4 Types of Chemical Reactions and Solution Stoichiometry

Contents

Yellow lead(II) iodide is produced when lead(II) nitrate is mixed with potassium iodide.

Much of the chemistry that affects each of us occurs among substances dissolved in water. For example, virtually all the chemistry that makes life possible occurs in an aqueous environment. Also, various medical tests involve aqueous reactions, depending heavily on analyses of blood and other body fluids. In addition to the common tests for sugar, cholesterol, and iron, analyses for specific chemical markers allow detection of many diseases before obvious symptoms occur.

Aqueous chemistry is also important in our environment. In recent years, contamination of the groundwater by substances such as chloroform and nitrates has been widely publicized. Water is essential for life, and the maintenance of an ample supply of clean water is crucial to all civilization.

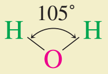
To understand the chemistry that occurs in such diverse places as the human body, the atmosphere, the groundwater, the oceans, the local water treatment plant, your hair as you shampoo it, and so on, we must understand how substances dissolved in water react with each other.

However, before we can understand solution reactions, we need to discuss the nature of solutions in which water is the dissolving medium, or *solvent.* These solutions are called **aqueous solutions.** In this chapter we will study the nature of materials after they are dissolved in water and various types of reactions that occur among these substances. You will see that the procedures developed in Chapter 3 to deal with chemical reactions work very well for reactions that take place in aqueous solutions. To understand the types of reactions that occur in aqueous solutions, we must first explore the types of species present. This requires an understanding of the nature of water.

4.1 Water, the Common Solvent

Water is one of the most important substances on earth. It is essential for sustaining the reactions that keep us alive, but it also affects our lives in many indirect ways. Water helps moderate the earth's temperature; it cools automobile engines, nuclear power plants, and many industrial processes; it provides a means of transportation on the earth's surface and a medium for the growth of a myriad of creatures we use as food; and much more.

One of the most valuable properties of water is its ability to dissolve many different substances. For example, salt "disappears" when you sprinkle it into the water used to cook vegetables, as does sugar when you add it to your iced tea. In each case the "disappearing" substance is obviously still present—you can taste it. What happens when a solid dissolves? To understand this process, we need to consider the nature of water. Liquid water consists of a collection of H_2O molecules. An individual H_2O molecule is "bent" or V-shaped, with an H—O—H angle of approximately 105 degrees:



The O—H bonds in the water molecule are covalent bonds formed by electron sharing between the oxygen and hydrogen atoms. However, the electrons of the bond are not shared equally between these atoms. For reasons we will discuss in later chapters, oxygen has a greater attraction for electrons than does hydrogen. If the electrons were shared equally between the two atoms, both would be electrically neutral because, on average, the number of electrons around each would equal the number of protons in that nucleus.

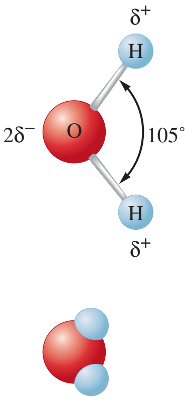


FIGURE 4.1
(top) The water molecule is polar. (bottom) A space-filling model of the water molecule.

However, because the oxygen atom has a greater attraction for electrons, the shared electrons tend to spend more time close to the oxygen than to either of the hydrogens. Thus the oxygen atom gains a slight excess of negative charge, and the hydrogen atoms become slightly positive. This is shown in Fig. 4.1, where δ (delta) indicates a *partial* charge (*less than one unit of charge*). Because of this unequal charge distribution, water is said to be a **polar molecule.** It is this polarity that gives water its great ability to dissolve compounds.

A schematic of an ionic solid dissolving in water is shown in Fig. 4.2. Note that the "positive ends" of the water molecules are attracted to the negatively charged anions and that the "negative ends" are attracted to the positively charged cations. This process is called **hydration.** The hydration of its ions tends to cause a salt to "fall apart" in the water, or to dissolve. The strong forces present among the positive and negative ions of the solid are replaced by strong water–ion interactions.

It is very important to recognize that when ionic substances (salts) dissolve in water, they break up into the *individual* cations and anions. For instance, when ammonium nitrate (NH_4NO_3) dissolves in water, the resulting solution contains NH_4^+ and NO_3^- ions moving around independently. This process can be represented as

$$NH_4NO_3(s) \xrightarrow{H_2O(l)} NH_4^+(aq) + NO_3^-(aq)$$

where (*aq*) designates that the ions are hydrated by unspecified numbers of water molecules.

The **solubility** of ionic substances in water varies greatly. For example, sodium chloride is quite soluble in water, whereas silver chloride (contains Ag^+ and Cl^- ions) is only very slightly soluble. The differences in the solubilities of ionic compounds in water typically depend on the relative attractions of the ions for each other (these forces hold the solid together) and the attractions of the ions for water molecules (which cause the solid to disperse [dissolve] in water). Solubility is a complex topic that we will explore in much more detail in Chapter 11. However, the most important thing to remember at

Visualization: The Dissolution of a Solid in a Liquid

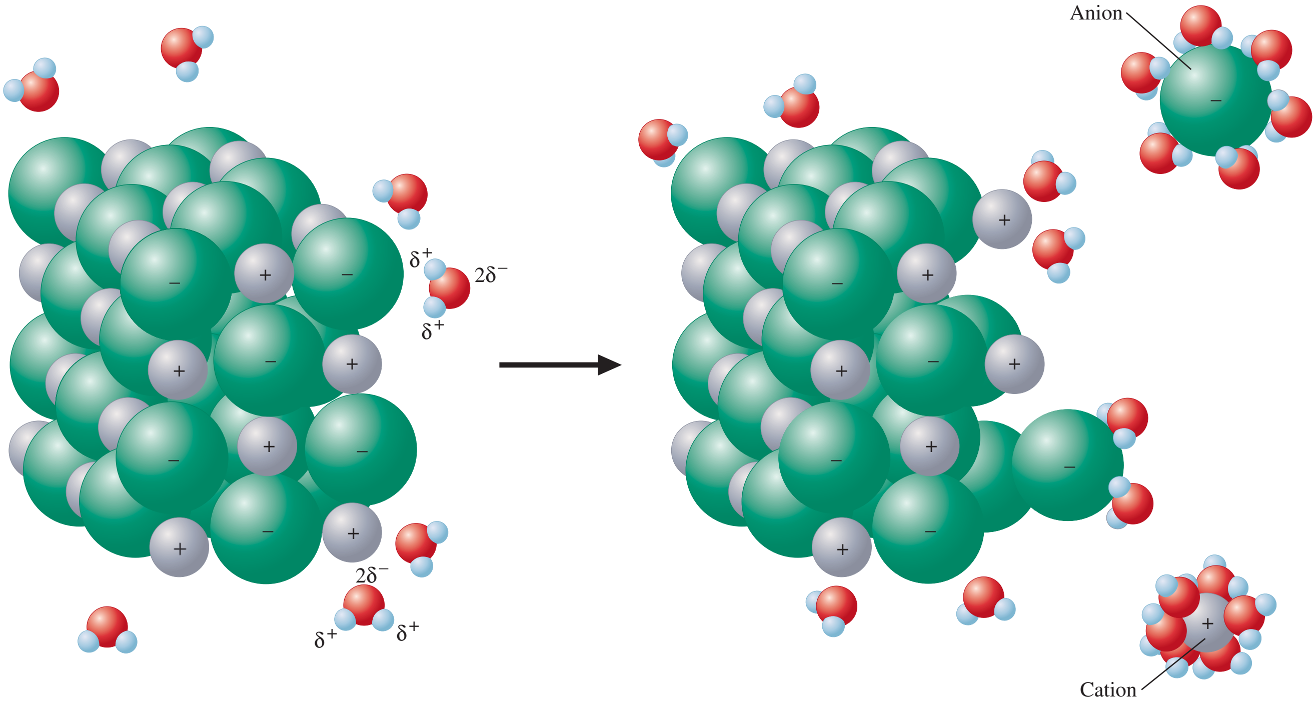


FIGURE 4.2
Polar water molecules interact with the positive and negative ions of a salt, assisting in the dissolving process.

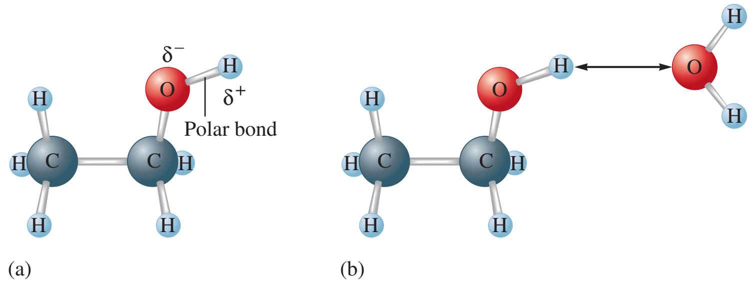


FIGURE 4.3
(a) The ethanol molecule contains a polar O—H bond similar to those in the water molecule. (b) The polar water molecule interacts strongly with the polar O—H bond in ethanol. This is a case of "like dissolving like."

this point is that when an ionic solid does dissolve in water, the ions become hydrated and are dispersed (move around independently).

Water also dissolves many nonionic substances. Ethanol (C_2H_5OH), for example, is very soluble in water. Wine, beer, and mixed drinks are aqueous solutions of ethanol and other substances. Why is ethanol so soluble in water? The answer lies in the structure of the alcohol molecules, which is shown in Fig. 4.3(a). The molecule contains a polar O—H bond like those in water, which makes it very compatible with water. The interaction of water with ethanol is represented in Fig. 4.3(b).

Many substances do not dissolve in water. Pure water will not, for example, dissolve animal fat, because fat molecules are nonpolar and do not interact effectively with polar water molecules. In general, polar and ionic substances are expected to be more soluble in water than nonpolar substances. "Like dissolves like" is a useful rule for predicting solubility. We will explore the basis for this generalization when we discuss the details of solution formation in Chapter 11.

4.2 The Nature of Aqueous Solutions: Strong and Weak Electrolytes

As we discussed in Chapter 2, a solution is a homogeneous mixture. It is the same throughout (the first sip of a cup of coffee is the same as the last), but its composition can be varied by changing the amount of dissolved substances (one can make weak or strong coffee). In this section we will consider what happens when a substance, the **solute,** is dissolved in liquid water, the **solvent.**

Visualization: Electrolytes

One useful property for characterizing a solution is its **electrical conductivity,** its ability to conduct an electric current. This characteristic can be checked conveniently by using an apparatus like the ones shown in Figure 4.4. If the solution in the container conducts electricity, the bulb lights. Pure water is not an electrical conductor. However, some aqueous solutions conduct current very efficiently, and the bulb shines very brightly; these solutions contain **strong electrolytes.** Other solutions conduct only a small current, and the bulb glows dimly; these solutions contain **weak electrolytes.** Some solutions permit no current to flow, and the bulb remains unlit; these solutions contain **nonelectrolytes.**

An *electrolyte* is a substance that when dissolved in water produces a solution that can conduct electricity.

The basis for the conductivity properties of solutions was first correctly identified by Svante Arrhenius (1859–1927), then a Swedish graduate student in physics, who carried out research on the nature of solutions at the University of Uppsala in the early 1880s. Arrhenius came to believe that the conductivity of solutions arose from the presence of ions, an idea that was at first scorned by the majority of the scientific establishment. However, in the late 1890s when atoms were found to contain charged particles, the ionic theory suddenly made sense and became widely accepted.

