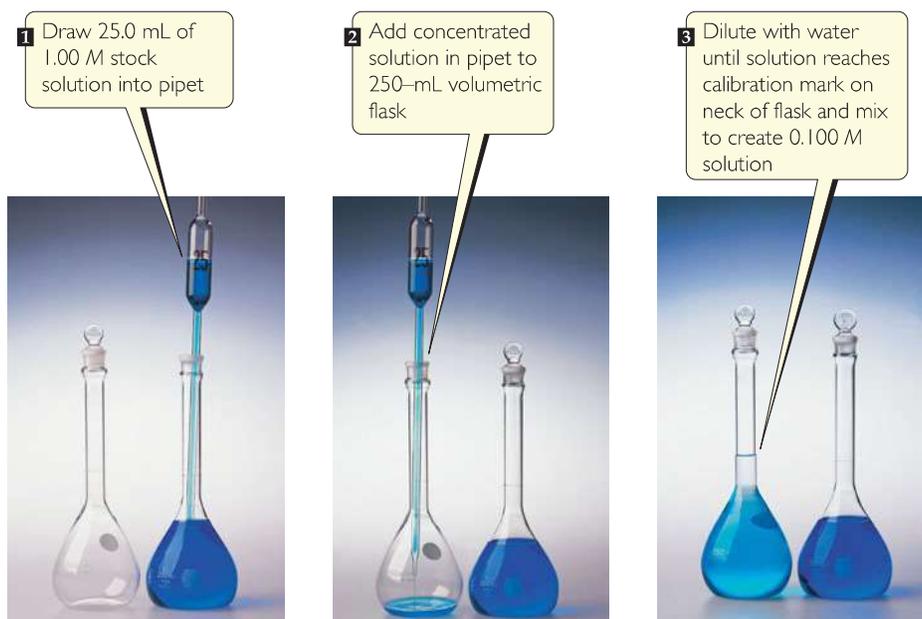
In laboratory situations, calculations of this sort are often made with an equation derived by remembering that the number of moles of solute is the same in both the concentrated and dilute solutions and that $\text{moles} = \text{molarity} \times \text{liters}$:

$$\begin{aligned}\text{Moles solute in conc soln} &= \text{moles solute in dilute soln} \\ M_{\text{conc}} \times V_{\text{conc}} &= M_{\text{dil}} \times V_{\text{dil}}\end{aligned}\quad [4.34]$$

Although we derived Equation 4.34 in terms of liters, any volume unit can be used as long as it is used on both sides of the equation. For example, in the calculation we did for the CuSO_4 solution, we have

$$(1.00 \text{ M})(V_{\text{conc}}) = (0.100 \text{ M})(250. \text{ mL})$$

Solving for V_{conc} gives $V_{\text{conc}} = 25.0 \text{ mL}$ as before.



▲ **FIGURE 4.17** Preparing 250 mL of 0.100 M CuSO_4 by dilution of 1.00 M CuSO_4 .

CHEMISTRY AND LIFE

DRINKING TOO MUCH WATER
CAN KILL YOU

For a long time dehydration was considered a potential danger for people engaged in extended vigorous activity. Thus, athletes were encouraged to drink lots of water while engaged in active sport. The trend toward extensive hydration has spread throughout society, so that today many people carry water bottles everywhere and dutifully keep well hydrated.

In some circumstances, however, drinking too much water is a greater danger than not drinking enough. Excess water consumption can lead to *hyponatremia*, a condition in which the concentration of sodium ion in the blood is too low. In the past decade at least four marathon runners have died from hyponatremia-related trauma, and dozens more have become seriously ill. For example, a first-time

marathoner named Hillary Bellamy, running in the Marine Corps marathon in 2003, collapsed near mile 22 and died the next day. One physician who treated her said that she died from hyponatremia-induced brain swelling, the result of drinking too much water before and during the race.

The normal blood sodium level is 135 to 145 mM (*millimolar*). When that level drops to 125 mM, dizziness and confusion set in. A concentration below 120 mM can be critical. Dangerously low levels can occur in any active athlete who is sweating out salt (NaCl) at the same time that excessive amounts of NaCl-free water are being drunk to compensate for water loss. The condition affects women more than men because of differences in body composition and patterns of metabolism. Drinking a sport drink that contains some electrolytes helps to prevent hyponatremia.

RELATED EXERCISES: 4.63, 4.64

SAMPLE EXERCISE 4.14 Preparing a Solution by Dilution

How many milliliters of 3.0 M H₂SO₄ are needed to make 450 mL of 0.10 M H₂SO₄?

SOLUTION

Analyze We need to dilute a concentrated solution. We are given the molarity of a more concentrated solution (3.0 M) and the volume and molarity of a more dilute one containing the same solute (450 mL of 0.10 M solution). We must calculate the volume of the concentrated solution needed to prepare the dilute solution.

Plan We can calculate the number of moles of solute, H₂SO₄, in the dilute solution and then calculate the volume of the concentrated solution needed to supply this amount of solute. Alternatively, we can directly apply Equation 4.34. Let's compare the two methods.

Solve Calculating the moles of H₂SO₄ in the dilute solution:

$$\begin{aligned} \text{Moles H}_2\text{SO}_4 \text{ in dilute solution} &= (0.450 \text{ L soln}) \left(\frac{0.10 \text{ mol H}_2\text{SO}_4}{1 \text{ L soln}} \right) \\ &= 0.045 \text{ mol H}_2\text{SO}_4 \end{aligned}$$

Calculating the volume of the concentrated solution that contains 0.045 mol H₂SO₄:

$$\text{L conc soln} = (0.045 \text{ mol H}_2\text{SO}_4) \left(\frac{1 \text{ L soln}}{3.0 \text{ mol H}_2\text{SO}_4} \right) = 0.015 \text{ L soln}$$

Converting liters to milliliters gives 15 mL.

If we apply Equation 4.34, we get the same result:

$$\begin{aligned} (3.0 \text{ M})(V_{\text{conc}}) &= (0.10 \text{ M})(450 \text{ mL}) \\ (V_{\text{conc}}) &= \frac{(0.10 \text{ M})(450 \text{ mL})}{3.0 \text{ M}} = 15 \text{ mL} \end{aligned}$$

Either way, we see that if we start with 15 mL of 3.0 M H₂SO₄ and dilute it to a total volume of 450 mL, the desired 0.10 M solution will be obtained.

Check The calculated volume seems reasonable because a small volume of concentrated solution is used to prepare a large volume of dilute solution.

Comment The first approach can also be used to find the final concentration when two solutions of different concentrations are mixed, whereas the second approach, using Equation 4.34, can be used only for diluting a concentrated solution with pure solvent.

PRACTICE EXERCISE

(a) What volume of 2.50 M lead(II) nitrate solution contains 0.0500 mol of Pb²⁺? (b) How many milliliters of 5.0 M K₂Cr₂O₇ solution must be diluted to prepare 250 mL of 0.10 M solution? (c) If 10.0 mL of a 10.0 M stock solution of NaOH is diluted to 250 mL, what is the concentration of the resulting stock solution?

Answers: (a) 0.0200 L = 20.0 mL, (b) 5.0 mL, (c) 0.40 M

4.6 SOLUTION STOICHIOMETRY AND CHEMICAL ANALYSIS

In Chapter 3 we learned that given the chemical equation for a reaction and the amount of one reactant consumed in the reaction, you can calculate the quantities of other reactants and products. In this section we extend this concept to reactions involving solutions.

Recall that the coefficients in a balanced equation give the relative number of moles of reactants and products. ∞ (Section 3.6) To use this information, we must convert the masses of substances involved in a reaction into moles. When dealing with pure substances, as we were in Chapter 3, we use molar mass to convert between grams and moles of the substances. This conversion is not valid when working with a solution because both solute and solvent contribute to its mass. However, if we know the solute concentration, we can use molarity and volume to determine the number of moles (moles solute = $M \times V$). **▼ FIGURE 4.18** summarizes this approach to using stoichiometry for the reaction between a pure substance and a solution.

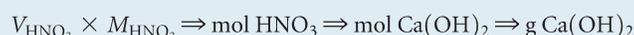
SAMPLE EXERCISE 4.15 Using Mass Relations in a Neutralization Reaction

How many grams of $\text{Ca}(\text{OH})_2$ are needed to neutralize 25.0 mL of 0.100 M HNO_3 ?

SOLUTION

Analyze The reactants are an acid, HNO_3 , and a base, $\text{Ca}(\text{OH})_2$. The volume and molarity of HNO_3 are given, and we are asked how many grams of $\text{Ca}(\text{OH})_2$ are needed to neutralize this quantity of HNO_3 .