Visualization: Electrolyte Behavior

As Arrhenius postulated, the extent to which a solution can conduct an electric current depends directly on the number of ions present. Some materials, such as sodium chloride, readily produce ions in aqueous solution and thus are strong electrolytes. Other substances,

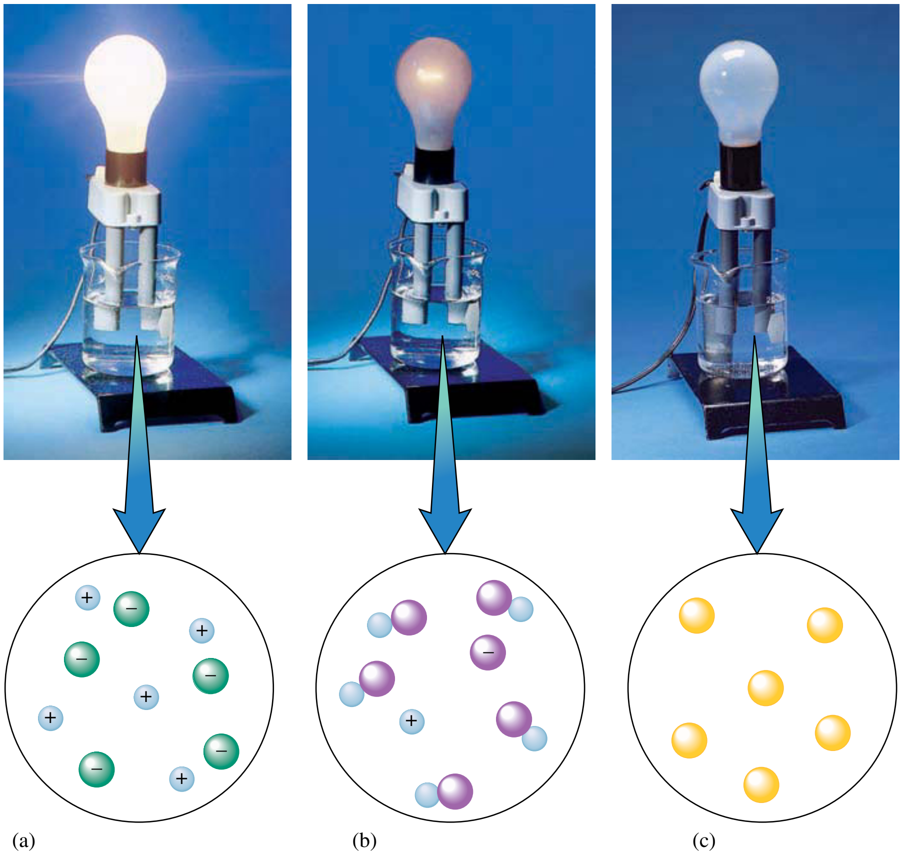


FIGURE 4.4
Electrical conductivity of aqueous solutions. The circuit will be completed and will allow current to flow only when there are charge carriers (ions) in the solution. *Note:* Water molecules are present but not shown in these pictures. (a) A hydrochloric acid solution, which is a strong electrolyte, contains ions that readily conduct the current and give a brightly lit bulb. (b) An acetic acid solution, which is a weak electrolyte, contains only a few ions and does not conduct as much current as a strong electrolyte. The bulb is only dimly lit. (c) A sucrose solution, which is a nonelectrolyte, contains no ions and does not conduct a current. The bulb remains unlit.

such as acetic acid, produce relatively few ions when dissolved in water and are weak electrolytes. A third class of materials, such as sugar, form virtually no ions when dissolved in water and are nonelectrolytes.

Strong Electrolytes

Strong electrolytes are substances that are completely ionized when they are dissolved in water, as represented in Fig. 4.4(a). We will consider several classes of strong electrolytes: (1) soluble salts, (2) strong acids, and (3) strong bases.

As shown in Fig. 4.2, a salt consists of an array of cations and anions that separate and become hydrated when the salt dissolves. For example, when NaCl dissolves in water, it produces hydrated Na^+ and Cl^- ions in the solution (see Fig. 4.5). Virtually no NaCl

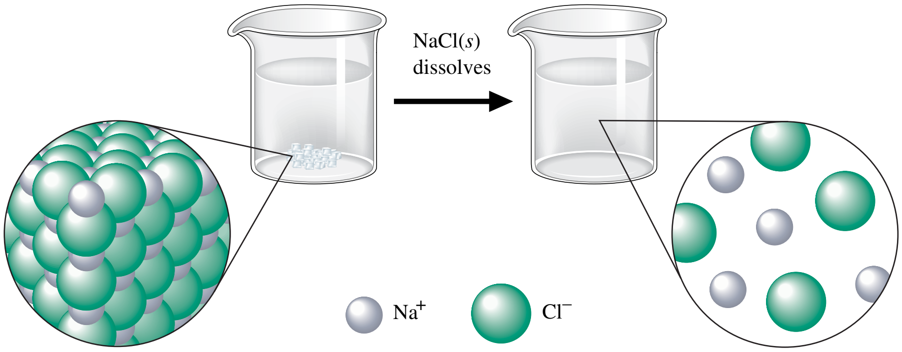


FIGURE 4.5
When solid NaCl dissolves, the Na^+ and Cl^- ions are randomly dispersed in the water.

units are present. Thus NaCl is a strong electrolyte. It is important to recognize that these aqueous solutions contain millions of water molecules that we will not include in our molecular-level drawings.

One of Arrhenius's most important discoveries concerned the nature of acids. Acidity was first associated with the sour taste of citrus fruits. In fact, the word *acid* comes directly from the Latin word *acidus,* meaning "sour." The mineral acids sulfuric acid (H_2SO_4) and nitric acid (HNO_3), so named because they were originally obtained by the treatment of minerals, were discovered around 1300.

Although acids were known for hundreds of years before the time of Arrhenius, no one had recognized their essential nature. In his studies of solutions, Arrhenius found that when the substances HCl, HNO_3, and H_2SO_4 were dissolved in water, they behaved as strong electrolytes. He postulated that this was the result of ionization reactions in water, for example:

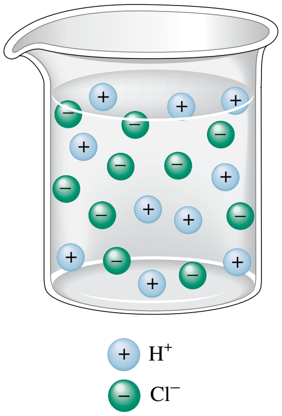


FIGURE 4.6
HCl(*aq*) is completely ionized.

$$\mathrm{HCl} \xrightarrow{\mathrm{H_2O}} \mathrm{H^+}(aq) + \mathrm{Cl^-}(aq)$$
$$\mathrm{HNO_3} \xrightarrow{\mathrm{H_2O}} \mathrm{H^+}(aq) + \mathrm{NO_3^-}(aq)$$
$$\mathrm{H_2SO_4} \xrightarrow{\mathrm{H_2O}} \mathrm{H^+}(aq) + \mathrm{HSO_4^-}(aq)$$

The Arrhenius definition of an acid is a substance that produces H^+ ions in solution.

Thus Arrhenius proposed that an ***acid*** *is a substance that produces H^+ ions (protons) when it is dissolved in water.*

Strong electrolytes dissociate (ionize) completely in aqueous solution.

Studies of conductivity show that when HCl, HNO_3, and H_2SO_4 are placed in water, *virtually every molecule ionizes.* These substances are strong electrolytes and are thus called **strong acids.** All three are very important chemicals, and much more will be said about them as we proceed. However, at this point the following facts are important:

Perchloric acid, $HClO_4(aq)$, is another strong acid.

> Sulfuric acid, nitric acid, and hydrochloric acid are aqueous solutions and should be written in chemical equations as $H_2SO_4(aq)$, $HNO_3(aq)$, and $HCl(aq)$, respectively, although they often appear without the (aq) symbol.
>
> A strong acid is one that completely dissociates into its ions. Thus, if 100 molecules of HCl are dissolved in water, 100 H^+ ions and 100 Cl^- ions are produced. Virtually no HCl molecules exist in aqueous solutions (see Fig. 4.6).
>
> Sulfuric acid is a special case. The formula H_2SO_4 indicates that this acid can produce two H^+ ions per molecule when dissolved in water. However, only the first H^+ ion is completely dissociated. The second H^+ ion can be pulled off under certain conditions, which we will discuss later. Thus an aqueous solution of H_2SO_4 contains mostly H^+ ions and HSO_4^- ions.

Another important class of strong electrolytes consists of the **strong bases,** soluble ionic compounds containing the hydroxide ion (OH^-). When these compounds are dissolved in water, the cations and OH^- ions separate and move independently. Solutions containing bases have a bitter taste and a slippery feel. The most common basic solutions are those produced when solid sodium hydroxide (NaOH) or potassium hydroxide (KOH) is dissolved in water to produce ions, as follows (see Fig. 4.7):

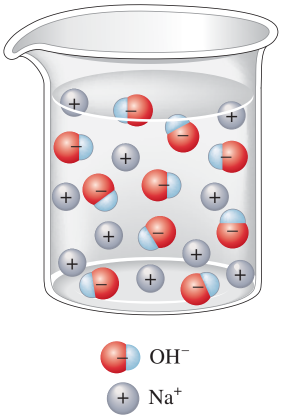


FIGURE 4.7
An aqueous solution of sodium hydroxide.

$$\mathrm{NaOH}(s) \xrightarrow{\mathrm{H_2O}} \mathrm{Na^+}(aq) + \mathrm{OH^-}(aq)$$
$$\mathrm{KOH}(s) \xrightarrow{\mathrm{H_2O}} \mathrm{K^+}(aq) + \mathrm{OH^-}(aq)$$

Weak Electrolytes

Weak electrolytes dissociate (ionize) only to a small extent in aqueous solution.

Weak electrolytes are substances that exhibit a small degree of ionization in water. That is, they produce relatively few ions when dissolved in water, as shown in Fig. 4.4(b). The most common weak electrolytes are weak acids and weak bases.

CHEMICAL IMPACT

Arrhenius: A Man with Solutions

Science is a human endeavor, subject to human frailties and governed by personalities, politics, and prejudices. One of the best illustrations of the often bumpy path of the advancement of scientific knowledge is the story of Swedish chemist Svante Arrhenius.

When Arrhenius began studies toward his doctorate at the University of Uppsala around 1880, he chose to investigate the passage of electricity through solutions, a mystery that had baffled scientists for a century. The first experiments had been done in the 1770s by Cavendish, who compared the conductivity of salt solution with that of rain water using his own physiologic reaction to the electric shocks he received! Arrhenius had an array of instruments to measure electric current, but the process of carefully weighing, measuring, and recording data from a multitude of experiments was a tedious one.

After his long series of experiments was performed, Arrhenius quit his laboratory bench and returned to his country

Svante August Arrhenius.

The main acidic component of vinegar is acetic acid ($HC_2H_3O_2$). The formula is written to indicate that acetic acid has two chemically distinct types of hydrogen atoms. Formulas for acids are often written with the acidic hydrogen atom or atoms (any that will produce H^+ ions in solution) listed first. If any nonacidic hydrogens are present, they are written later in the formula. Thus the formula $HC_2H_3O_2$ indicates one acidic and three nonacidic hydrogen atoms. The dissociation reaction for acetic acid in water can be written as follows:

$$HC_2H_3O_2(aq) \xrightleftharpoons{H_2O} H^+(aq) + C_2H_3O_2^-(aq)$$

Acetic acid is very different from the strong acids because only about 1% of its molecules dissociate in aqueous solutions at typical concentrations. For example, in a solution containing 0.1 mole of $HC_2H_3O_2$ per liter, for every 100 molecules of $HC_2H_3O_2$ originally dissolved in water, approximately 99 molecules of $HC_2H_3O_2$ remain intact (see Fig. 4.8). That is, only one molecule out of every 100 dissociates (to produce one H^+ ion and one $C_2H_3O_2^-$ ion).

Because acetic acid is a weak electrolyte, it is called a **weak acid.** Any acid, such as acetic acid, that *dissociates (ionizes) only to a slight extent in aqueous solutions is called a weak acid.* In Chapter 14 we will explore the subject of weak acids in detail.

The most common weak base is ammonia (NH_3). When ammonia is dissolved in water, it reacts as follows:

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

The solution is *basic* because OH^- ions are produced. Ammonia is called a **weak base** because *the resulting solution is a weak electrolyte;* that is, very few ions are formed. In fact, in a solution containing 0.1 mole of NH_3 per liter, for every 100 molecules of NH_3

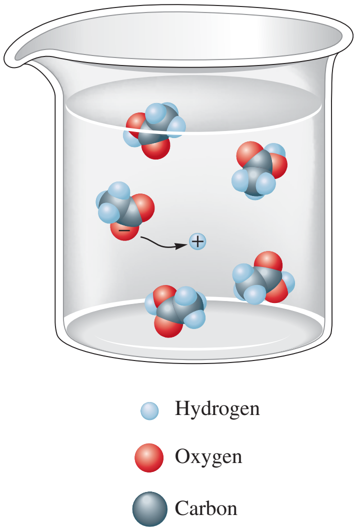


FIGURE 4.8
Acetic acid ($HC_2H_3O_2$) exists in water mostly as undissociated molecules. Only a small percentage of the molecules are ionized.

home to try to formulate a model that could account for his data. He wrote, “I got the idea in the night of the 17th of May in the year 1883, and I could not sleep that night until I had worked through the whole problem.” His idea was that ions were responsible for conducting electricity through a solution.

Back at Uppsala, Arrhenius took his doctoral dissertation containing the new theory to his advisor, Professor Cleve, an eminent chemist and the discoverer of the elements holmium and thulium. Cleve’s uninterested response was what Arrhenius had expected. It was in keeping with Cleve’s resistance to new ideas—he had not even accepted Mendeleev’s periodic table, introduced 10 years earlier.

It is a long-standing custom that before a doctoral degree is granted, the dissertation must be defended before a panel of professors. Although this procedure is still followed at most universities today, the problems are usually worked out in private with the evaluating professors before the actual defense. However, when Arrhenius did it, the dissertation defense was an open debate, which could be rancorous and humiliating. Knowing that it would be unwise to antagonize his professors, Arrhenius downplayed his convictions about his new theory as he defended his dissertation. His diplomacy paid off: He was awarded his degree, albeit reluctantly, because the professors still did not believe his model and considered him to be a marginal scientist, at best.

Such a setback could have ended his scientific career, but Arrhenius was a crusader; he was determined to see his theory triumph. He promptly embarked on a political campaign, enlisting the aid of several prominent scientists, to get his theory accepted.

Ultimately, the ionic theory triumphed. Arrhenius’s fame spread, and honors were heaped on him, culminating in the Nobel Prize in chemistry in 1903. Not one to rest on his laurels, Arrhenius turned to new fields, including astronomy; he formulated a new theory that the solar system may have come into being through the collision of stars. His exceptional versatility led him to study the use of serums to fight disease, energy resources and conservation, and the origin of life.

Additional insight on Arrhenius and his scientific career can be obtained from his address on receiving the Willard Gibbs Award. See *Journal of the American Chemical Society* 36 (1912): 353.

originally dissolved, only one NH_4^+ ion and one OH^- ion are produced; 99 molecules of NH_3 remain unreacted (see Fig. 4.9).

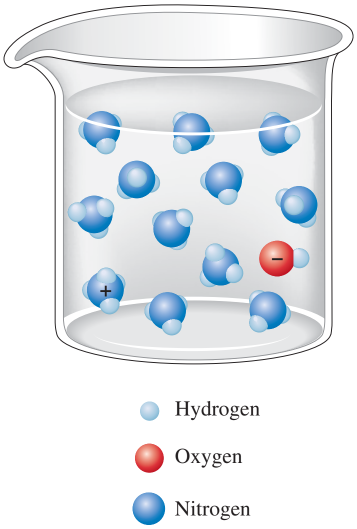


FIGURE 4.9
The reaction of NH_3 in water.

Nonelectrolytes

Nonelectrolytes are substances that dissolve in water but do not produce any ions, as shown in Fig. 4.4(c). An example of a nonelectrolyte is ethanol (see Fig. 4.3 for the structural formula). When ethanol dissolves, entire C_2H_5OH molecules are dispersed in the water. Since the molecules do not break up into ions, the resulting solution does not conduct an electric current. Another common nonelectrolyte is table sugar (sucrose, $C_{12}H_{22}O_{11}$), which is very soluble in water but which produces no ions when it dissolves. The sucrose molecules remain intact.

4.3 The Composition of Solutions

Chemical reactions often take place when two solutions are mixed. To perform stoichiometric calculations in such cases, we must know two things: (1) the *nature of the reaction,* which depends on the exact forms the chemicals take when dissolved, and (2) the *amounts of chemicals* present in the solutions, usually expressed as concentrations.

The concentration of a solution can be described in many different ways, as we will see in Chapter 11. At this point we will consider only the most commonly used expression of concentration, **molarity** (M), which is defined as *moles of solute per volume of solution in liters:*

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

A solution that is 1.0 molar (written as 1.0 M) contains 1.0 mole of solute per liter of solution.

Sample Exercise 4.1

Calculation of Molarity I

Calculate the molarity of a solution prepared by dissolving 11.5 g of solid NaOH in enough water to make 1.50 L of solution.

Solution

To find the molarity of the solution, we first compute the number of moles of solute using the molar mass of NaOH (40.00 g/mol):

$$11.5\ \cancel{\text{g NaOH}} \times \frac{1\ \text{mol NaOH}}{40.00\ \cancel{\text{g NaOH}}} = 0.288\ \text{mol NaOH}$$

Then we divide by the volume of the solution in liters:

$$\text{Molarity} = \frac{\text{mol solute}}{\text{L solution}} = \frac{0.288\ \text{mol NaOH}}{1.50\ \text{L solution}} = 0.192\ M\ \text{NaOH}$$

See Exercises 4.21 and 4.22.

Sample Exercise 4.2

Calculation of Molarity II

Calculate the molarity of a solution prepared by dissolving 1.56 g of gaseous HCl in enough water to make 26.8 mL of solution.

Solution

First we calculate the number of moles of HCl (molar mass = 36.46 g/mol):

$$1.56\ \cancel{\text{g HCl}} \times \frac{1\ \text{mol HCl}}{36.46\ \cancel{\text{g HCl}}} = 4.28 \times 10^{-2}\ \text{mol HCl}$$

Next we must change the volume of the solution to liters:

$$26.8\ \cancel{\text{mL}} \times \frac{1\ \text{L}}{1000\ \cancel{\text{mL}}} = 2.68 \times 10^{-2}\ \text{L}$$

Finally, we divide the moles of solution by the liters of solution:

$$\text{Molarity} = \frac{4.28 \times 10^{-2}\ \text{mol HCl}}{2.68 \times 10^{-2}\ \text{L solution}} = 1.60\ M\ \text{HCl}$$

See Exercises 4.21 and 4.22.

It is important to realize that the conventional description of a solution's concentration may not accurately reflect the true composition of the solution. Solution concentration is always given in terms of the form of the solute *before* it dissolves. For example, when a solution is described as being 1.0 M NaCl, this means that the solution was prepared by dissolving 1.0 mole of solid NaCl in enough water to make 1.0 liter of solution; it does not mean that the solution contains 1.0 mole of NaCl units. Actually, the solution contains 1.0 mole of Na^+ ions and 1.0 mole of Cl^- ions. This situation is further illustrated in Sample Exercise 4.3.

Sample Exercise 4.3

Concentrations of Ions I

Give the concentration of each type of ion in the following solutions:

a. 0.50 M $Co(NO_3)_2$
b. 1 M $Fe(ClO_4)_3$

An aqueous solution of $Co(NO_3)_2$.

Solution

a. When solid $Co(NO_3)_2$ dissolves, the cobalt(II) cation and the nitrate anions separate:

$$Co(NO_3)_2(s) \xrightarrow{H_2O} Co^{2+}(aq) + 2NO_3^-(aq)$$

For each mole of $Co(NO_3)_2$ that is dissolved, the solution contains 1 mol Co^{2+} ions and 2 mol NO_3^- ions. Thus a solution that is 0.50 M $Co(NO_3)_2$ contains 0.50 M Co^{2+} and (2×0.50) M NO_3^- or 1.0 M NO_3^-.

b. When solid $Fe(ClO_4)_3$ dissolves, the iron(III) cation and the perchlorate anions separate:

$$Fe(ClO_4)_3(s) \xrightarrow{H_2O} Fe^{3+}(aq) + 3ClO_4^-(aq)$$

Thus a solution that is described as 1 M $Fe(ClO_4)_3$ actually contains 1 M Fe^{3+} ions and 3 M ClO_4^- ions.

See Exercises 14.23 and 14.24.

Often chemists need to determine the number of moles of solute present in a given volume of a solution of known molarity. The procedure for doing this is easily derived from the definition of molarity. If we multiply the molarity of a solution by the volume (in liters) of a particular sample of the solution, we get the moles of solute present in that sample:

$$M = \frac{\text{moles of solute}}{\text{liters of solution}}$$

$$\text{Liters of solution} \times \text{molarity} = \cancel{\text{liters of solution}} \times \frac{\text{moles of solute}}{\cancel{\text{liters of solution}}} = \text{moles of solute}$$

This procedure is demonstrated in Sample Exercises 4.4 and 4.5.

Sample Exercise 4.4

Concentrations of Ions II

Calculate the number of moles of Cl^- ions in 1.75 L of 1.0×10^{-3} M $ZnCl_2$.

Solution

When solid $ZnCl_2$ dissolves, it produces ions as follows:

$$ZnCl_2(s) \xrightarrow{H_2O} Zn^{2+}(aq) + 2Cl^-(aq)$$

Thus a 1.0×10^{-3} M $ZnCl_2$ solution contains 1.0×10^{-3} M Zn^{2+} ions and 2.0×10^{-3} M Cl^- ions. To calculate the moles of Cl^- ions in 1.75 L of the 1.0×10^{-3} M $ZnCl_2$ solution, we must multiply the volume times the molarity:

$$\begin{aligned}1.75 \text{ L solution} \times 2.0 \times 10^{-3}\ M\ Cl^- &= 1.75\ \cancel{\text{L solution}} \times \frac{2.0 \times 10^{-3} \text{ mol } Cl^-}{\cancel{\text{L solution}}} \\ &= 3.5 \times 10^{-3} \text{ mol } Cl^-\end{aligned}$$

See Exercise 4.25.

Sample Exercise 4.5

Concentration and Volume

Typical blood serum is about 0.14 M NaCl. What volume of blood contains 1.0 mg NaCl?

Solution

We must first determine the number of moles represented by 1.0 mg NaCl (molar mass = 58.45 g/mol):

$$1.0\ \cancel{\text{mg NaCl}} \times \frac{1\ \cancel{\text{g NaCl}}}{1000\ \cancel{\text{mg NaCl}}} \times \frac{1 \text{ mol NaCl}}{58.45\ \cancel{\text{g NaCl}}} = 1.7 \times 10^{-5} \text{ mol NaCl}$$

Next, we must determine what volume of 0.14 M NaCl solution contains 1.7×10^{-5} mol NaCl. There is some volume, call it V, that when multiplied by the molarity of this solution will yield 1.7×10^{-5} mol NaCl. That is:

$$V \times \frac{0.14 \text{ mol NaCl}}{\text{L solution}} = 1.7 \times 10^{-5} \text{ mol NaCl}$$

We want to solve for the volume:

$$V = \frac{1.7 \times 10^{-5} \cancel{\text{mol NaCl}}}{\dfrac{0.14 \cancel{\text{mol NaCl}}}{\text{L solution}}} = 1.2 \times 10^{-4} \text{ L solution}$$

Thus 0.12 mL of blood contains 1.7×10^{-5} mol NaCl or 1.0 mg NaCl.

See Exercises 4.27 and 4.28.

A **standard solution** is a *solution whose concentration is accurately known.* Standard solutions, often used in chemical analysis, can be prepared as shown in Fig. 4.10 and in Sample Exercise 4.6.

Sample Exercise 4.6 Solutions of Known Concentration

To analyze the alcohol content of a certain wine, a chemist needs 1.00 L of an aqueous 0.200 M $K_2Cr_2O_7$ (potassium dichromate) solution. How much solid $K_2Cr_2O_7$ must be weighed out to make this solution?

Solution

We must first determine the moles of $K_2Cr_2O_7$ required:

$$1.00 \cancel{\text{L solution}} \times \frac{0.200 \text{ mol } K_2Cr_2O_7}{\cancel{\text{L solution}}} = 0.200 \text{ mol } K_2Cr_2O_7$$

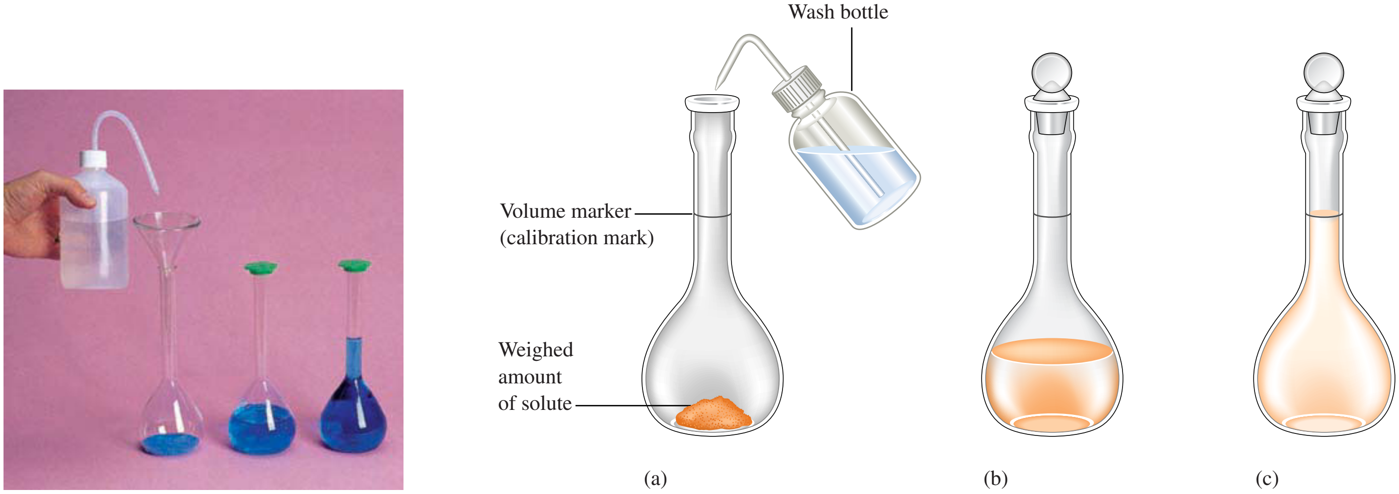


FIGURE 4.10
Steps involved in the preparation of a standard aqueous solution. (a) Put a weighed amount of a substance (the solute) into the volumetric flask, and add a small quantity of water. (b) Dissolve the solid in the water by gently swirling the flask (*with the stopper in place*). (c) Add more water (with gentle swirling) until the level of the solution just reaches the mark etched on the neck of the flask. Then mix the solution thoroughly by inverting the flask several times.

This amount can be converted to grams using the molar mass of $K_2Cr_2O_7$ (294.18 g/mol).

$$0.200\ \cancel{\text{mol } K_2Cr_2O_7} \times \frac{294.20\text{ g } K_2Cr_2O_7}{\cancel{\text{mol } K_2Cr_2O_7}} = 58.8\text{ g } K_2Cr_2O_7$$

Thus, to make 1.00 L of 0.200 M $K_2Cr_2O_7$, the chemist must weigh out 58.8 g $K_2Cr_2O_7$, transfer it to a 1.00-L volumetric flask, and add distilled water to the mark on the flask.