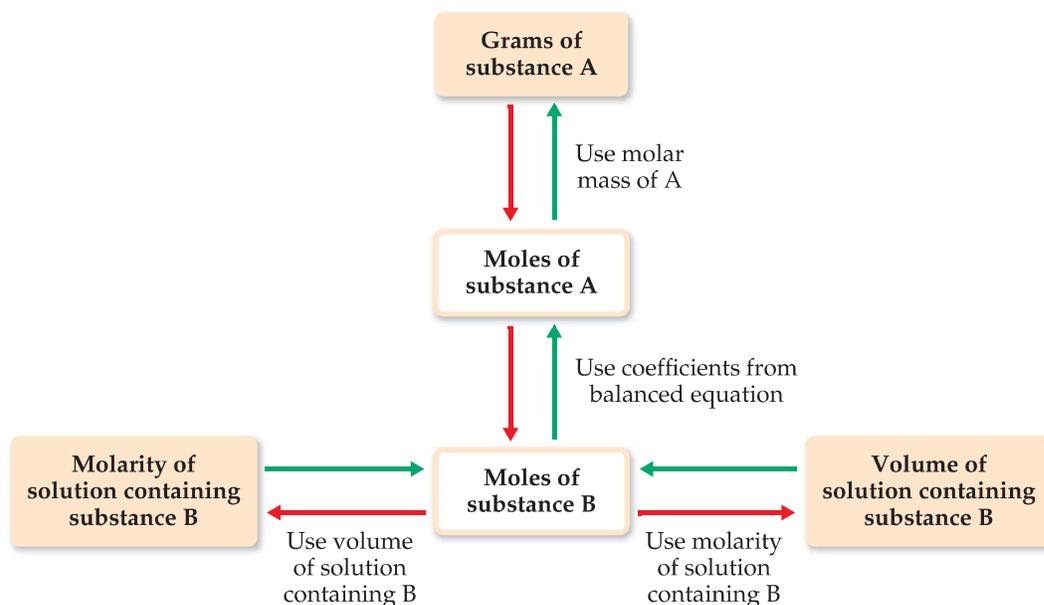
Plan Following the steps outlined by the green arrows in Figure 4.18, we use the molarity and volume of the HNO_3 solution (substance B in Figure 4.18) to calculate the number of moles of HNO_3 . We then use the balanced equation to relate moles of HNO_3 to moles of $\text{Ca}(\text{OH})_2$ (substance A). Finally, we use the molar mass to convert moles to grams of $\text{Ca}(\text{OH})_2$:



Solve The product of the molar concentration of a solution and its volume in liters gives the number of moles of solute:

$$\begin{aligned} \text{Moles HNO}_3 &= V_{\text{HNO}_3} \times M_{\text{HNO}_3} = (0.0250 \cancel{\text{L}}) \left(\frac{0.100 \text{ mol HNO}_3}{\cancel{\text{L}}} \right) \\ &= 2.50 \times 10^{-3} \text{ mol HNO}_3 \end{aligned}$$

► FIGURE 4.18 Procedure for solving stoichiometry problems involving reactions between a pure substance A and a solution containing a known concentration of substance B. Starting from a known mass of substance A, we follow the red arrows to determine either the volume of the solution containing B (if the molarity of B is known) or the molarity of the solution containing B (if the volume of B is known). Starting from either a known volume or known molarity of the solution containing B, we follow the green arrows to determine the mass of substance A.



Because this is a neutralization reaction, HNO_3 and $\text{Ca}(\text{OH})_2$ react to form H_2O and the salt containing Ca^{2+} and NO_3^- :



Thus, $2 \text{ mol HNO}_3 \approx \text{mol Ca}(\text{OH})_2$. Therefore,

$$\begin{aligned} \text{Grams Ca}(\text{OH})_2 &= (2.50 \times 10^{-3} \text{ mol HNO}_3) \left(\frac{1 \text{ mol Ca}(\text{OH})_2}{2 \text{ mol HNO}_3} \right) \left(\frac{74.1 \text{ g Ca}(\text{OH})_2}{1 \text{ mol Ca}(\text{OH})_2} \right) \\ &= 0.0926 \text{ g Ca}(\text{OH})_2 \end{aligned}$$

Check The answer is reasonable because a small volume of dilute acid requires only a small amount of base to neutralize it.

PRACTICE EXERCISE

- (a) How many grams of NaOH are needed to neutralize 20.0 mL of 0.150 M H_2SO_4 solution?
 (b) How many liters of 0.500 M $\text{HCl}(aq)$ are needed to react completely with 0.100 mol of $\text{Pb}(\text{NO}_3)_2(aq)$, forming a precipitate of $\text{PbCl}_2(s)$?

Answers: (a) 0.240 g, (b) 0.400 L

Titration

To determine the concentration of a particular solute in a solution, chemists often carry out a **titration**, which involves combining a solution where the solute concentration is not known with a reagent solution of known concentration, called a **standard solution**. Just enough standard solution is added to completely react with the solute in the solution of unknown concentration. The point at which stoichiometrically equivalent quantities are brought together is known as the **equivalence point**.

Titration can be conducted using neutralization, precipitation, or oxidation-reduction reactions. ▼ **FIGURE 4.19** illustrates a typical neutralization titration, one between a HCl solution of unknown concentration and a NaOH solution we know to have a concentration of 0.100 M (our standard solution). To determine the HCl concentration, we first add a specific volume of the HCl solution, 20.0 mL in this example, to a flask. Next

GO FIGURE

How would the volume of standard solution added change if that solution were $\text{Ba}(\text{OH})_2(aq)$ instead of $\text{NaOH}(aq)$?

1 20.0 mL of acid solution added to flask

2 A few drops of acid-base indicator added

3 Standard NaOH solution added from buret

4 Solution becomes basic on passing equivalence point, triggering indicator color change

Initial volume reading

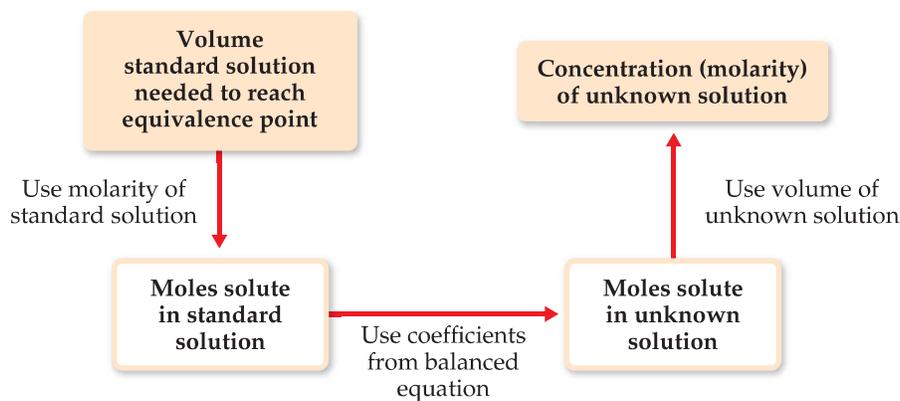
Buret

Final volume reading

▲ **FIGURE 4.19** Procedure for titrating an acid against a standard solution of NaOH.

The acid-base indicator, phenolphthalein, is colorless in acidic solution but takes on a pink color in basic solution.

► **FIGURE 4.20** Procedure for determining the concentration of a solution from titration with a standard solution.



a few drops of an acid–base indicator are added. The acid–base indicator is a dye that changes color on passing the equivalence point.* For example, the dye phenolphthalein is colorless in acidic solution but pink in basic solution. The standard solution is then slowly added until the solution turns pink, telling us that the neutralization reaction between HCl and NaOH is complete. The standard solution is added from a *buret* so that we can accurately determine the added volume of NaOH solution. Knowing the volumes of both solutions and the concentration of the standard solution we can calculate the concentration of the unknown solution as diagrammed in ▲ **FIGURE 4.20**.

SAMPLE EXERCISE 4.16 Determining Solution Concentration by an Acid–Base Titration

One commercial method used to peel potatoes is to soak them in a NaOH solution for a short time, then remove them and spray off the peel. The NaOH concentration is normally 3 to 6 *M*, and the solution must be analyzed periodically. In one such analysis, 45.7 mL of 0.500 *M* H₂SO₄ is required to neutralize 20.0 mL of NaOH solution. What is the concentration of the NaOH solution?

SOLUTION

Analyze We are given the volume (45.7 mL) and molarity (0.500 *M*) of an H₂SO₄ solution (the standard solution) that reacts completely with 20.0 mL of NaOH solution. We are asked to calculate the molarity of the NaOH solution.

Plan Following the steps of Figure 4.20, we use the H₂SO₄ volume and molarity to calculate the number of moles of H₂SO₄. Then we can use this quantity and the balanced equation for the reaction to calculate moles of NaOH. Finally, we can use moles of NaOH and the NaOH volume to calculate NaOH molarity.

Solve The number of moles of H₂SO₄ is the product of the volume and molarity of this solution:

$$\begin{aligned} \text{Moles H}_2\text{SO}_4 &= (45.7 \text{ mL soln}) \left(\frac{1 \text{ L soln}}{1000 \text{ mL soln}} \right) \left(\frac{0.500 \text{ mol H}_2\text{SO}_4}{\text{L soln}} \right) \\ &= 2.28 \times 10^{-2} \text{ mol H}_2\text{SO}_4 \end{aligned}$$

Acids react with metal hydroxides to form water and a salt. Thus, the balanced equation for the neutralization reaction is



According to the balanced equation, 1 mol H₂SO₄ \approx 2 mol NaOH. Therefore,

$$\begin{aligned} \text{Moles NaOH} &= (2.28 \times 10^{-2} \text{ mol H}_2\text{SO}_4) \left(\frac{2 \text{ mol NaOH}}{1 \text{ mol H}_2\text{SO}_4} \right) \\ &= 4.56 \times 10^{-2} \text{ mol NaOH} \end{aligned}$$

*More precisely, the color change of an indicator signals the end point of the titration, which if the proper indicator is chosen lies very near the equivalence point. Acid–base titrations are discussed in more detail in Section 17.3.