See Exercises 4.29a and c and 4.30c and e.

Dilution

Visualization: Dilution

Dilution with water does not alter the numbers of moles of solute present.

To save time and space in the laboratory, routinely used solutions are often purchased or prepared in concentrated form (called *stock solutions*). Water is then added to achieve the molarity desired for a particular solution. This process is called **dilution.** For example, the common acids are purchased as concentrated solutions and diluted as needed. A typical dilution calculation involves determining how much water must be added to an amount of stock solution to achieve a solution of the desired concentration. The key to doing these calculations is to remember that

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

because only water (no solute) is added to accomplish the dilution.

For example, suppose we need to prepare 500. mL of 1.00 M acetic acid ($HC_2H_3O_2$) from a 17.4 M stock solution of acetic acid. What volume of the stock solution is required? The first step is to determine the number of moles of acetic acid in the final solution by multiplying the volume by the molarity (remembering that the volume must be changed to liters):

$$500.\ \cancel{\text{mL solution}} \times \frac{1\ \cancel{\text{L solution}}}{1000\ \cancel{\text{mL solution}}} \times \frac{1.00\text{ mol } HC_2H_3O_2}{\cancel{\text{L solution}}} = 0.500\text{ mol } HC_2H_3O_2$$

Thus we need to use a volume of 17.4 M acetic acid that contains 0.500 mol $HC_2H_3O_2$. That is,

$$V \times \frac{17.4\text{ mol } HC_2H_3O_2}{\text{L solution}} = 0.500\text{ mol } HC_2H_3O_2$$

Solving for V gives

$$V = \frac{0.500\ \cancel{\text{mol } HC_2H_3O_2}}{\dfrac{17.4\ \cancel{\text{mol } HC_2H_3O_2}}{\text{L solution}}} = 0.0287\text{ L or } 28.7\text{ mL solution}$$

Thus, to make 500 mL of a 1.00 M acetic acid solution, we can take 28.7 mL of 17.4 M acetic acid and dilute it to a total volume of 500 mL with distilled water.

A dilution procedure typically involves two types of glassware: a pipet and a volumetric flask. A *pipet* is a device for accurately measuring and transferring a given volume of solution. There are two common types of pipets: *volumetric* (or *transfer*) *pipets* and *measuring pipets,* as shown in Fig. 4.11. Volumetric pipets come in specific sizes, such as 5 mL, 10 mL, 25 mL, and so on. Measuring pipets are used to measure volumes for which a volumetric pipet is not available. For example, we would use a measuring pipet as shown in Fig. 4.12 on page 139 to deliver 28.7 mL of 17.4 M acetic acid into a 500-mL volumetric flask and then add water to the mark to perform the dilution described above.

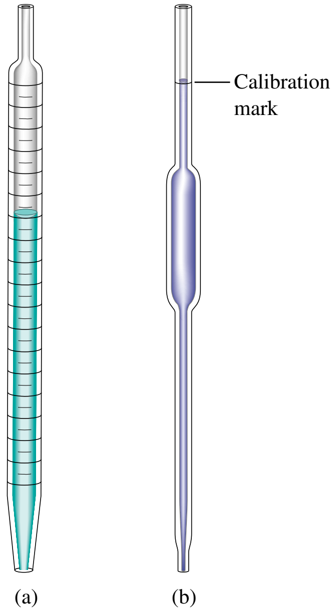


FIGURE 4.11
(a) A measuring pipet is graduated and can be used to measure various volumes of liquid accurately. (b) A volumetric (transfer) pipet is designed to measure one volume accurately. When filled to the mark, it delivers the volume indicated on the pipet.

CHEMICAL IMPACT

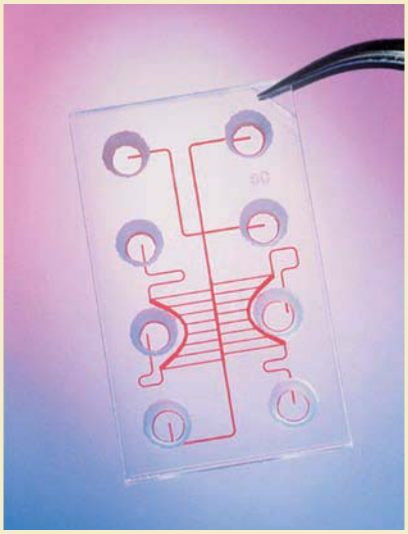
Tiny Laboratories

One of the major impacts of modern technology is to make things smaller. The best example is the computer. Calculations that 30 years ago required a machine the size of a large room now can be carried out on a hand-held calculator. This tendency toward miniaturization is also having a major impact on the science of chemical analysis. Using the techniques of computer chip makers, researchers are now constructing minuscule laboratories on the surface of a tiny chip made of silicon, glass, or plastic (see photo). Instead of electrons, 10^{-6} to 10^{-9} L of liquids moves between reaction chambers on the chip through tiny capillaries. The chips typically contain no moving parts. Instead of conventional pumps, the chip-based laboratories use voltage differences to move liquids that contain ions from one reaction chamber to another.

Microchip laboratories have many advantages. They require only tiny amounts of sample. This is especially advantageous for expensive, difficult-to-prepare materials or in cases such as criminal investigations, where only small amounts of evidence may exist. The chip laboratories also minimize contamination because they represent a “closed system” once the material has been introduced to the chip. In addition, the chips can be made to be disposable to prevent cross-contamination of different samples.

The chip laboratories present some difficulties not found in macroscopic laboratories. The main problem concerns the large surface area of the capillaries and reaction chambers relative to the sample volume. Molecules or biological cells in the sample solution encounter so much “wall” that they may undergo unwanted reactions with the wall materials. Glass seems to present the least of these problems, and the walls of silicon chip laboratories can be protected by formation of relatively inert silicon dioxide. Because plastic is inexpensive, it seems a good choice for disposable chips, but plastic also is the most reactive with the samples and the least durable of the available materials.

Caliper Technologies Corporation, of Palo Alto, California, is working toward creating a miniature chemistry laboratory about the size of a toaster that can be used with “plug-in” chip-based laboratories. Various chips would be furnished with the unit that would be appropriate for different types of analyses. The entire unit would be connected to a computer to collect and analyze the data. There is even the possibility that these “laboratories” could be used in the home to perform analyses such as blood sugar and blood cholesterol and to check for the presence of bacteria such as *E. coli* and many others. This would revolutionize the health care industry.



Plastic chips such as this one made by Caliper Technologies are being used to perform laboratory procedures traditionally done with test tubes.

Adapted from “The Incredible Shrinking Laboratory,” by Corinna Wu, as appeared in *Science News,* Vol. 154, August 15, 1998, p. 104.

Sample Exercise 4.7 Concentration and Volume

What volume of 16 *M* sulfuric acid must be used to prepare 1.5 L of a 0.10 *M* H_2SO_4 solution?

Solution

We must first determine the moles of H_2SO_4 in 1.5 L of 0.10 *M* H_2SO_4:

$$1.5\ \cancel{\text{L solution}} \times \frac{0.10\ \text{mol H}_2\text{SO}_4}{\cancel{\text{L solution}}} = 0.15\ \text{mol H}_2\text{SO}_4$$

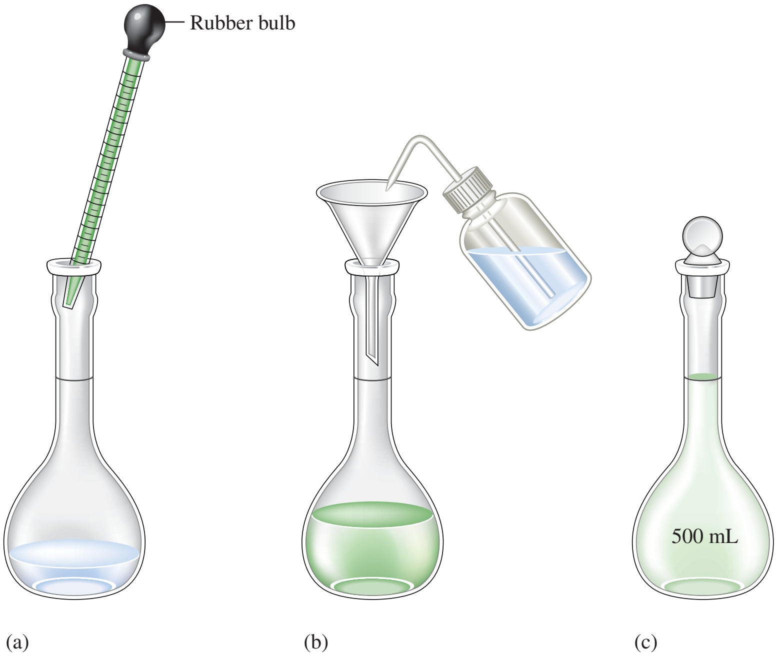


FIGURE 4.12
(a) A measuring pipet is used to transfer 28.7 mL of 17.4 *M* acetic acid solution to a volumetric flask. (b) Water is added to the flask to the calibration mark. (c) The resulting solution is 1.00 *M* acetic acid.

Next we must find the volume of 16 *M* H_2SO_4 that contains 0.15 mol H_2SO_4:

$$V \times \frac{16 \text{ mol } H_2SO_4}{\text{L solution}} = 0.15 \text{ mol } H_2SO_4$$

Solving for *V* gives

$$V = \frac{0.15 \cancel{\text{mol } H_2SO_4}}{\dfrac{16 \cancel{\text{mol } H_2SO_4}}{1 \text{ L solution}}} = 9.4 \times 10^{-3} \text{ L or } 9.4 \text{ mL solution}$$

In diluting an acid, "Do what you oughta, always add acid to water."

Thus, to make 1.5 L of 0.10 *M* H_2SO_4 using 16 *M* H_2SO_4, we must take 9.4 mL of the concentrated acid and dilute it with water to 1.5 L. The correct way to do this is to add the 9.4 mL of acid to about 1 L of distilled water and then dilute to 1.5 L by adding more water.

See Exercises 4.29b and d and 4.30a, b, and d.

As noted earlier, the central idea in performing the calculations associated with dilutions is to recognize that the moles of solute are not changed by the dilution. Another way to express this condition is by the following equation:

$$M_1V_1 = M_2V_2$$

where M_1 and V_1 represent the molarity and volume of the original solution (before dilution) and M_2 and V_2 represent the molarity and volume of the diluted solution. This equation makes sense because

$$\begin{aligned} M_1 \times V_1 &= \text{mol solute before dilution} \\ &= \text{mol solute after dilution} = M_2 \times V_2 \end{aligned}$$

Repeat Sample Exercise 4.7 using the equation $M_1V_1 = M_2V_2$. Note that in doing so

$$M_1 = 16\,M \qquad M_2 = 0.10\,M \qquad V_2 = 1.5\text{ L}$$

and V_1 is the unknown quantity sought. The equation $M_1V_1 = M_2V_2$ always holds for a dilution. This equation will be easy for you to remember if you understand where it comes from.

4.4 Types of Chemical Reactions

Although we have considered many reactions so far in this text, we have examined only a tiny fraction of the millions of possible chemical reactions. To make sense of all these reactions, we need some system for grouping reactions into classes. Although there are many different ways to do this, we will use the system most commonly used by practicing chemists:

Types of Solution Reactions

- Precipitation reactions
- Acid–base reactions
- Oxidation–reduction reactions

Virtually all reactions can be put into one of these classes. We will define and illustrate each type in the following sections.

FIGURE 4.13
When yellow aqueous potassium chromate is added to a colorless barium nitrate solution, yellow barium chromate precipitates.

A *precipitation reaction* also can be called a *double displacement reaction.*

Visualization: Precipitation Reactions

The quantitative aspects of precipitation reactions are covered in Chapter 15.

When ionic compounds dissolve in water, the *resulting solution contains the separated ions.*

4.5 Precipitation Reactions

When two solutions are mixed, an insoluble substance sometimes forms; that is, a solid forms and separates from the solution. Such a reaction is called a **precipitation reaction,** and the solid that forms is called a **precipitate.** For example, a precipitation reaction occurs when an aqueous solution of potassium chromate, $K_2CrO_4(aq)$, which is yellow, is added to a colorless aqueous solution containing barium nitrate, $Ba(NO_3)_2(aq)$. As shown in Fig. 4.13, when these solutions are mixed, a yellow solid forms. What is the equation that describes this chemical change? To write the equation, we must know the identities of the reactants and products. The reactants have already been described: $K_2CrO_4(aq)$ and $Ba(NO_3)_2(aq)$. Is there some way we can predict the identities of the products? In particular, what is the yellow solid?

The best way to predict the identity of this solid is to think carefully about what products are possible. To do this, we need to know what species are present in the solution after the two reactant solutions are mixed. First, let's think about the nature of each reactant solution. The designation $Ba(NO_3)_2(aq)$ means that barium nitrate (a white solid) has been dissolved in water. Notice that barium nitrate contains the Ba^{2+} and NO_3^- ions. *Remember: In virtually every case, when a solid containing ions dissolves in water, the ions separate* and move around independently. That is, $Ba(NO_3)_2(aq)$ does not contain $Ba(NO_3)_2$ units; it contains separated Ba^{2+} and NO_3^- ions. See Fig. 4.14(a).

Similarly, since solid potassium chromate contains the K^+ and CrO_4^{2-} ions, an aqueous solution of potassium chromate (which is prepared by dissolving solid K_2CrO_4 in water) contains these separated ions, as shown in Fig. 4.14(b).

We can represent the mixing of $K_2CrO_4(aq)$ and $Ba(NO_3)_2(aq)$ in two ways. First, we can write

$$K_2CrO_4(aq) + Ba(NO_3)_2(aq) \longrightarrow \text{products}$$

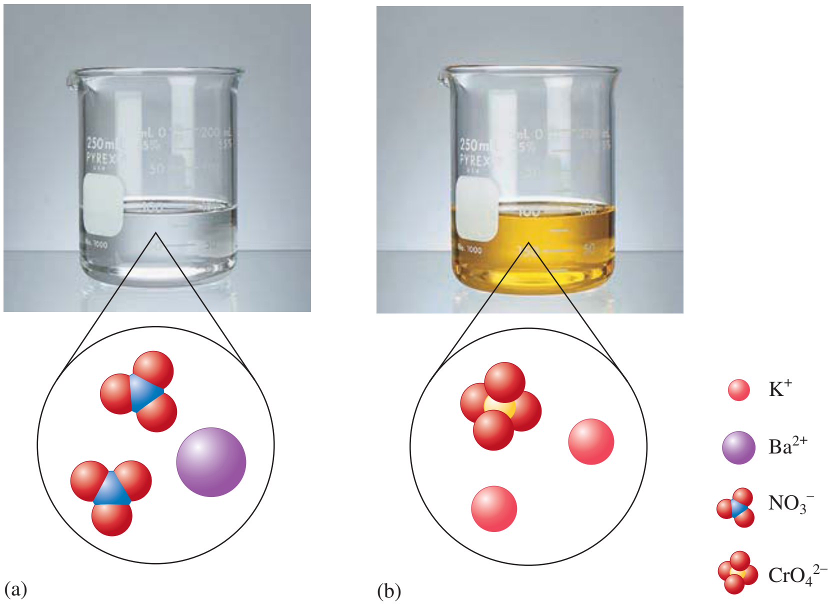


FIGURE 4.14
Reactant solutions: (a) $Ba(NO_3)_2(aq)$ and (b) $K_2CrO_4(aq)$.

However, a much more accurate representation is

$$\underbrace{2K^+(aq) + CrO_4^{2-}(aq)}_{\text{The ions in } K_2CrO_4(aq)} + \underbrace{Ba^{2+}(aq) + 2NO_3^-(aq)}_{\text{The ions in } Ba(NO_3)_2(aq)} \longrightarrow \text{products}$$

Thus the mixed solution contains the ions:

$$K^+ \qquad CrO_4^{2-} \qquad Ba^{2+} \qquad NO_3^-$$

as illustrated in Fig. 4.15(a).

How can some or all of these ions combine to form a yellow solid? This is not an easy question to answer. In fact, predicting the products of a chemical reaction is one of the hardest things a beginning chemistry student is asked to do. Even an experienced chemist, when confronted with a new reaction, is often not sure what will happen. The chemist tries to think of the various possibilities, considers the likelihood of each

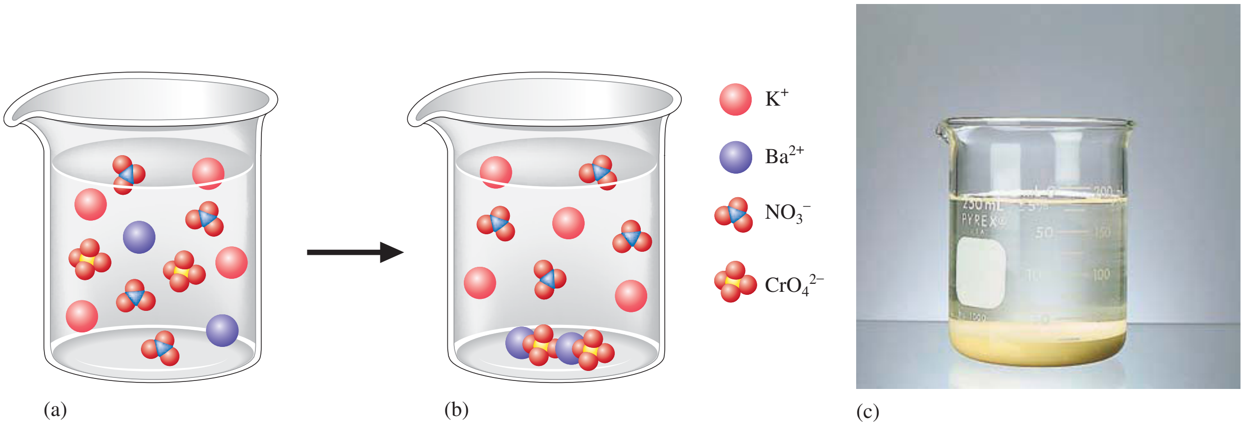


FIGURE 4.15
The reaction of $K_2CrO_4(aq)$ and $Ba(NO_3)_2(aq)$. (a) The molecular-level "picture" of the mixed solution before any reaction has occurred. (b) The molecular-level "picture" of the solution after the reaction has occurred to form $BaCrO_4(s)$. *Note:* $BaCrO_4(s)$ is not molecular. It actually contains Ba^{2+} and CrO_4^{2-} ions packed together in a lattice. (c) A photo of the solution after the reaction has occurred, showing the solid $BaCrO_4$ on the bottom.

possibility, and then makes a prediction (an educated guess). Only after identifying each product *experimentally* is the chemist sure what reaction has taken place. However, an educated guess is very useful because it provides a place to start. It tells us what kinds of products we are most likely to find. We already know some things that will help us predict the products of the above reaction.

1. When ions form a solid compound, the compound must have a zero net charge. Thus the products of this reaction must contain *both anions and cations.* For example, K^+ and Ba^{2+} could not combine to form the solid, nor could CrO_4^{2-} and NO_3^-.
2. Most ionic materials contain only two types of ions: one type of cation and one type of anion (for example, NaCl, KOH, Na_2SO_4, K_2CrO_4, $Co(NO_3)_2$, NH_4Cl, Na_2CO_3).

The possible combinations of a given cation and a given anion from the list of ions K^+, CrO_4^{2-}, Ba^{2+}, and NO_3^- are

$$K_2CrO_4 \qquad KNO_3 \qquad BaCrO_4 \qquad Ba(NO_3)_2$$

Which of these possibilities is most likely to represent the yellow solid? We know it's not K_2CrO_4 or $Ba(NO_3)_2$. They are the reactants. They were present (dissolved) in the separate solutions that were mixed. The only real possibilities for the solid that formed are

$$KNO_3 \quad \text{and} \quad BaCrO_4$$

To decide which of these most likely represents the yellow solid, we need more facts. An experienced chemist knows that the K^+ ion and the NO_3^- ion are both colorless. Thus, if the solid is KNO_3, it should be white, not yellow. On the other hand, the CrO_4^{2-} ion is yellow (note in Fig. 4.14 that $K_2CrO_4(aq)$ is yellow). Thus the yellow solid is almost certainly $BaCrO_4$. Further tests show that this is the case.

So far we have determined that one product of the reaction between $K_2CrO_4(aq)$ and $Ba(NO_3)_2(aq)$ is $BaCrO_4(s)$, but what happened to the K^+ and NO_3^- ions? The answer is that these ions are left dissolved in the solution; KNO_3 does not form a solid when the K^+ and NO_3^- ions are present in this much water. In other words, if we took solid KNO_3 and put it in the same quantity of water as is present in the mixed solution, it would dissolve. Thus, when we mix $K_2CrO_4(aq)$ and $Ba(NO_3)_2(aq)$, $BaCrO_4(s)$ forms, but KNO_3 is left behind in solution (we write it as $KNO_3(aq)$). Thus the overall equation for this precipitation reaction using the formulas of the reactants and products is

$$K_2CrO_4(aq) + Ba(NO_3)_2(aq) \longrightarrow BaCrO_4(s) + 2KNO_3(aq)$$

As long as water is present, the KNO_3 remains dissolved as separated ions. (See Fig. 4.15 to help visualize what is happening in this reaction. Note the solid $BaCrO_4$ on the bottom of the container, while the K^+ and NO_3^- ions remain dispersed in the solution.) If we removed the solid $BaCrO_4$ and then evaporated the water, white solid KNO_3 would be obtained; the K^+ and NO_3^- ions would assemble themselves into solid KNO_3 when the water is removed.

FIGURE 4.16
Precipitation of silver chloride by mixing solutions of silver nitrate and potassium chloride. The K^+ and NO_3^- ions remain in solution.

Now let's consider another example. When an aqueous solution of silver nitrate is added to an aqueous solution of potassium chloride, a white precipitate forms, as shown in Fig. 4.16. We can represent what we know so far as

$$AgNO_3(aq) + KCl(aq) \longrightarrow \text{unknown white solid}$$

Remembering that when ionic substances dissolve in water, the ions separate, we can write

$$\underbrace{Ag^+, NO_3^-}_{\substack{\text{In silver}\\\text{nitrate}\\\text{solution}}} + \underbrace{K^+, Cl^-}_{\substack{\text{In potassium}\\\text{chloride}\\\text{solution}}} \longrightarrow \underbrace{Ag^+, NO_3^-, K^+, Cl^-}_{\substack{\text{Combined solution,}\\\text{before reaction}}} \longrightarrow \text{white solid}$$

Since we know the white solid must contain both positive and negative ions, the possible compounds that can be assembled from this collection of ions are

$$AgNO_3 \qquad KCl \qquad AgCl \qquad KNO_3$$

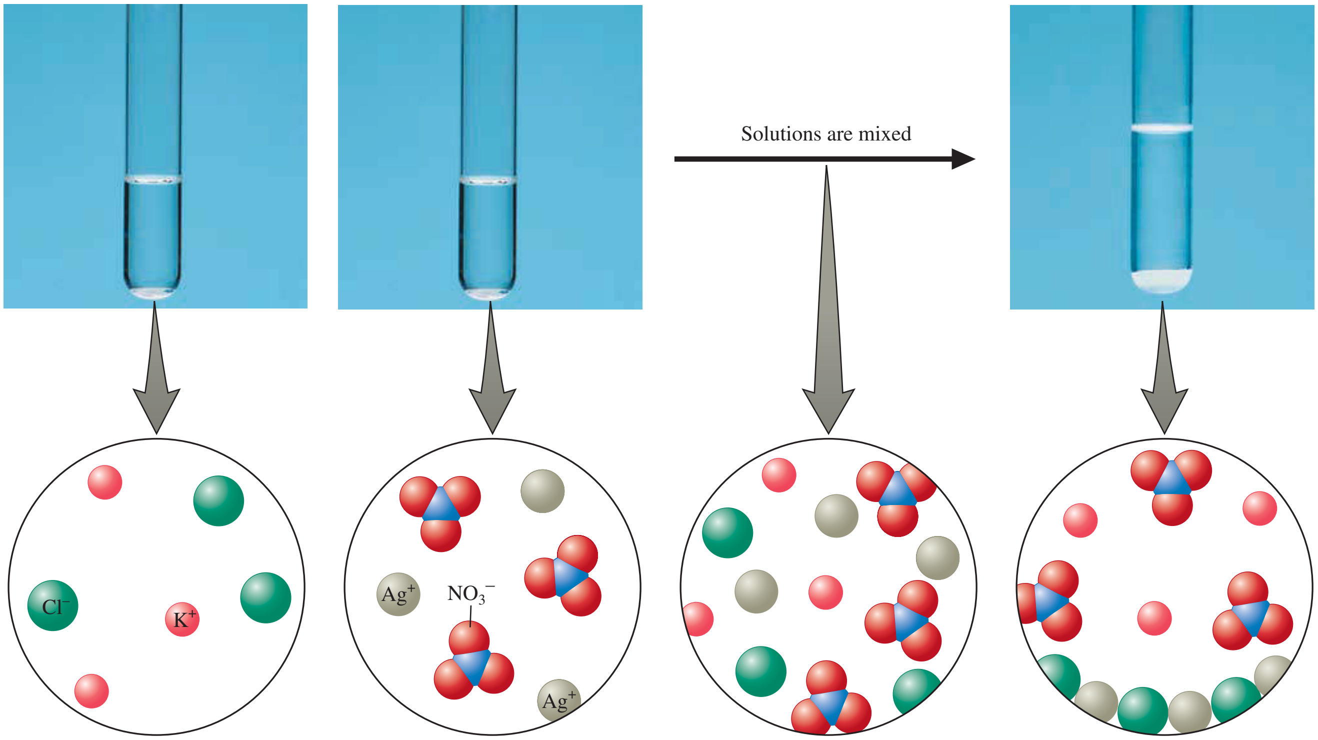


FIGURE 4.17

Photos and accompanying molecular-level representations illustrating the reaction of KCl(aq) with $AgNO_3$(aq) to form AgCl(s). Note that it is not possible to have a photo of the mixed solution before the reaction occurs, because it is an imaginary step that we use to help visualize the reaction. Actually, the reaction occurs immediately when the two solutions are mixed.