Knowing the number of moles of NaOH in 20.0 mL of solution allows us to calculate the molarity of this solution:

$$\begin{aligned}\text{Molarity NaOH} &= \frac{\text{mol NaOH}}{\text{L soln}} = \left(\frac{4.56 \times 10^{-2} \text{ mol NaOH}}{20.0 \text{ mL soln}} \right) \left(\frac{1000 \text{ mL soln}}{1 \text{ L soln}} \right) \\ &= 2.28 \frac{\text{mol NaOH}}{\text{L soln}} = 2.28 \text{ M}\end{aligned}$$

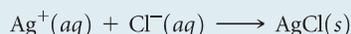
PRACTICE EXERCISE

What is the molarity of an NaOH solution if 48.0 mL neutralizes 35.0 mL of 0.144 M H₂SO₄?

Answer: 0.210 M

SAMPLE EXERCISE 4.17 Determining the Quantity of Solute by Titration

The quantity of Cl⁻ in a municipal water supply is determined by titrating the sample with Ag⁺. The precipitation reaction taking place during the titration is



The end point in this type of titration is marked by a change in color of a special type of indicator. (a) How many grams of chloride ion are in a sample of the water if 20.2 mL of 0.100 M Ag⁺ is needed to react with all the chloride in the sample? (b) If the sample has a mass of 10.0 g, what percent Cl⁻ does it contain?

SOLUTION

Analyze We are given the volume (20.2 mL) and molarity (0.100 M) of a solution of Ag⁺ and the chemical equation for reaction of this ion with Cl⁻. We are asked to calculate the number of grams of Cl⁻ in the sample and the mass percent of Cl⁻ in the sample.

(a) Plan We can use the procedure outlined by the green arrows in Figure 4.18. We begin by using the volume and molarity of Ag⁺ to calculate the number of moles of Ag⁺ used in the titration. We then use the balanced equation to determine the moles of Cl⁻ in the sample and from that the grams of Cl⁻.

Solve

$$\begin{aligned}\text{Moles Ag}^+ &= (20.2 \text{ mL soln}) \left(\frac{1 \text{ L soln}}{1000 \text{ mL soln}} \right) \left(\frac{0.100 \text{ mol Ag}^+}{\text{L soln}} \right) \\ &= 2.02 \times 10^{-3} \text{ mol Ag}^+\end{aligned}$$

From the balanced equation we see that 1 mol Ag⁺ \approx 1 mol Cl⁻. Using this information and the molar mass of Cl, we have

$$\begin{aligned}\text{Grams Cl}^- &= (2.02 \times 10^{-3} \text{ mol Ag}^+) \left(\frac{1 \text{ mol Cl}^-}{1 \text{ mol Ag}^+} \right) \left(\frac{35.5 \text{ g Cl}^-}{\text{mol Cl}^-} \right) \\ &= 7.17 \times 10^{-2} \text{ g Cl}^-\end{aligned}$$

(b) Plan To calculate the percentage of Cl⁻ in the sample, we compare the number of grams of Cl⁻ in the sample, 7.17 \times 10⁻² g, with the original mass of the sample, 10.0 g.

Solve

$$\text{Percent Cl}^- = \frac{7.17 \times 10^{-2} \text{ g}}{10.0 \text{ g}} \times 100\% = 0.717\% \text{ Cl}^-$$

Comment Chloride ion is one of the most common ions in water and sewage. Ocean water contains 1.92% Cl⁻. Whether water containing Cl⁻ tastes salty depends on the other ions present. If the only accompanying ions are Na⁺, a salty taste may be detected with as little as 0.03% Cl⁻.

PRACTICE EXERCISE

A sample of an iron ore is dissolved in acid, and the iron is converted to Fe^{2+} . The sample is then titrated with 47.20 mL of 0.02240 M MnO_4^- solution. The oxidation-reduction reaction that occurs during titration is



(a) How many moles of MnO_4^- were added to the solution? (b) How many moles of Fe^{2+} were in the sample? (c) How many grams of iron were in the sample? (d) If the sample had a mass of 0.8890 g, what is the percentage of iron in the sample?

Answers: (a) 1.057×10^{-3} mol MnO_4^- , (b) 5.286×10^{-3} mol Fe^{2+} , (c) 0.2952 g, (d) 33.21%

SAMPLE INTEGRATIVE EXERCISE Putting Concepts Together

Note: Integrative exercises require skills from earlier chapters as well as ones from the present chapter.

A sample of 70.5 mg of potassium phosphate is added to 15.0 mL of 0.050 M silver nitrate, resulting in the formation of a precipitate. (a) Write the molecular equation for the reaction. (b) What is the limiting reactant in the reaction? (c) Calculate the theoretical yield, in grams, of the precipitate that forms.

SOLUTION

(a) Potassium phosphate and silver nitrate are both ionic compounds. Potassium phosphate contains K^+ and PO_4^{3-} ions, so its chemical formula is K_3PO_4 . Silver nitrate contains Ag^+ and NO_3^- ions, so its chemical formula is AgNO_3 . Because both reactants are strong electrolytes, the solution contains K^+ , PO_4^{3-} , Ag^+ , and NO_3^- ions before the reaction occurs. According to the solubility guidelines in Table 4.1, Ag^+ and PO_4^{3-} form an insoluble compound, so Ag_3PO_4 will precipitate from the solution. In contrast, K^+ and NO_3^- will remain in solution because KNO_3 is water soluble. Thus, the balanced molecular equation for the reaction is



(b) To determine the limiting reactant, we must examine the number of moles of each reactant. ∞ (Section 3.7) The number of moles of K_3PO_4 is calculated from the mass of the sample using the molar mass as a conversion factor. ∞ (Section 3.4) The molar mass of K_3PO_4 is $3(39.1) + 31.0 + 4(16.0) = 212.3$ g/mol. Converting milligrams to grams and then to moles, we have

$$(70.5 \text{ mg } \text{K}_3\text{PO}_4) \left(\frac{10^{-3} \text{ g } \text{K}_3\text{PO}_4}{1 \text{ mg } \text{K}_3\text{PO}_4} \right) \left(\frac{1 \text{ mol } \text{K}_3\text{PO}_4}{212.3 \text{ g } \text{K}_3\text{PO}_4} \right) = 3.32 \times 10^{-4} \text{ mol } \text{K}_3\text{PO}_4$$

We determine the number of moles of AgNO_3 from the volume and molarity of the solution. (Section 4.5) Converting milliliters to liters and then to moles, we have

$$(15.0 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left(\frac{0.050 \text{ mol } \text{AgNO}_3}{\text{L}} \right) = 7.5 \times 10^{-4} \text{ mol } \text{AgNO}_3$$

Comparing the amounts of the two reactants, we find that there are $(7.5 \times 10^{-4}) / (3.32 \times 10^{-4}) = 2.3$ times as many moles of AgNO_3 as there are moles of K_3PO_4 . According to the balanced equation, however, 1 mol K_3PO_4 requires 3 mol AgNO_3 . Thus, there is insufficient AgNO_3 to consume the K_3PO_4 , and AgNO_3 is the limiting reactant.

(c) The precipitate is Ag_3PO_4 , whose molar mass is $3(107.9) + 31.0 + 4(16.0) = 418.7$ g/mol. To calculate the number of grams of Ag_3PO_4 that could be produced in this reaction (the theoretical yield), we use the number of moles of the limiting reactant, converting mol $\text{AgNO}_3 \Rightarrow$ mol $\text{Ag}_3\text{PO}_4 \Rightarrow$ g Ag_3PO_4 . We use the coefficients in the balanced equation to convert moles of AgNO_3 to moles Ag_3PO_4 , and we use the molar mass of Ag_3PO_4 to convert the number of moles of this substance to grams.

$$(7.5 \times 10^{-4} \text{ mol } \text{AgNO}_3) \left(\frac{1 \text{ mol } \text{Ag}_3\text{PO}_4}{3 \text{ mol } \text{AgNO}_3} \right) \left(\frac{418.7 \text{ g } \text{Ag}_3\text{PO}_4}{1 \text{ mol } \text{Ag}_3\text{PO}_4} \right) = 0.10 \text{ g } \text{Ag}_3\text{PO}_4$$

The answer has only two significant figures because the quantity of AgNO_3 is given to only two significant figures.

CHAPTER SUMMARY AND KEY TERMS

INTRODUCTION AND SECTION 4.1 Solutions in which water is the dissolving medium are called **aqueous solutions**. The component of the solution that is present in the greatest quantity is the **solvent**. The other components are **solutes**.

Any substance whose aqueous solution contains ions is called an **electrolyte**. Any substance that forms a solution containing no ions is a **nonelectrolyte**. Electrolytes that are present in solution entirely as ions are **strong electrolytes**, whereas those that are present partly as ions and partly as molecules are **weak electrolytes**. Ionic compounds dissociate into ions when they dissolve, and they are strong electrolytes. The solubility of ionic substances is made possible by **solvation**, the interaction of ions with polar solvent molecules. Most molecular compounds are nonelectrolytes, although some are weak electrolytes, and a few are strong electrolytes. When representing the ionization of a weak electrolyte in solution, half-arrows in both directions are used, indicating that the forward and reverse reactions can achieve a chemical balance called a **chemical equilibrium**.

SECTION 4.2 **Precipitation reactions** are those in which an insoluble product, called a **precipitate**, forms. Solubility guidelines help determine whether or not an ionic compound will be soluble in water. (The **solubility** of a substance is the amount that dissolves in a given quantity of solvent.) Reactions such as precipitation reactions, in which cations and anions appear to exchange partners, are called **exchange reactions**, or **metathesis reactions**.

Chemical equations can be written to show whether dissolved substances are present in solution predominantly as ions or molecules. When the complete chemical formulas of all reactants and products are used, the equation is called a **molecular equation**. A **complete ionic equation** shows all dissolved strong electrolytes as their component ions. In a **net ionic equation**, those ions that go through the reaction unchanged (**spectator ions**) are omitted.

SECTION 4.3 Acids and bases are important electrolytes. **Acids** are proton donors; they increase the concentration of $\text{H}^+(\text{aq})$ in aqueous solutions to which they are added. **Bases** are proton acceptors; they increase the concentration of $\text{OH}^-(\text{aq})$ in aqueous solutions. Those acids and bases that are strong electrolytes are called **strong acids** and **strong bases**, respectively. Those that are weak electrolytes are **weak acids** and **weak bases**. When solutions of acids and bases are mixed, a neutralization reaction occurs. The **neutralization reaction** between an acid and a metal hydroxide produces water and a **salt**. Gases can

also be formed as a result of neutralization reactions. The reaction of a sulfide with an acid forms $\text{H}_2\text{S}(\text{g})$; the reaction between a carbonate and an acid forms $\text{CO}_2(\text{g})$.

SECTION 4.4 **Oxidation** is the loss of electrons by a substance, whereas **reduction** is the gain of electrons by a substance. **Oxidation numbers** keep track of electrons during chemical reactions and are assigned to atoms using specific rules. The oxidation of an element results in an increase in its oxidation number, whereas reduction is accompanied by a decrease in oxidation number. Oxidation is always accompanied by reduction, giving **oxidation-reduction**, or **redox reactions**.

Many metals are oxidized by O_2 , acids, and salts. The redox reactions between metals and acids as well as those between metals and salts are called **displacement reactions**. The products of these displacement reactions are always an element (H_2 or a metal) and a salt. Comparing such reactions allows us to rank metals according to their ease of oxidation. A list of metals arranged in order of decreasing ease of oxidation is called an **activity series**. Any metal on the list can be oxidized by ions of metals (or H^+) below it in the series.

SECTION 4.5 The **concentration** of a solution expresses the amount of a solute dissolved in the solution. One of the common ways to express the concentration of a solute is in terms of molarity. The **molarity** of a solution is the number of moles of solute per liter of solution. Molarity makes it possible to interconvert solution volume and number of moles of solute. Solutions of known molarity can be formed either by weighing out the solute and diluting it to a known volume or by the **dilution** of a more concentrated solution of known concentration (a stock solution). Adding solvent to the solution (the process of dilution) decreases the concentration of the solute without changing the number of moles of solute in the solution ($M_{\text{conc}} \times V_{\text{conc}} = M_{\text{dil}} \times V_{\text{dil}}$).

SECTION 4.6 In the process called **titration**, we combine a solution of known concentration (a **standard solution**) with a solution of unknown concentration to determine the unknown concentration or the quantity of solute in the unknown. The point in the titration at which stoichiometrically equivalent quantities of reactants are brought together is called the **equivalence point**. An indicator can be used to show the end point of the titration, which coincides closely with the equivalence point.

KEY SKILLS

- Recognize compounds as acids or bases, and as strong, weak, or nonelectrolytes. (Sections 4.1 and 4.3)
- Recognize reactions by type and be able to predict the products of simple acid–base, precipitation, and redox reactions. (Sections 4.2–4.4)
- Be able to calculate molarity and use it to convert between moles of a substance in solution and volume of the solution. (Section 4.5)
- Understand how to carry out a dilution to achieve a desired solution concentration. (Section 4.5)
- Understand how to perform and interpret the results of a titration. (Section 4.6)

KEY EQUATIONS

$$\text{Molarity} = \frac{\text{moles solute}}{\text{volume of solution in liters}} \quad [4.32]$$

Molarity is the most commonly used unit of concentration in chemistry.

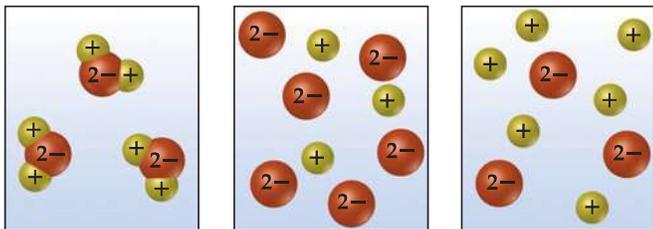
$$M_{\text{conc}} \times V_{\text{conc}} = M_{\text{dil}} \times V_{\text{dil}} \quad [4.34]$$

When adding solvent to a concentrated solution to make a dilute solution, molarities and volumes of both concentrated and dilute solutions can be calculated if three of the quantities are known.

EXERCISES

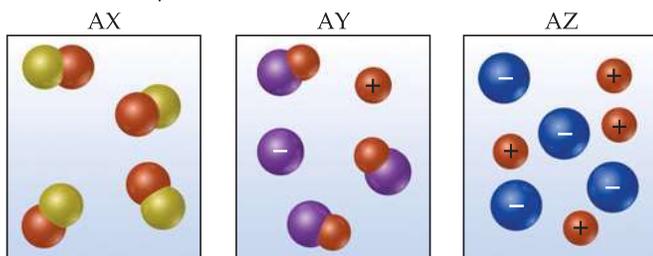
VISUALIZING CONCEPTS

4.1 Which of the following schematic drawings best describes a solution of Li_2SO_4 in water (water molecules not shown for simplicity)? [Section 4.1]



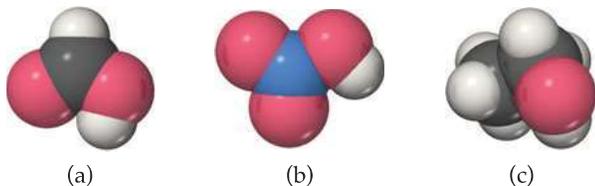
(a) (b) (c)

4.2 Aqueous solutions of three different substances, AX, AY, and AZ, are represented by the three accompanying diagrams. Identify each substance as a strong electrolyte, weak electrolyte, or non-electrolyte. [Section 4.1]



(a) (b) (c)

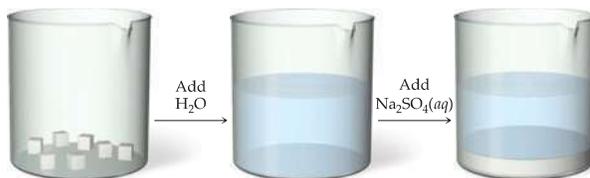
4.3 Use the molecular representations shown here to classify each compound as either a nonelectrolyte, a weak electrolyte, or a strong electrolyte (see inside back cover for element color scheme). [Sections 4.1 and 4.3]



(a) (b) (c)

4.4 A 0.1 M solution of acetic acid, CH_3COOH , causes the light-bulb in the apparatus of Figure 4.2 to glow about as brightly as a 0.001 M solution of HBr. How do you account for this fact? [Section 4.1]

4.5 You are presented with a white solid and told that due to careless labeling it is not clear if the substance is barium chloride, lead chloride, or zinc chloride. When you transfer the solid to a beaker and add water, the solid dissolves to give a clear solution. Next a $\text{Na}_2\text{SO}_4(aq)$ solution is added and a white precipitate forms. What is the identity of the unknown white solid? [Section 4.2]



4.6 We have seen that ions in aqueous solution are stabilized by the attractions between the ions and the water molecules. Why then do some pairs of ions in solution form precipitates? [Section 4.2]

4.7 Which of the following ions will *always* be a spectator ion in a precipitation reaction? (a) Cl^- , (b) NO_3^- , (c) NH_4^+ , (d) S^{2-} , (e) SO_4^{2-} . Explain briefly. [Section 4.2]

4.8 The labels have fallen off three bottles containing powdered samples of metals; one contains zinc, one lead, and the other platinum. You have three solutions at your disposal: 1 M sodium nitrate, 1 M nitric acid, and 1 M nickel nitrate. How could you use these solutions to determine the identities of each metal powder? [Section 4.4]

4.9 Explain how a redox reaction involves electrons in the same way that a neutralization reaction involves protons. [Sections 4.3 and 4.4]

4.10 If you want to double the concentration of a solution, how could you do it? [Section 4.5]

GENERAL PROPERTIES OF AQUEOUS SOLUTIONS (section 4.1)

4.11 When asked what causes electrolyte solutions to conduct electricity, a student responds that it is due to the movement of electrons through the solution. Is the student correct? If not, what is the correct response?

4.12 When methanol, CH_3OH , is dissolved in water, a nonconducting solution results. When acetic acid, CH_3COOH , dissolves in water, the solution is weakly conducting and acidic in nature. Describe what happens upon dissolution in the two cases, and account for the different results.

4.13 We have learned in this chapter that many ionic solids dissolve in water as strong electrolytes, that is, as separated ions in solution. What properties of water facilitate this process? Would you expect ionic compounds to be soluble in elemental liquids like bromine or mercury, just as they are in water? Explain.

4.14 What does it mean to say that ions are solvated when an ionic substance dissolves in water?

4.15 Specify what ions are present in solution upon dissolving each of the following substances in water: (a) ZnCl_2 , (b) HNO_3 , (c) $(\text{NH}_4)_2\text{SO}_4$, (d) $\text{Ca}(\text{OH})_2$.