Visualization: Reactions of Silver I

Since $AgNO_3$ and KCl are the substances dissolved in the two reactant solutions, we know that they do not represent the white solid product. Therefore, the only real possibilities are

$$AgCl \quad \text{and} \quad KNO_3$$

From the first example considered, we know that KNO_3 is quite soluble in water. Thus solid KNO_3 will not form when the reactant solids are mixed. The product must be AgCl(s) (which can be proved by experiment to be true). The overall equation for the reaction now can be written

$$AgNO_3(aq) + KCl(aq) \longrightarrow AgCl(s) + KNO_3(aq)$$

Figure 4.17 shows the result of mixing aqueous solutions of $AgNO_3$ and KCl, including a microscopic visualization of the reaction.

Notice that in these two examples we had to apply both concepts (solids must have a zero net charge) and facts (KNO_3 is very soluble in water, CrO_4^{2-} is yellow, and so on). Doing chemistry requires both understanding ideas and remembering key information. Predicting the identity of the solid product in a precipitation reaction requires knowledge of the solubilities of common ionic substances. As an aid in predicting the products of precipitation reactions, some simple solubility rules are given in Table 4.1. You should memorize these rules.

The phrase *slightly soluble* used in the solubility rules in Table 4.1 means that the tiny amount of solid that dissolves is not noticeable. The solid appears to be insoluble to the naked eye. Thus the terms *insoluble* and *slightly soluble* are often used interchangeably.

Note that the information in Table 4.1 allows us to predict that AgCl is the white solid formed when solutions of $AgNO_3$ and KCl are mixed. Rules 1 and 2 indicate that KNO_3 is soluble, and Rule 3 states that AgCl is insoluble.

TABLE 4.1 Simple Rules for the Solubility of Salts in Water

1. Most nitrate (NO_3^-) salts are soluble.
2. Most salts containing the alkali metal ions (Li^+, Na^+, K^+, Cs^+, Rb^+) and the ammonium ion (NH_4^+) are soluble.
3. Most chloride, bromide, and iodide salts are soluble. Notable exceptions are salts containing the ions Ag^+, Pb^{2+}, and Hg_2^{2+}.
4. Most sulfate salts are soluble. Notable exceptions are $BaSO_4$, $PbSO_4$, Hg_2SO_4, and $CaSO_4$.
5. Most hydroxide salts are only slightly soluble. The important soluble hydroxides are NaOH and KOH. The compounds $Ba(OH)_2$, $Sr(OH)_2$, and $Ca(OH)_2$ are marginally soluble.
6. Most sulfide (S^{2-}), carbonate (CO_3^{2-}), chromate (CrO_4^{2-}), and phosphate (PO_4^{3-}) salts are only slightly soluble.

Visualization: Solubility Rules

When solutions containing ionic substances are mixed, it will be helpful in determining the products if you think in terms of *ion interchange.* For example, in the preceding discussion we considered the results of mixing $AgNO_3(aq)$ and $KCl(aq)$. In determining the products, we took the cation from one reactant and combined it with the anion of the other reactant:

$$Ag^+ + NO_3^- + K^+ + Cl^- \longrightarrow$$

Possible solid products

The solubility rules in Table 4.1 allow us to predict whether either product forms as a solid.

To begin, focus on the ions in solution before any reaction occurs.

The key to dealing with the chemistry of an aqueous solution is first to *focus on the actual components of the solution before any reaction occurs* and then to figure out how these components will react with each other. Sample Exercise 4.8 illustrates this process for three different reactions.

Sample Exercise 4.8 Predicting Reaction Products

Using the solubility rules in Table 4.1, predict what will happen when the following pairs of solutions are mixed.

a. $KNO_3(aq)$ and $BaCl_2(aq)$
b. $Na_2SO_4(aq)$ and $Pb(NO_3)_2(aq)$
c. $KOH(aq)$ and $Fe(NO_3)_3(aq)$

Lead sulfate is a white solid.

Solution

a. The formula $KNO_3(aq)$ represents an aqueous solution obtained by dissolving solid KNO_3 in water to form a solution containing the hydrated ions $K^+(aq)$ and $NO_3^-(aq)$. Likewise, $BaCl_2(aq)$ represents a solution formed by dissolving solid $BaCl_2$ in water to produce $Ba^{2+}(aq)$ and $Cl^-(aq)$. When these two solutions are mixed, the resulting solution contains the ions K^+, NO_3^-, Ba^{2+}, and Cl^-. All ions are hydrated, but the (aq) is omitted for simplicity. To look for possible solid products, combine the cation from one reactant with the anion from the other:

$$K^+ + NO_3^- + Ba^{2+} + Cl^- \longrightarrow$$

Possible solid products

Solid $Fe(OH)_3$ forms when aqueous KOH and $Fe(NO_3)_3$ are mixed.

Note from Table 4.1 that the rules predict that both KCl and $Ba(NO_3)_2$ are soluble in water. Thus no precipitate forms when $KNO_3(aq)$ and $BaCl_2(aq)$ are mixed. All the ions remain dissolved in solution. No chemical reaction occurs.

b. Using the same procedures as in part a, we find that the ions present in the combined solution before any reaction occurs are Na^+, SO_4^{2-}, Pb^{2+}, and NO_3^-. The possible salts that could form precipitates are

$$Na^+ \quad + \quad SO_4^{2-} \quad + \quad Pb^{2+} \quad + \quad NO_3^- \quad \longrightarrow$$

The compound $NaNO_3$ is soluble, but $PbSO_4$ is insoluble (see Rule 4 in Table 4.1). When these solutions are mixed, $PbSO_4$ will precipitate from the solution. The balanced equation is

$$Na_2SO_4(aq) + Pb(NO_3)_2(aq) \longrightarrow PbSO_4(s) + 2NaNO_3(aq)$$

c. The combined solution (before any reaction occurs) contains the ions K^+, OH^-, Fe^{3+}, and NO_3^-. The salts that might precipitate are KNO_3 and $Fe(OH)_3$. The solubility rules in Table 4.1 indicate that both K^+ and NO_3^- salts are soluble. However, $Fe(OH)_3$ is only slightly soluble (Rule 5) and hence will precipitate. The balanced equation is

$$3KOH(aq) + Fe(NO_3)_3(aq) \longrightarrow Fe(OH)_3(s) + 3KNO_3(aq)$$

See Exercises 4.37 and 4.38.

4.6 Describing Reactions in Solution

In this section we will consider the types of equations used to represent reactions in solution. For example, when we mix aqueous potassium chromate with aqueous barium nitrate, a reaction occurs to form a precipitate ($BaCrO_4$) and dissolved potassium nitrate. So far we have written the overall or **formula equation** for this reaction:

$$K_2CrO_4(aq) + Ba(NO_3)_2(aq) \longrightarrow BaCrO_4(s) + 2KNO_3(aq)$$

Although the formula equation shows the reactants and products of the reaction, it does not give a correct picture of what actually occurs in solution. As we have seen, aqueous solutions of potassium chromate, barium nitrate, and potassium nitrate contain individual ions, not collections of ions, as implied by the formula equation. Thus the **complete ionic equation**

A strong electrolyte is a substance that completely breaks apart into ions when dissolved in water.

$$2K^+(aq) + CrO_4^{2-}(aq) + Ba^{2+}(aq) + 2NO_3^-(aq) \longrightarrow BaCrO_4(s) + 2K^+(aq) + 2NO_3^-(aq)$$

better represents the actual forms of the reactants and products in solution. *In a complete ionic equation, all substances that are strong electrolytes are represented as ions.*

The complete ionic equation reveals that only some of the ions participate in the reaction. The K^+ and NO_3^- ions are present in solution both before and after the reaction. The ions that do not participate directly in the reaction are called **spectator ions.** The ions that participate in this reaction are the Ba^{2+} and CrO_4^{2-} ions, which combine to form solid $BaCrO_4$:

Net ionic equations include only those components that undergo changes in the reaction.

$$Ba^{2+}(aq) + CrO_4^{2-}(aq) \longrightarrow BaCrO_4(s)$$

This equation, called the **net ionic equation,** includes only those solution components directly involved in the reaction. Chemists usually write the net ionic equation for a reaction in solution because it gives the actual forms of the reactants and products and includes only the species that undergo a change.

Three Types of Equations Are Used to Describe Reactions in Solution

- The **formula equation** gives the overall reaction stoichiometry but not necessarily the actual forms of the reactants and products in solution.
- The **complete ionic equation** represents as ions all reactants and products that are strong electrolytes.
- The **net ionic equation** includes only those solution components undergoing a change. Spectator ions are not included.

Sample Exercise 4.9

Writing Equations for Reactions

For each of the following reactions, write the formula equation, the complete ionic equation, and the net ionic equation.

a. Aqueous potassium chloride is added to aqueous silver nitrate to form a silver chloride precipitate plus aqueous potassium nitrate.
b. Aqueous potassium hydroxide is mixed with aqueous iron(III) nitrate to form a precipitate of iron(III) hydroxide and aqueous potassium nitrate.

Solution

a. Formula Equation

$$\mathrm{KCl}(aq) + \mathrm{AgNO_3}(aq) \longrightarrow \mathrm{AgCl}(s) + \mathrm{KNO_3}(aq)$$

Complete Ionic Equation

(*Remember:* Any ionic compound dissolved in water will be present as the separated ions.)

$$\underset{\substack{\uparrow\\ \text{Spectator}\\ \text{ion}}}{\mathrm{K}^+}(aq) + \mathrm{Cl}^-(aq) + \mathrm{Ag}^+(aq) + \underset{\substack{\uparrow\\ \text{Spectator}\\ \text{ion}}}{\mathrm{NO_3}^-}(aq) \longrightarrow \underset{\substack{\uparrow\\ \text{Solid,}\\ \text{not written}\\ \text{as separate ions}}}{\mathrm{AgCl}(s)} + \underset{\substack{\uparrow\\ \text{Spectator}\\ \text{ion}}}{\mathrm{K}^+}(aq) + \underset{\substack{\uparrow\\ \text{Spectator}\\ \text{ion}}}{\mathrm{NO_3}^-}(aq)$$

Canceling the spectator ions

$$\cancel{\mathrm{K}^+}(aq) + \mathrm{Cl}^-(aq) + \mathrm{Ag}^+(aq) + \cancel{\mathrm{NO_3}^-}(aq) \longrightarrow \mathrm{AgCl}(s) + \cancel{\mathrm{K}^+}(aq) + \cancel{\mathrm{NO_3}^-}(aq)$$

gives the following net ionic equation.

Net Ionic Equation

$$\mathrm{Cl}^-(aq) + \mathrm{Ag}^+(aq) \longrightarrow \mathrm{AgCl}(s)$$

b. Formula Equation

$$3\mathrm{KOH}(aq) + \mathrm{Fe(NO_3)_3}(aq) \longrightarrow \mathrm{Fe(OH)_3}(s) + 3\mathrm{KNO_3}(aq)$$

Complete Ionic Equation

$$3\mathrm{K}^+(aq) + 3\mathrm{OH}^-(aq) + \mathrm{Fe}^{3+}(aq) + 3\mathrm{NO_3}^-(aq) \longrightarrow \mathrm{Fe(OH)_3}(s) + 3\mathrm{K}^+(aq) + 3\mathrm{NO_3}^-(aq)$$

Net Ionic Equation

$$3\mathrm{OH}^-(aq) + \mathrm{Fe}^{3+}(aq) \longrightarrow \mathrm{Fe(OH)_3}(s)$$

See Exercises 4.39 through 4.44.

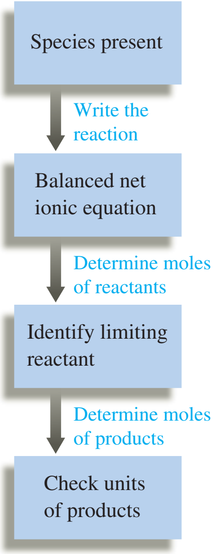
4.7 Stoichiometry of Precipitation Reactions

In Chapter 3 we covered the principles of chemical stoichiometry: the procedures for calculating quantities of reactants and products involved in a chemical reaction. Recall that in performing these calculations we first convert all quantities to moles and then use the coefficients of the balanced equation to assemble the appropriate mole ratios. In cases where reactants are mixed we must determine which reactant is limiting, since the reactant that is consumed first will limit the amounts of products formed. *These same principles apply to reactions that take place in solutions.* However, two points about solution reactions need special emphasis. The first is that it is sometimes difficult to tell immediately what reaction will occur when two solutions are mixed. Usually we must do some thinking about the various possibilities and then decide what probably will happen. The first step in this process *always* should be to write down the species that are actually present in the solution, as we did in Section 4.5. The second special point about solution reactions is that to obtain the moles of reactants we must use the volume of the solution and its molarity. This procedure was covered in Section 4.3.

We will introduce stoichiometric calculations for reactions in solution in Sample Exercise 4.10.

Sample Exercise 4.10 Determining the Mass of Product Formed

Calculate the mass of solid NaCl that must be added to 1.50 L of a 0.100 *M* $AgNO_3$ solution to precipitate all the Ag^+ ions in the form of AgCl.