4.16 Specify what ions are present upon dissolving each of the following substances in water: (a) MgI_2 , (b) $\text{Al}(\text{NO}_3)_3$, (c) HClO_4 , (d) NaCH_3COO .

4.17 Formic acid, HCOOH , is a weak electrolyte. What solute particles are present in an aqueous solution of this compound? Write the chemical equation for the ionization of HCOOH .

4.18 Acetone, CH_3COCH_3 , is a nonelectrolyte; hypochlorous acid, HClO , is a weak electrolyte; and ammonium chloride, NH_4Cl , is a strong electrolyte. (a) What are the solute particles present in aqueous solutions of each compound? (b) If 0.1 mol of each compound is dissolved in solution, which one contains 0.2 mol of solute particles, which contains 0.1 mol of solute particles, and which contains somewhere between 0.1 and 0.2 mol of solute particles?

PRECIPITATION REACTIONS (section 4.2)

- 4.19 Using solubility guidelines, predict whether each of the following compounds is soluble or insoluble in water: (a) MgBr_2 , (b) PbI_2 , (c) $(\text{NH}_4)_2\text{CO}_3$, (d) $\text{Sr}(\text{OH})_2$, (e) ZnSO_4 .
- 4.20 Predict whether each of the following compounds is soluble in water: (a) AgI , (b) Na_2CO_3 , (c) BaCl_2 , (d) $\text{Al}(\text{OH})_3$, (e) $\text{Zn}(\text{CH}_3\text{COO})_2$.
- 4.21 Will precipitation occur when the following solutions are mixed? If so, write a balanced chemical equation for the reaction. (a) Na_2CO_3 and AgNO_3 , (b) NaNO_3 and NiSO_4 , (c) FeSO_4 and $\text{Pb}(\text{NO}_3)_2$.
- 4.22 Identify the precipitate (if any) that forms when the following solutions are mixed, and write a balanced equation for each reaction. (a) NaCH_3COO and HCl , (b) KOH and $\text{Cu}(\text{NO}_3)_2$, (c) Na_2S and CdSO_4 .
- 4.23 Name the spectator ions in any reactions that may be involved when each of the following pairs of solutions are mixed.
 (a) $\text{Na}_2\text{CO}_3(\text{aq})$ and $\text{MgSO}_4(\text{aq})$
 (b) $\text{Pb}(\text{NO}_3)_2(\text{aq})$ and $\text{Na}_2\text{S}(\text{aq})$
 (c) $(\text{NH}_4)_3\text{PO}_4(\text{aq})$ and $\text{CaCl}_2(\text{aq})$
- 4.24 Write balanced net ionic equations for the reactions that occur in each of the following cases. Identify the spectator ion or ions in each reaction.
- (a) $\text{Cr}_2(\text{SO}_4)_3(\text{aq}) + (\text{NH}_4)_2\text{CO}_3(\text{aq}) \longrightarrow$
 (b) $\text{Ba}(\text{NO}_3)_2(\text{aq}) + \text{K}_2\text{SO}_4(\text{aq}) \longrightarrow$
 (c) $\text{Fe}(\text{NO}_3)_2(\text{aq}) + \text{KOH}(\text{aq}) \longrightarrow$
- 4.25 Separate samples of a solution of an unknown salt are treated with dilute solutions of HBr , H_2SO_4 , and NaOH . A precipitate forms in all three cases. Which of the following cations could the solution contain: K^+ , Pb^{2+} , Ba^{2+} ?
- 4.26 Separate samples of a solution of an unknown ionic compound are treated with dilute AgNO_3 , $\text{Pb}(\text{NO}_3)_2$, and BaCl_2 . Precipitates form in all three cases. Which of the following could be the anion of the unknown salt: Br^- , CO_3^{2-} , NO_3^- ?
- 4.27 You know that an unlabeled bottle contains a solution of one of the following: AgNO_3 , CaCl_2 , or $\text{Al}_2(\text{SO}_4)_3$. A friend suggests that you test a portion of the solution with $\text{Ba}(\text{NO}_3)_2$ and then with NaCl solutions. Explain how these two tests together would be sufficient to determine which salt is present in the solution.
- 4.28 Three solutions are mixed together to form a single solution. One contains 0.2 mol $\text{Pb}(\text{CH}_3\text{COO})_2$, the second contains 0.1 mol Na_2S , and the third contains 0.1 mol CaCl_2 . (a) Write the net ionic equations for the precipitation reaction or reactions that occur. (b) What are the spectator ions in the solution?

ACIDS, BASES, AND NEUTRALIZATION REACTIONS (section 4.3)

- 4.29 Which of the following solutions has the largest concentration of solvated protons: (a) 0.2 M LiOH , (b) 0.2 M HI , (c) 1.0 M methyl alcohol (CH_3OH)? Explain
- 4.30 Which of the following solutions is the most basic? (a) 0.6 M NH_3 , (b) 0.150 M KOH , (c) 0.100 M $\text{Ba}(\text{OH})_2$. Explain.
- 4.31 What is the difference between (a) a monoprotic acid and a diprotic acid, (b) a weak acid and a strong acid, (c) an acid and a base?
- 4.32 Explain the following observations: (a) NH_3 contains no OH^- ions, and yet its aqueous solutions are basic; (b) HF is called a weak acid, and yet it is very reactive; (c) although sulfuric acid is a strong electrolyte, an aqueous solution of H_2SO_4 contains more HSO_4^- ions than SO_4^{2-} ions.
- 4.33 Is there any correlation between the anions that form when each of the strong acids in Table 4.2 dissociates and the anions that normally form soluble ionic compounds (Table 4.1)? Which anions if any are exceptions to the general trend?
- 4.34 What is the relationship between the solubility rules in Table 4.1 and the list of strong bases in Table 4.2? Another way of asking this question is, why is $\text{Cd}(\text{OH})_2$, for example, not listed as a strong base in Table 4.2?
- 4.35 Label each of the following substances as an acid, base, salt, or none of the above. Indicate whether the substance exists in aqueous solution entirely in molecular form, entirely as ions, or as a mixture of molecules and ions. (a) HF , (b) acetonitrile, CH_3CN , (c) NaClO_4 , (d) $\text{Ba}(\text{OH})_2$.
- 4.36 An aqueous solution of an unknown solute is tested with litmus paper and found to be acidic. The solution is weakly conducting compared with a solution of NaCl of the same concentration.
- Which of the following substances could the unknown be: KOH , NH_3 , HNO_3 , KClO_2 , H_3PO_3 , CH_3COCH_3 (acetone)?
- 4.37 Classify each of the following substances as a nonelectrolyte, weak electrolyte, or strong electrolyte in water: (a) H_2SO_3 , (b) $\text{C}_2\text{H}_5\text{OH}$ (ethanol), (c) NH_3 , (d) KClO_3 , (e) $\text{Cu}(\text{NO}_3)_2$.
- 4.38 Classify each of the following aqueous solutions as a nonelectrolyte, weak electrolyte, or strong electrolyte: (a) LiClO_4 , (b) HClO , (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (propanol), (d) HClO_3 , (e) CuSO_4 , (f) $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (sucrose).
- 4.39 Complete and balance the following molecular equations, and then write the net ionic equation for each:
 (a) $\text{HBr}(\text{aq}) + \text{Ca}(\text{OH})_2(\text{aq}) \longrightarrow$
 (b) $\text{Cu}(\text{OH})_2(\text{s}) + \text{HClO}_4(\text{aq}) \longrightarrow$
 (c) $\text{Al}(\text{OH})_3(\text{s}) + \text{HNO}_3(\text{aq}) \longrightarrow$
- 4.40 Write the balanced molecular and net ionic equations for each of the following neutralization reactions:
 (a) Aqueous acetic acid is neutralized by aqueous barium hydroxide.
 (b) Solid chromium(III) hydroxide reacts with nitrous acid.
 (c) Aqueous nitric acid and aqueous ammonia react.
- 4.41 Write balanced molecular and net ionic equations for the following reactions, and identify the gas formed in each: (a) solid cadmium sulfide reacts with an aqueous solution of sulfuric acid; (b) solid magnesium carbonate reacts with an aqueous solution of perchloric acid.
- 4.42 Because the oxide ion is basic, metal oxides react readily with acids. (a) Write the net ionic equation for the following reaction:
 $\text{FeO}(\text{s}) + 2 \text{HClO}_4(\text{aq}) \longrightarrow \text{Fe}(\text{ClO}_4)_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$

(b) Based on the equation in part (a), write the net ionic equation for the reaction that occurs between NiO(s) and an aqueous solution of nitric acid.

- 4.43** Magnesium carbonate, magnesium oxide, and magnesium hydroxide are all white solids that react with acidic solutions. (a) Write a balanced molecular equation and a net ionic equation for the reaction that occurs when each substance reacts with a hydrochloric acid solution. (b) By observing the reactions in part (a) could you distinguish any of the three

magnesium substances from the other two? If so how? (c) If excess HCl(aq) is added, would the clear solutions left behind after the reaction is complete contain the same or different ions in each case?

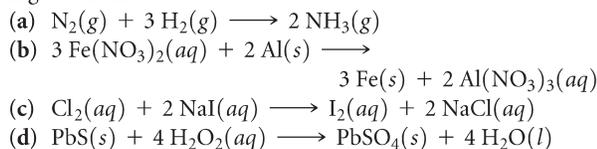
- 4.44** As K₂O dissolves in water, the oxide ion reacts with water molecules to form hydroxide ions. Write the molecular and net ionic equations for this reaction. Based on the definitions of acid and base, what ion is the base in this reaction? What is the acid? What is the spectator ion in the reaction?

OXIDATION-REDUCTION REACTIONS (section 4.4)

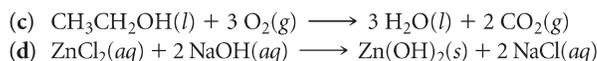
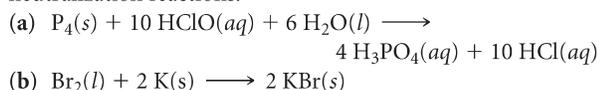
- 4.45** Define oxidation and reduction in terms of (a) electron transfer and (b) oxidation numbers.
- 4.46** Can oxidation occur without oxygen? Can oxidation occur without reduction?
- 4.47** Which region of the periodic table shown here contains the most readily oxidized elements? Which region contains the least readily oxidized?

- 4.48** Determine the oxidation number of sulfur in each of the following substances: (a) barium sulfate, BaSO₄, (b) sulfurous acid, H₂SO₃, (c) strontium sulfide, SrS, (d) hydrogen sulfide, H₂S. (e) Based on these compounds what is the range of oxidation numbers seen for sulfur? Is there any relationship between the range of accessible oxidation states and sulfur's position on the periodic table?
- 4.49** Determine the oxidation number for the indicated element in each of the following substances: (a) S in SO₂, (b) C in COCl₂, (c) Mn in KMnO₄, (d) Br in HBrO, (e) As in As₄, (f) O in K₂O₂.
- 4.50** Determine the oxidation number for the indicated element in each of the following compounds: (a) Co in LiCoO₂, (b) Al in NaAlH₄, (c) C in CH₃OH (methanol), (d) N in GaN, (e) Cl in HClO₂, (f) Cr in BaCrO₄.

- 4.51** Which element is oxidized and which is reduced in the following reactions?



- 4.52** Which of the following are redox reactions? For those that are, indicate which element is oxidized and which is reduced. For those that are not, indicate whether they are precipitation or neutralization reactions.



- 4.53** Write balanced molecular and net ionic equations for the reactions of (a) manganese with dilute sulfuric acid, (b) chromium with hydrobromic acid, (c) tin with hydrochloric acid, (d) aluminum with formic acid, HCOOH.
- 4.54** Write balanced molecular and net ionic equations for the reactions of (a) hydrochloric acid with nickel, (b) dilute sulfuric acid with iron, (c) hydrobromic acid with magnesium, (d) acetic acid, CH₃COOH, with zinc.

- 4.55** Using the activity series (Table 4.5), write balanced chemical equations for the following reactions. If no reaction occurs, simply write NR. (a) Iron metal is added to a solution of copper(II) nitrate; (b) zinc metal is added to a solution of magnesium sulfate; (c) hydrobromic acid is added to tin metal; (d) hydrogen gas is bubbled through an aqueous solution of nickel(II) chloride; (e) aluminum metal is added to a solution of cobalt(II) sulfate.

- 4.56** Using the activity series (Table 4.5), write balanced chemical equations for the following reactions. If no reaction occurs, simply write NR. (a) Nickel metal is added to a solution of copper(II) nitrate; (b) a solution of zinc nitrate is added to a solution of magnesium sulfate; (c) hydrochloric acid is added to gold metal; (d) chromium metal is immersed in an aqueous solution of cobalt(II) chloride; (e) hydrogen gas is bubbled through a solution of silver nitrate.

- 4.57** The metal cadmium tends to form Cd²⁺ ions. The following observations are made: (i) When a strip of zinc metal is placed in CdCl₂(aq), cadmium metal is deposited on the strip. (ii) When a strip of cadmium metal is placed in Ni(NO₃)₂(aq), nickel metal is deposited on the strip. (a) Write net ionic equations to explain each of the preceding observations. (b) What can you conclude about the position of cadmium in the activity series? (c) What experiments would you need to perform to locate more precisely the position of cadmium in the activity series?

- 4.58** (a) Use the following reactions to prepare an activity series for the halogens:



(b) Relate the positions of the halogens in the periodic table with their locations in this activity series. (c) Predict whether a reaction occurs when the following reagents are mixed: Cl₂(aq) and KI(aq); Br₂(aq) and LiCl(aq).

CONCENTRATIONS OF SOLUTIONS (section 4.5)

- 4.59** (a) Is the concentration of a solution an intensive or an extensive property? (b) What is the difference between 0.50 mol HCl and 0.50 M HCl?
- 4.60** (a) Suppose you prepare 500 mL of a 0.10 M solution of some salt and then spill some of it. What happens to the concentration of the solution left in the container? (b) Suppose you prepare 500 mL of a 0.10 M aqueous solution of some salt and let it sit out, uncovered, for a long time, and some water evaporates. What happens to the concentration of the solution left in the container? (c) A certain volume of a 0.50 M solution contains 4.5 g of a salt. What mass of the salt is present in the same volume of a 2.50 M solution?
- 4.61** (a) Calculate the molarity of a solution that contains 0.175 mol ZnCl_2 in exactly 150 mL of solution. (b) How many moles of HCl are present in 35.0 mL of a 4.50 M solution of nitric acid? (c) How many milliliters of 6.00 M NaOH solution are needed to provide 0.325 mol of NaOH?
- 4.62** (a) Calculate the molarity of a solution made by dissolving 12.5 grams of Na_2CrO_4 in enough water to form exactly 550 mL of solution. (b) How many moles of KBr are present in 150 mL of a 0.275 M solution? (c) How many milliliters of 6.1 M HCl solution are needed to obtain 0.100 mol of HCl?
- 4.63** The average adult human male has a total blood volume of 5.0 L. If the concentration of sodium ion in this average individual is 0.135 M, what is the mass of sodium ion circulating in the blood?
- 4.64** A person suffering from hyponatremia has a sodium ion concentration in the blood of 0.118 M and a total blood volume of 4.6 L. What mass of sodium chloride would need to be added to the blood to bring the sodium ion concentration up to 0.138 M, assuming no change in blood volume?
- 4.65** The concentration of alcohol ($\text{CH}_3\text{CH}_2\text{OH}$) in blood, called the “blood alcohol concentration” or BAC, is given in units of grams of alcohol per 100 mL of blood. The legal definition of intoxication, in many states of the United States, is that the BAC is 0.08 or higher. What is the concentration of alcohol, in terms of molarity, in blood if the BAC is 0.08?
- 4.66** The average adult male has a total blood volume of 5.0 L. After drinking a few beers, he has a BAC of 0.10 (see Exercise 4.65). What mass of alcohol is circulating in his blood?
- 4.67** Calculate (a) the number of grams of solute in 0.250 L of 0.175 M KBr, (b) the molar concentration of a solution containing 14.75 g of $\text{Ca}(\text{NO}_3)_2$ in 1.375 L, (c) the volume of 1.50 M Na_3PO_4 in milliliters that contains 2.50 g of solute.
- 4.68** (a) How many grams of solute are present in 15.0 mL of 0.736 M $\text{K}_2\text{Cr}_2\text{O}_7$? (b) If 14.00 g of $(\text{NH}_4)_2\text{SO}_4$ is dissolved in enough water to form 250 mL of solution, what is the molarity of the solution? (c) How many milliliters of 0.0455 M CuSO_4 contain 3.65 g of solute?
- 4.69** (a) Which will have the highest concentration of potassium ion: 0.20 M KCl, 0.15 M K_2CrO_4 , or 0.080 M K_3PO_4 ? (b) Which will contain the greater number of moles of potassium ion: 30.0 mL of 0.15 M K_2CrO_4 or 25.0 mL of 0.080 M K_3PO_4 ?
- 4.70** In each of the following pairs, indicate which has the higher concentration of I^- ion: (a) 0.10 M BaI_2 or 0.25 M KI solution, (b) 100 mL of 0.10 M KI solution or 200 mL of 0.040 M ZnI_2 solution, (c) 3.2 M HI solution or a solution made by dissolving 145 g of NaI in water to make 150 mL of solution.
- 4.71** Indicate the concentration of each ion or molecule present in the following solutions: (a) 0.25 M NaNO_3 , (b) 1.3×10^{-2} M MgSO_4 , (c) 0.0150 M $\text{C}_6\text{H}_{12}\text{O}_6$, (d) a mixture of 45.0 mL of 0.272 M NaCl and 65.0 mL of 0.0247 M $(\text{NH}_4)_2\text{CO}_3$. Assume that the volumes are additive.
- 4.72** Indicate the concentration of each ion present in the solution formed by mixing (a) 42.0 mL of 0.170 M NaOH and 37.6 mL of 0.400 M NaOH, (b) 44.0 mL of 0.100 M and Na_2SO_4 and 25.0 mL of 0.150 M KCl, (c) 3.60 g KCl in 75.0 mL of 0.250 M CaCl_2 solution. Assume that the volumes are additive.
- 4.73** (a) You have a stock solution of 14.8 M NH_3 . How many milliliters of this solution should you dilute to make 1000.0 mL of 0.250 M NH_3 ? (b) If you take a 10.0-mL portion of the stock solution and dilute it to a total volume of 0.500 L, what will be the concentration of the final solution?
- 4.74** (a) How many milliliters of a stock solution of 6.0 M HNO_3 would you have to use to prepare 110 mL of 0.500 M HNO_3 ? (b) If you dilute 10.0 mL of the stock solution to a final volume of 0.250 L, what will be the concentration of the diluted solution?
- 4.75** (a) Starting with solid sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, describe how you would prepare 250 mL of a 0.250 M sucrose solution. (b) Describe how you would prepare 350.0 mL of 0.100 M $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ starting with 3.00 L of 1.50 M $\text{C}_{12}\text{H}_{22}\text{O}_{11}$.
- 4.76** (a) How would you prepare 175.0 mL of 0.150 M AgNO_3 solution starting with pure AgNO_3 ? (b) An experiment calls for you to use 100 mL of 0.50 M HNO_3 solution. All you have available is a bottle of 3.6 M HNO_3 . How would you prepare the desired solution?
- 4.77** Pure acetic acid, known as glacial acetic acid, is a liquid with a density of 1.049 g/mL at 25 °C. Calculate the molarity of a solution of acetic acid made by dissolving 20.00 mL of glacial acetic acid at 25 °C in enough water to make 250.0 mL of solution.
- 4.78** Glycerol, $\text{C}_3\text{H}_8\text{O}_3$, is a substance used extensively in the manufacture of cosmetics, foodstuffs, antifreeze, and plastics. Glycerol is a water-soluble liquid with a density of 1.2656 g/mL at 15 °C. Calculate the molarity of a solution of glycerol made by dissolving 50.000 mL glycerol at 15 °C in enough water to make 250.00 mL of solution.