Solution

When added to the $AgNO_3$ solution (which contains Ag^+ and NO_3^- ions), the solid NaCl dissolves to yield Na^+ and Cl^- ions. Thus the mixed solution contains the ions

$$Ag^+ \qquad NO_3^- \qquad Na^+ \qquad Cl^-$$

Note from Table 4.1 that $NaNO_3$ is soluble and AgCl is insoluble. Therefore, solid AgCl forms according to the following net ionic equation:

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$

In this case we must add enough Cl^- ions to react with all the Ag^+ ions present. Thus we must calculate the moles of Ag^+ ions present in 1.50 L of a 0.100 *M* $AgNO_3$ solution (remember that a 0.100 *M* $AgNO_3$ solution contains 0.100 *M* Ag^+ ions and 0.100 *M* NO_3^- ions):

$$1.50\ \cancel{L} \times \frac{0.100\ \text{mol Ag}^+}{\cancel{L}} = 0.150\ \text{mol Ag}^+$$

Because Ag^+ and Cl^- react in a 1:1 ratio, 0.150 mol Cl^- ions and thus 0.150 mol NaCl are required. We calculate the mass of NaCl required as follows:

$$0.150\ \cancel{\text{mol NaCl}} \times \frac{58.45\ \text{g NaCl}}{\cancel{\text{mol NaCl}}} = 8.77\ \text{g NaCl}$$

See Exercise 4.47.

Notice from Sample Exercise 4.10 that the procedures for doing stoichiometric calculations for solution reactions are very similar to those for other types of reactions. It is useful to think in terms of the following steps for reactions in solution.

Solving Stoichiometry Problems for Reactions in Solution

1 Identify the species present in the combined solution, and determine what reaction occurs.

2 Write the balanced net ionic equation for the reaction.

3 Calculate the moles of reactants.

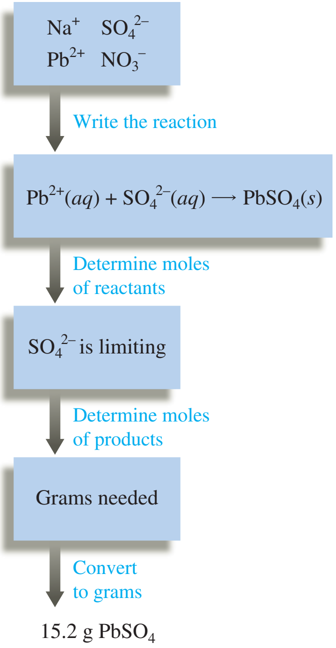
4 Determine which reactant is limiting.

5 Calculate the moles of product or products, as required.

6 Convert to grams or other units, as required.

Sample Exercise 4.11 Determining the Mass of Product Formed

When aqueous solutions of Na_2SO_4 and $Pb(NO_3)_2$ are mixed, $PbSO_4$ precipitates. Calculate the mass of $PbSO_4$ formed when 1.25 L of 0.0500 M $Pb(NO_3)_2$ and 2.00 L of 0.0250 M Na_2SO_4 are mixed.



Solution

1 *Identify the species present in the combined solution, and determine what reaction occurs.* When the aqueous solutions of Na_2SO_4 (containing Na^+ and SO_4^{2-} ions) and $Pb(NO_3)_2$ (containing Pb^{2+} and NO_3^- ions) are mixed, the resulting solution contains the ions Na^+, SO_4^{2-}, Pb^{2+}, and NO_3^-. Since $NaNO_3$ is soluble and $PbSO_4$ is insoluble (see Rule 4 in Table 4.1), solid $PbSO_4$ will form.

2 *Write the balanced net ionic equation for the reaction.* The net ionic equation is

$$Pb^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s)$$

3 *Calculate the moles of reactants.* Since 0.0500 M $Pb(NO_3)_2$ contains 0.0500 M Pb^{2+} ions, we can calculate the moles of Pb^{2+} ions in 1.25 L of this solution as follows:

$$1.25\ \cancel{L} \times \frac{0.0500\ \text{mol Pb}^{2+}}{\cancel{L}} = 0.0625\ \text{mol Pb}^{2+}$$

The 0.0250 M Na_2SO_4 solution contains 0.0250 M SO_4^{2-} ions, and the number of moles of SO_4^{2-} ions in 2.00 L of this solution is

$$2.00\ \cancel{L} \times \frac{0.0250\ \text{mol SO}_4^{2-}}{\cancel{L}} = 0.0500\ \text{mol SO}_4^{2-}$$

4 *Determine which reactant is limiting.* Because Pb^{2+} and SO_4^{2-} react in a 1:1 ratio, the amount of SO_4^{2-} will be limiting (0.0500 mol SO_4^{2-} is less than 0.0625 mol Pb^{2+}).

5 *Calculate the moles of product.* Since the Pb^{2+} ions are present in excess, only 0.0500 mol of solid $PbSO_4$ will be formed.

6 *Convert to grams of product.* The mass of $PbSO_4$ formed can be calculated using the molar mass of $PbSO_4$ (303.3 g/mol):

$$0.0500\ \cancel{\text{mol PbSO}_4} \times \frac{303.3\ \text{g PbSO}_4}{1\ \cancel{\text{mol PbSO}_4}} = 15.2\ \text{g PbSO}_4$$

See Exercises 4.49 and 4.50.

4.8 Acid–Base Reactions

Visualization: Proton Transfer

The Brønsted–Lowry concept of acids and bases will be discussed in detail in Chapter 14.

Earlier in this chapter we considered Arrhenius's concept of acids and bases: An acid is a substance that produces H^+ ions when dissolved in water, and a base is a substance that produces OH^- ions. Although these ideas are fundamentally correct, it is convenient to have a more general definition of a base, which includes substances that do not contain OH^- ions. Such a definition was provided by Johannes N. Brønsted (1879–1947) and Thomas M. Lowry (1874–1936), who defined acids and bases as follows:

An **acid** is a proton donor.

A **base** is a proton acceptor.

How do we know when to expect an acid–base reaction? One of the most difficult tasks for someone inexperienced in chemistry is to predict what reaction might occur when two solutions are mixed. With precipitation reactions, we found that the best way to deal with this problem is to focus on the species actually present in the mixed solution. This idea also applies to acid–base reactions. For example, when an aqueous solution of hydrogen chloride (HCl) is mixed with an aqueous solution of sodium hydroxide (NaOH), the combined solution contains the ions H^+, Cl^-, Na^+, and OH^-. The separated ions are present because HCl is a strong acid and NaOH is a strong base. How can we predict what reaction occurs, if any? First, will NaCl precipitate? From Table 4.1 we can see that NaCl is soluble in water and thus will not precipitate. Therefore, the Na^+ and Cl^- ions are spectator ions. On the other hand, because water is a nonelectrolyte, large quantities of H^+ and OH^- ions cannot coexist in solution. They react to form H_2O molecules:

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

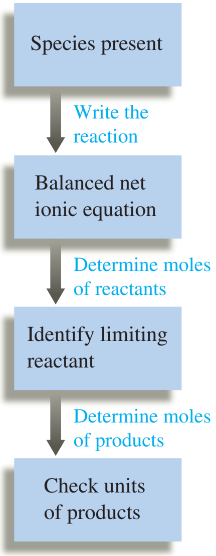
This is the net ionic equation for the reaction that occurs when aqueous solutions of HCl and NaOH are mixed.

Next, consider mixing an aqueous solution of acetic acid ($HC_2H_3O_2$) with an aqueous solution of potassium hydroxide (KOH). In our earlier discussion of conductivity we said that an aqueous solution of acetic acid is a weak electrolyte. This tells us that acetic acid does not dissociate into ions to any great extent. In fact, in 0.1 M $HC_2H_3O_2$ approximately 99% of the $HC_2H_3O_2$ molecules remain undissociated. However, when solid KOH is dissolved in water, it dissociates completely to produce K^+ and OH^- ions. Therefore, in the solution formed by mixing aqueous solutions of $HC_2H_3O_2$ and KOH, *before any reaction occurs,* the principal species are $HC_2H_3O_2$, K^+, and OH^-. What reaction will occur? A possible precipitation reaction could occur between K^+ and OH^-. However, we know that KOH is soluble, so precipitation does not occur. Another possibility is a reaction involving the hydroxide ion (a proton acceptor) and some proton donor. Is there a source of protons in the solution? The answer is yes—the $HC_2H_3O_2$ molecules. The OH^- ion has such a strong affinity for protons that it can strip them from the $HC_2H_3O_2$ molecules. The net ionic equation for this reaction is

$$OH^-(aq) + HC_2H_3O_2(aq) \longrightarrow H_2O(l) + C_2H_3O_2^-(aq)$$

This reaction illustrates a very important general principle: *The hydroxide ion is such a strong base that for purposes of stoichiometric calculations it can be assumed to react completely with any weak acid that we will encounter.* Of course, OH^- ions also react completely with the H^+ ions in solutions of strong acids.

We will now deal with the stoichiometry of acid–base reactions in aqueous solutions. The procedure is fundamentally the same as that used previously for precipitation reactions.



Performing Calculations for Acid–Base Reactions

➡ **1 List the species present in the combined solution *before any reaction occurs,* and decide what reaction will occur.**

2 Write the balanced net ionic equation for this reaction.

3 Calculate the moles of reactants. For reactions in solution, use the volumes of the original solutions and their molarities.

4 Determine the limiting reactant where appropriate.

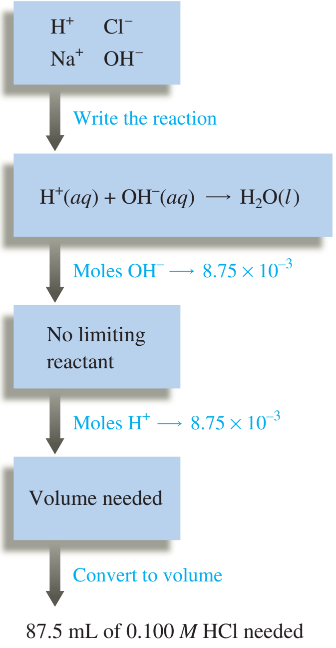
5 Calculate the moles of the required reactant or product.

6 Convert to grams or volume (of solution), as required.

An acid–base reaction is often called a **neutralization reaction.** When just enough base is added to react exactly with the acid in a solution, we say the acid has been *neutralized.*

Sample Exercise 4.12 Neutralization Reactions I

What volume of a 0.100 *M* HCl solution is needed to neutralize 25.0 mL of 0.350 *M* NaOH?



Solution

1 *List the species present in the combined solution before any reaction occurs, and decide what reaction will occur.* The species present in the mixed solutions before any reaction occurs are

$$\underbrace{H^+ \quad Cl^-}_{\text{From HCl}(aq)} \qquad\qquad \underbrace{Na^+ \quad OH^-}_{\text{From NaOH}(aq)}$$

What reaction will occur? The two possibilities are

$$Na^+(aq) + Cl^-(aq) \longrightarrow NaCl(s)$$
$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

Since we know that NaCl is soluble, the first reaction does not take place (Na^+ and Cl^- are spectator ions). However, as we have seen before, the reaction of the H^+ and OH^- ions to form H_2O does occur.

2 *Write the balanced net ionic equation.* The balanced net ionic equation for this reaction is

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

3 *Calculate the moles of reactants.* The number of moles of OH^- ions in the 25.0-mL sample of 0.350 *M* NaOH is

$$25.0\ \cancel{\text{mL NaOH}} \times \frac{1\ \cancel{\text{L}}}{1000\ \cancel{\text{mL}}} \times \frac{0.350\ \text{mol OH}^-}{\cancel{\text{L NaOH}}} = 8.75 \times 10^{-3}\ \text{mol OH}^-$$

4 *Determine the limiting reactant.* This problem requires the addition of just enough H^+ ions to react exactly with the OH^- ions present. Thus we need not be concerned with determining a limiting reactant.

5 *Calculate the moles of reactant needed.* Since H^+ and OH^- ions react in a 1:1 ratio, 8.75×10^{-3} mol H^+ ions is required to neutralize the OH^- ions present.

6 *Convert to volume required.* The volume V of 0.100 *M* HCl required to furnish 8.75×10^{-3} mol H^+ ions can be calculated as follows:

$$V \times \frac{0.100\ \text{mol H}^+}{\text{L}} = 8.75 \times 10^{-3}\ \text{mol H}^+$$

Solving for V gives

$$V = \frac{8.75 \times 10^{-3}\ \cancel{\text{mol H}^+}}{\dfrac{0.100\ \cancel{\text{mol H}^+}}{\text{L}}} = 8.75 \times 10^{-2}\ \text{L}$$

Thus 8.75×10^{-2} L (87.5 mL) of 0.100 *M* HCl is required to neutralize 25.0 mL of 0.350 *M* NaOH.