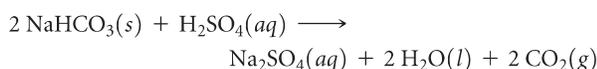
SOLUTION STOICHIOMETRY AND CHEMICAL ANALYSIS (section 4.6)

- 4.79** What mass of KCl is needed to precipitate the silver ions from 15.0 mL of 0.200 M AgNO_3 solution?
- 4.80** What mass of NaOH is needed to precipitate the Cd^{2+} ions from 35.0 mL of 0.500 M $\text{Cd}(\text{NO}_3)_2$ solution?
- 4.81** (a) What volume of 0.115 M HClO_4 solution is needed to neutralize 50.00 mL of 0.0875 M NaOH? (b) What volume of 0.128 M HCl is needed to neutralize 2.87 g of $\text{Mg}(\text{OH})_2$? (c) If 25.8 mL of AgNO_3 is needed to precipitate all the Cl^- ions in a

785-mg sample of KCl (forming AgCl), what is the molarity of the AgNO₃ solution? (d) If 45.3 mL of 0.108 M HCl solution is needed to neutralize a solution of KOH, how many grams of KOH must be present in the solution?

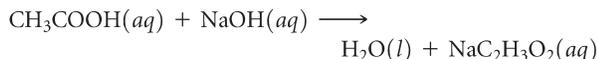
- 4.82 (a) How many milliliters of 0.120 M HCl are needed to completely neutralize 50.0 mL of 0.101 M Ba(OH)₂ solution? (b) How many milliliters of 0.125 M H₂SO₄ are needed to neutralize 0.200 g of NaOH? (c) If 55.8 mL of BaCl₂ solution is needed to precipitate all the sulfate ion in a 752-mg sample of Na₂SO₄, what is the molarity of the solution? (d) If 42.7 mL of 0.208 M HCl solution is needed to neutralize a solution of Ca(OH)₂, how many grams of Ca(OH)₂ must be in the solution?

- 4.83 Some sulfuric acid is spilled on a lab bench. You can neutralize the acid by sprinkling sodium bicarbonate on it and then mopping up the resultant solution. The sodium bicarbonate reacts with sulfuric acid as follows:



Sodium bicarbonate is added until the fizzing due to the formation of CO₂(g) stops. If 27 mL of 6.0 M H₂SO₄ was spilled, what is the minimum mass of NaHCO₃ that must be added to the spill to neutralize the acid?

- 4.84 The distinctive odor of vinegar is due to acetic acid, CH₃COOH, which reacts with sodium hydroxide in the following fashion:



If 3.45 mL of vinegar needs 42.5 mL of 0.115 M NaOH to reach the equivalence point in a titration, how many grams of acetic acid are in a 1.00-qt sample of this vinegar?

- 4.85 A 4.36-g sample of an unknown alkali metal hydroxide is dissolved in 100.0 mL of water. An acid–base indicator is added and the resulting solution is titrated with 2.50 M HCl(aq)

solution. The indicator changes color signaling that the equivalence point has been reached after 17.0 mL of the hydrochloric acid solution has been added. (a) What is the molar mass of the metal hydroxide? (b) What is the identity of the alkali metal cation: Li⁺, Na⁺, K⁺, Rb⁺, or Cs⁺?

- 4.86 An 8.65-g sample of an unknown group 2A metal hydroxide is dissolved in 85.0 mL of water. An acid–base indicator is added and the resulting solution is titrated with 2.50 M HCl(aq) solution. The indicator changes color signaling that the equivalence point has been reached after 56.9 mL of the hydrochloric acid solution has been added. (a) What is the molar mass of the metal hydroxide? (b) What is the identity of the metal cation: Ca²⁺, Sr²⁺, Ba²⁺?

- 4.87 A solution of 100.0 mL of 0.200 M KOH is mixed with a solution of 200.0 mL of 0.150 M NiSO₄. (a) Write the balanced chemical equation for the reaction that occurs. (b) What precipitate forms? (c) What is the limiting reactant? (d) How many grams of this precipitate form? (e) What is the concentration of each ion that remains in solution?

- 4.88 A solution is made by mixing 15.0 g of Sr(OH)₂ and 55.0 mL of 0.200 M HNO₃. (a) Write a balanced equation for the reaction that occurs between the solutes. (b) Calculate the concentration of each ion remaining in solution. (c) Is the resultant solution acidic or basic?

- 4.89 A 0.5895-g sample of impure magnesium hydroxide is dissolved in 100.0 mL of 0.2050 M HCl solution. The excess acid then needs 19.85 mL of 0.1020 M NaOH for neutralization. Calculate the percent by mass of magnesium hydroxide in the sample, assuming that it is the only substance reacting with the HCl solution.

- 4.90 A 1.248-g sample of limestone rock is pulverized and then treated with 30.00 mL of 1.035 M HCl solution. The excess acid then requires 11.56 mL of 1.010 M NaOH for neutralization. Calculate the percent by mass of calcium carbonate in the rock, assuming that it is the only substance reacting with the HCl solution.

ADDITIONAL EXERCISES

- 4.91 Gold is one of the few metals that can be obtained by panning, where a simple pan is used to separate gold from other deposits found in or near a stream bed. What two properties of gold make it possible to find gold, but not metals like copper, silver, lead, and aluminum, by panning?
- 4.92 The accompanying photo shows the reaction between a solution of Cd(NO₃)₂ and one of Na₂S. What is the identity of the precipitate? What ions remain in solution? Write the net ionic equation for the reaction.



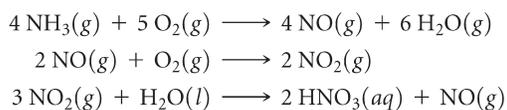
- 4.93 Suppose you have a solution that might contain any or all of the following cations: Ni^{2+} , Ag^+ , Sr^{2+} , and Mn^{2+} . Addition of HCl solution causes a precipitate to form. After filtering off the precipitate, H_2SO_4 solution is added to the resulting solution and another precipitate forms. This is filtered off, and a solution of NaOH is added to the resulting solution. No precipitate is observed. Which ions are present in each of the precipitates? Which of the four ions listed above must be absent from the original solution?
- 4.94 You choose to investigate some of the solubility guidelines for two ions not listed in Table 4.1, the chromate ion (CrO_4^{2-}) and the oxalate ion ($\text{C}_2\text{O}_4^{2-}$). You are given 0.01 M solutions (A, B, C, D) of four water-soluble salts:

Solution	Solute	Color of Solution
A	Na_2CrO_4	Yellow
B	$(\text{NH}_4)_2\text{C}_2\text{O}_4$	Colorless
C	AgNO_3	Colorless
D	CaCl_2	Colorless

When these solutions are mixed, the following observations are made:

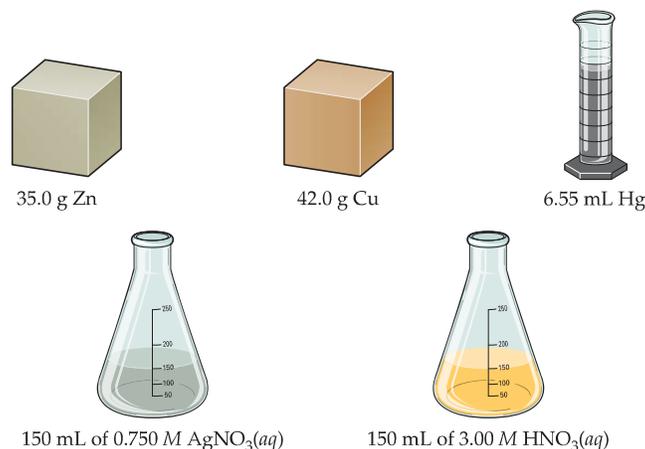
Expt Number	Solutions Mixed	Result
1	A + B	No precipitate, yellow solution
2	A + C	Red precipitate forms
3	A + D	Yellow precipitate forms
4	B + C	White precipitate forms
5	B + D	White precipitate forms
6	C + D	White precipitate forms

- (a) Write a net ionic equation for the reaction that occurs in each of the experiments. (b) Identify the precipitate formed, if any, in each of the experiments.
- 4.95 Antacids are often used to relieve pain and promote healing in the treatment of mild ulcers. Write balanced net ionic equations for the reactions between the $\text{HCl}(aq)$ in the stomach and each of the following substances used in various antacids: (a) $\text{Al}(\text{OH})_3(s)$, (b) $\text{Mg}(\text{OH})_2(s)$, (c) $\text{MgCO}_3(s)$, (d) $\text{NaAl}(\text{CO}_3)(\text{OH})_2(s)$, (e) $\text{CaCO}_3(s)$.
- [4.96] The commercial production of nitric acid involves the following chemical reactions:



(a) Which of these reactions are redox reactions? (b) In each redox reaction identify the element undergoing oxidation and the element undergoing reduction.

- 4.97 Consider the following reagents: zinc, copper, mercury (density 13.6 g/mL), silver nitrate solution, nitric acid solution. (a) Given a 500-mL Erlenmeyer flask and a balloon can you combine two or more of the foregoing reagents to initiate a chemical reaction that will inflate the balloon? Write a balanced chemical equation to represent this process. What is the identity of the substance that inflates the balloon? (b) What is the theoretical yield of the substance that fills the balloon? (c) Can you combine two or more of the foregoing reagents to initiate a chemical reaction that will produce metallic silver? Write a balanced chemical equation to represent this process. What ions are left behind in solution? (d) What is the theoretical yield of silver?



- [4.98] Lanthanum metal forms cations with a charge of 3+. Consider the following observations about the chemistry of lanthanum: When lanthanum metal is exposed to air, a white solid (compound A) is formed that contains lanthanum and one other element. When lanthanum metal is added to water, gas bubbles are observed and a different white solid (compound B) is formed. Both A and B dissolve in hydrochloric acid to give a clear solution. When either of these solutions is evaporated, a soluble white solid (compound C) remains. If compound C is dissolved in water and sulfuric acid is added, a white precipitate (compound D) forms. (a) Propose identities for the substances A, B, C, and D. (b) Write net ionic equations for all the reactions described. (c) Based on the preceding observations, what can be said about the position of lanthanum in the activity series (Table 4.5)?

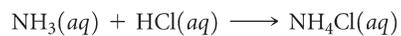
- 4.99 A 35.0-mL sample of 1.00 M KBr and a 60.0-mL sample of 0.600 M KBr are mixed. The solution is then heated to evaporate water until the total volume is 50.0 mL. What is the molarity of the KBr in the final solution?
- 4.100 Using modern analytical techniques, it is possible to detect sodium ions in concentrations as low as 50 pg/mL. What is this detection limit expressed in (a) molarity of Na^+ , (b) Na^+ ions per cubic centimeter?

- 4.101** Hard water contains Ca^{2+} , Mg^{2+} , and Fe^{2+} , which interfere with the action of soap and leave an insoluble coating on the insides of containers and pipes when heated. Water softeners replace these ions with Na^+ . (a) If 1500 L of hard water contains 0.020 M Ca^{2+} and 0.0040 M Mg^{2+} , how many moles of Na^+ are needed to replace these ions? (b) If the sodium is added to the water softener in the form of NaCl, how many grams of sodium chloride are needed?
- 4.102** Tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, has two acidic hydrogens. The acid is often present in wines and precipitates from solution as the wine ages. A solution containing an unknown concentration of the acid is titrated with NaOH. It requires 24.65 mL of 0.2500 M NaOH solution to titrate both acidic protons in 50.00 mL of the tartaric acid solution. Write a balanced net ionic equation for the neutralization reaction, and calculate the molarity of the tartaric acid solution.
- 4.103** (a) A strontium hydroxide solution is prepared by dissolving 10.45 g of $\text{Sr}(\text{OH})_2$ in water to make 50.00 mL of solution. What is the molarity of this solution? (b) Next the strontium hydroxide solution prepared in part (a) is used to titrate a nitric acid solution of unknown concentration. Write a balanced chemical equation to represent the reaction between strontium hydroxide and nitric acid solutions. (c) If 23.9 mL of the strontium hydroxide solution was needed to neutralize a 31.5 mL aliquot of the nitric acid solution, what is the concentration (molarity) of the acid?
- [4.104]** A solid sample of $\text{Zn}(\text{OH})_2$ is added to 0.350 L of 0.500 M aqueous HBr. The solution that remains is still acidic. It is then titrated with 0.500 M NaOH solution, and it takes 88.5 mL of the NaOH solution to reach the equivalence point. What mass of $\text{Zn}(\text{OH})_2$ was added to the HBr solution?

INTEGRATIVE EXERCISES

- 4.105** Suppose you have 5.00 g of powdered magnesium metal, 1.00 L of 2.00 M potassium nitrate solution, and 1.00 L of 2.00 M silver nitrate solution. (a) Which one of the solutions will react with the magnesium powder? (b) What is the net ionic equation that describes this reaction? (c) What volume of solution is needed to completely react with the magnesium? (d) What is the molarity of the Mg^{2+} ions in the resulting solution?
- 4.106** (a) By titration, 15.0 mL of 0.1008 M sodium hydroxide is needed to neutralize a 0.2053-g sample of an organic acid. What is the molar mass of the acid if it is monoprotic? (b) An elemental analysis of the acid indicates that it is composed of 5.89% H, 70.6% C, and 23.5% O by mass. What is its molecular formula?
- 4.107** A 3.455-g sample of a mixture was analyzed for barium ion by adding a small excess of sulfuric acid to an aqueous solution of the sample. The resultant reaction produced a precipitate of barium sulfate, which was collected by filtration, washed, dried, and weighed. If 0.2815 g of barium sulfate was obtained, what was the mass percentage of barium in the sample?
- 4.108** A tanker truck carrying 5.0×10^3 kg of concentrated sulfuric acid solution tips over and spills its load. If the sulfuric acid is 95.0% H_2SO_4 by mass and has a density of 1.84 g/mL, how many kilograms of sodium carbonate must be added to neutralize the acid?
- 4.109** A sample of 5.53 g of $\text{Mg}(\text{OH})_2$ is added to 25.0 mL of 0.200 M HNO_3 . (a) Write the chemical equation for the reaction that occurs. (b) Which is the limiting reactant in the reaction? (c) How many moles of $\text{Mg}(\text{OH})_2$, HNO_3 , and $\text{Mg}(\text{NO}_3)_2$ are present after the reaction is complete?
- 4.110** A sample of 1.50 g of lead(II) nitrate is mixed with 125 mL of 0.100 M sodium sulfate solution. (a) Write the chemical equation for the reaction that occurs. (b) Which is the limiting reactant in the reaction? (c) What are the concentrations of all ions that remain in solution after the reaction is complete?
- [4.111]** The average concentration of bromide ion in seawater is 65 mg of bromide ion per kg of seawater. What is the molarity of the bromide ion if the density of the seawater is 1.025 g/mL?
- [4.112]** The mass percentage of chloride ion in a 25.00-mL sample of seawater was determined by titrating the sample with silver nitrate, precipitating silver chloride. It took 42.58 mL of 0.2997 M silver nitrate solution to reach the equivalence point in the titration. What is the mass percentage of chloride ion in the seawater if its density is 1.025 g/mL?
- 4.113** The arsenic in a 1.22-g sample of a pesticide was converted to AsO_4^{3-} by suitable chemical treatment. It was then titrated using Ag^+ to form Ag_3AsO_4 as a precipitate. (a) What is the oxidation state of As in AsO_4^{3-} ? (b) Name Ag_3AsO_4 by analogy to the corresponding compound containing phosphorus in place of arsenic. (c) If it took 25.0 mL of 0.102 M Ag^+ to reach the equivalence point in this titration, what is the mass percentage of arsenic in the pesticide?
- [4.114]** The newest US standard for arsenate in drinking water, mandated by the Safe Drinking Water Act, required that by January 2006, public water supplies must contain no greater than 10 parts per billion (ppb) arsenic. If this arsenic is present as arsenate, AsO_4^{3-} , what mass of sodium arsenate would be present in a 1.00-L sample of drinking water that just meets the standard? Parts per billion is defined on a mass basis as
- $$\text{ppb} = \frac{\text{g solute}}{\text{g solution}} \times 10^9.$$

[4.115] Federal regulations set an upper limit of 50 parts per million (ppm) of NH_3 in the air in a work environment [that is, 50 molecules of $\text{NH}_3(g)$ for every million molecules in the air]. Air from a manufacturing operation was drawn through a solution containing 1.00×10^2 mL of 0.0105 M HCl. The NH_3 reacts with HCl as follows:



After drawing air through the acid solution for 10.0 min at a rate of 10.0 L/min, the acid was titrated. The remaining acid needed 13.1 mL of 0.0588 M NaOH to reach the equivalence point. (a) How many grams of NH_3 were drawn into the acid solution? (b) How many ppm of NH_3 were in the air? (Air has a density of 1.20 g/L and an average molar mass of 29.0 g/mol under the conditions of the experiment.) (c) Is this manufacturer in compliance with regulations?