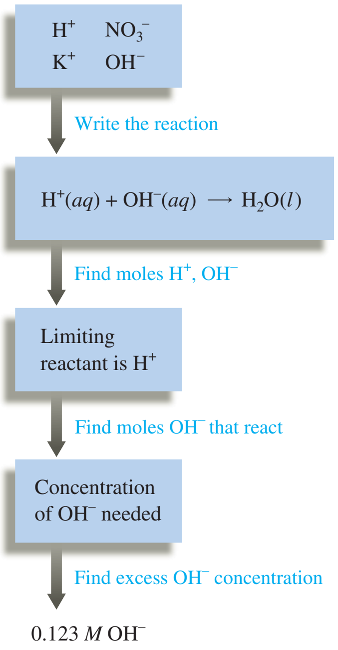
See Exercises 4.59 and 4.60.

Sample Exercise 4.13

Neutralization Reactions II

In a certain experiment, 28.0 mL of 0.250 *M* HNO_3 and 53.0 mL of 0.320 *M* KOH are mixed. Calculate the amount of water formed in the resulting reaction. What is the concentration of H^+ or OH^- ions in excess after the reaction goes to completion?

Solution



The species available for reaction are

$$\underbrace{H^+ \quad NO_3^-}_{\text{From } HNO_3 \text{ solution}} \qquad \underbrace{K^+ \quad OH^-}_{\text{From KOH solution}}$$

Since KNO_3 is soluble, K^+ and NO_3^- are spectator ions, so the net ionic equation is

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

We next compute the amounts of H^+ and OH^- ions present:

$$28.0\ \cancel{\text{mL } HNO_3} \times \frac{1\ \cancel{\text{L}}}{1000\ \cancel{\text{mL}}} \times \frac{0.250 \text{ mol } H^+}{\cancel{\text{L } HNO_3}} = 7.00 \times 10^{-3} \text{ mol } H^+$$

$$53.0\ \cancel{\text{mL KOH}} \times \frac{1\ \cancel{\text{L}}}{1000\ \cancel{\text{mL}}} \times \frac{0.320 \text{ mol } OH^-}{\cancel{\text{L KOH}}} = 1.70 \times 10^{-2} \text{ mol } OH^-$$

Since H^+ and OH^- react in a 1:1 ratio, the limiting reactant is H^+. This means that 7.00×10^{-3} mol H^+ ions will react with 7.00×10^{-3} mol OH^- ions to form 7.00×10^{-3} mol H_2O.

The amount of OH^- ions in excess is obtained from the following difference:

$$\text{Original amount} - \text{amount consumed} = \text{amount in excess}$$

$$1.70 \times 10^{-2} \text{ mol } OH^- - 7.00 \times 10^{-3} \text{ mol } OH^- = 1.00 \times 10^{-2} \text{ mol } OH^-$$

The volume of the combined solution is the sum of the individual volumes:

$$\text{Original volume of } HNO_3 + \text{original volume of KOH} = \text{total volume}$$

$$28.0 \text{ mL} + 53.0 \text{ mL} = 81.0 \text{ mL} = 8.10 \times 10^{-2} \text{ L}$$

Thus the molarity of OH^- ions in excess is

$$\frac{\text{mol } OH^-}{\text{L solution}} = \frac{1.00 \times 10^{-2} \text{ mol } OH^-}{8.10 \times 10^{-2} \text{ L}} = 0.123 \text{ M } OH^-$$

See Exercises 4.61 and 4.62.

Acid–Base Titrations

Volumetric analysis is a technique for determining the amount of a certain substance by doing a titration. A **titration** involves delivery (from a buret) of a measured volume of a solution of known concentration (the *titrant*) into a solution containing the substance being analyzed (the *analyte*). The titrant contains a substance that reacts in a known manner with the analyte. The point in the titration where enough titrant has been added to react exactly with the analyte is called the **equivalence point** or the **stoichiometric point.** This point is often marked by an **indicator,** a substance added at the beginning of the titration that changes color at (or very near) the equivalence point. The point where the indicator

Visualization: Neutralization of a Strong Acid by a Strong Base

Ideally, the endpoint and stoichiometric point should coincide.

actually changes color is called the **endpoint** of the titration. The goal is to choose an indicator such that the endpoint (where the indicator changes color) occurs exactly at the equivalence point (where just enough titrant has been added to react with all the analyte).

Visualization: Titrations

The following three requirements must be met for a titration to be successful:

1. The exact reaction between titrant and analyte must be known (and rapid).
2. The stoichiometric (equivalence) point must be marked accurately.
3. The volume of titrant required to reach the stoichiometric point must be known accurately.

When the analyte is a base or an acid, the required titrant is a strong acid or strong base, respectively. This procedure is called an *acid–base titration.* An indicator very commonly used for acid–base titrations is phenolphthalein, which is colorless in an acidic solution and pink in a basic solution. Thus, when an acid is titrated with a base, the phenolphthalein remains colorless until after the acid is consumed and the first drop of excess base is added. In this case, the endpoint (the solution changes from colorless to pink) occurs approximately one drop of base beyond the stoichiometric point. This type of titration is illustrated in the three photos in Fig. 4.18.

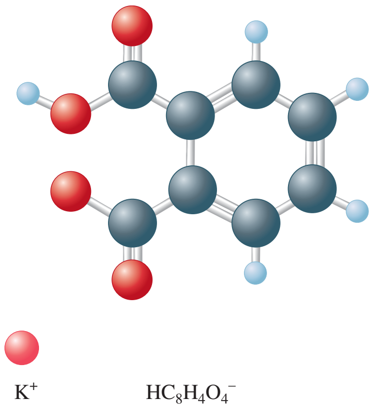
We will deal with the acid–base titrations only briefly here but will return to the topic of titrations and indicators in more detail in Chapter 15. The titration of an acid with a standard solution containing hydroxide ions is described in Sample Exercise 4.15. In Sample Exercise 4.14 we show how to determine accurately the concentration of a sodium hydroxide solution. This procedure is called *standardizing the solution.*

FIGURE 4.18

The titration of an acid with a base. (a) The titrant (the base) is in the buret, and the flask contains the acid solution along with a small amount of indicator. (b) As base is added drop by drop to the acid solution in the flask during the titration, the indicator changes color, but the color disappears on mixing. (c) The stoichiometric (equivalence) point is marked by a permanent indicator color change. The volume of base added is the difference between the final and initial buret readings.

Sample Exercise 4.14

Neutralization Titration



A student carries out an experiment to standardize (determine the exact concentration of) a sodium hydroxide solution. To do this, the student weighs out a 1.3009-g sample of potassium hydrogen phthalate ($KHC_8H_4O_4$, often abbreviated KHP). KHP (molar mass 204.22 g/mol) has one acidic hydrogen. The student dissolves the KHP in distilled water, adds phenolphthalein as an indicator, and titrates the resulting solution with the sodium hydroxide solution to the phenolphthalein endpoint. The difference between the final and initial buret readings indicates that 41.20 mL of the sodium hydroxide solution is required to react exactly with the 1.3009 g KHP. Calculate the concentration of the sodium hydroxide solution.

Solution

Aqueous sodium hydroxide contains the Na^+ and OH^- ions, and $KHC_8H_4O_4$ dissolves in water to give the K^+ and $HC_8H_4O_4^-$ ions. As the titration proceeds, the mixed solution contains the following ions: K^+, $HC_8H_4O_4^-$, Na^+, and OH^-. The OH^- will remove an H^+ from the $HC_8H_4O_4^-$ to give the following net ionic reaction:

$$HC_8H_4O_4^-(aq) + OH^-(aq) \longrightarrow H_2O(l) + C_8H_4O_4^{2-}(aq)$$

Since the reaction exhibits 1:1 stoichiometry, we know that 41.20 mL of the sodium hydroxide solution must contain exactly the same number of moles of OH^- as there are moles of $HC_8H_4O_4^-$ in 1.3009 g $KHC_8H_4O_4$.

We calculate the moles of $KHC_8H_4O_4$ in the usual way:

$$1.3009\ \cancel{\text{g KHC}_8\text{H}_4\text{O}_4} \times \frac{1\ \text{mol KHC}_8\text{H}_4\text{O}_4}{204.22\ \cancel{\text{g KHC}_8\text{H}_4\text{O}_4}} = 6.3701 \times 10^{-3}\ \text{mol KHC}_8\text{H}_4\text{O}_4$$

This means that 6.3701×10^{-3} mol OH^- must be added to react with the 6.3701×10^{-3} mol $HC_8H_4O_4^-$. Thus 41.20 mL (4.120×10^{-2} L) of the sodium hydroxide solution must contain 6.3701×10^{-3} mol OH^- (and Na^+), and the concentration of the sodium hydroxide solution is

$$\text{Molarity of NaOH} = \frac{\text{mol NaOH}}{\text{L solution}} = \frac{6.3701 \times 10^{-3}\ \text{mol NaOH}}{4.120 \times 10^{-2}\ \text{L}}$$
$$= 0.1546\ M$$

This standard sodium hydroxide solution can now be used in other experiments (see Sample Exercise 4.15).

See Exercises 4.63 and 4.66.

Sample Exercise 4.15

Neutralization Analysis

An environmental chemist analyzed the effluent (the released waste material) from an industrial process known to produce the compounds carbon tetrachloride (CCl_4) and benzoic acid ($HC_7H_5O_2$), a weak acid that has one acidic hydrogen atom per molecule. A sample of this effluent weighing 0.3518 g was shaken with water, and the resulting aqueous solution required 10.59 mL of 0.1546 *M* NaOH for neutralization. Calculate the mass percent of $HC_7H_5O_2$ in the original sample.

Solution

In this case, the sample was a mixture containing CCl_4 and $HC_7H_5O_2$, and it was titrated with OH^- ions. Clearly, CCl_4 is not an acid (it contains no hydrogen atoms), so we can assume it does not react with OH^- ions. However, $HC_7H_5O_2$ is an acid that donates one H^+ ion per molecule to react with an OH^- ion as follows:

$$HC_7H_5O_2(aq) + OH^-(aq) \longrightarrow H_2O(l) + C_7H_5O_2^-(aq)$$

Although $HC_7H_5O_2$ is a weak acid, the OH^- ion is such a strong base that we can assume that each OH^- ion added will react with a $HC_7H_5O_2$ molecule until all the benzoic acid is consumed.

We must first determine the number of moles of OH^- ions required to react with all the $HC_7H_5O_2$:

$$10.59\ \cancel{\text{mL NaOH}} \times \frac{\cancel{1\ \text{L}}}{1000\ \cancel{\text{mL}}} \times \frac{0.1546\ \text{mol OH}^-}{\cancel{\text{L NaOH}}} = 1.637 \times 10^{-3}\ \text{mol OH}^-$$

This number is also the number of moles of $HC_7H_5O_2$ present. The number of grams of the acid is calculated using its molar mass (122.12 g/mol):

$$1.637 \times 10^{-3}\ \cancel{\text{mol HC}_7\text{H}_5\text{O}_2} \times \frac{122.12\ \text{g HC}_7\text{H}_5\text{O}_2}{1\ \cancel{\text{mol HC}_7\text{H}_5\text{O}_2}} = 0.1999\ \text{g HC}_7\text{H}_5\text{O}_2$$

The mass percent of $HC_7H_5O_2$ in the original sample is

$$\frac{0.1999\ \cancel{\text{g}}}{0.3518\ \cancel{\text{g}}} \times 100 = 56.82\%$$

See Exercise 4.65.

The first step in the analysis of a complex solution is to write down the components and focus on the chemistry of each one. When a strong electrolyte is present, write it as separated ions.

In doing problems involving titrations, you must first decide what reaction is occurring. Sometimes this seems difficult because the titration solution contains several components. *The key to success is to first write down all the components in the solution and focus on the chemistry of each one.* We have been emphasizing this approach in dealing with the reactions between ions in solution. Make it a habit to write down the components of solutions before trying to decide what reaction(s) might take place as you attempt the end-of-chapter problems involving titrations.

4.9 Oxidation–Reduction Reactions

Visualization: Zinc and Iodine

Visualization: Barking Dogs: Reaction of Phosphorus

Visualization: Dry Ice and Magnesium

Visualization: Sugar and Potassium Chlorate

We have seen that many important substances are ionic. Sodium chloride, for example, can be formed by the reaction of elemental sodium and chlorine:

$$2\text{Na}(s) + \text{Cl}_2(g) \longrightarrow 2\text{NaCl}(s)$$

In this reaction, solid sodium, which contains neutral sodium atoms, reacts with chlorine gas, which contains diatomic Cl_2 molecules, to form the ionic solid NaCl, which contains Na^+ and Cl^- ions. This process is represented in Fig. 4.19. *Reactions like this one, in which one or more electrons are transferred, are called* ***oxidation–reduction reactions*** *or* ***redox reactions.***

Many important chemical reactions involve oxidation and reduction. Photosynthesis, which stores energy from the sun in plants by converting carbon dioxide and water to sugar, is a very important oxidation–reduction reaction. In fact, most reactions used for energy production are redox reactions. In humans, the oxidation of sugars, fats, and proteins provides the energy necessary for life. Combustion reactions, which provide most of the energy to power our civilization, also involve oxidation and reduction. An example is the reaction of methane with oxygen:

$$\text{CH}_4(g) + 2\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g) + \text{energy}$$

Even though none of the reactants or products in this reaction is ionic, the reaction is still assumed to involve a transfer of electrons from carbon to oxygen. To explain this, we must introduce the concept of oxidation states.

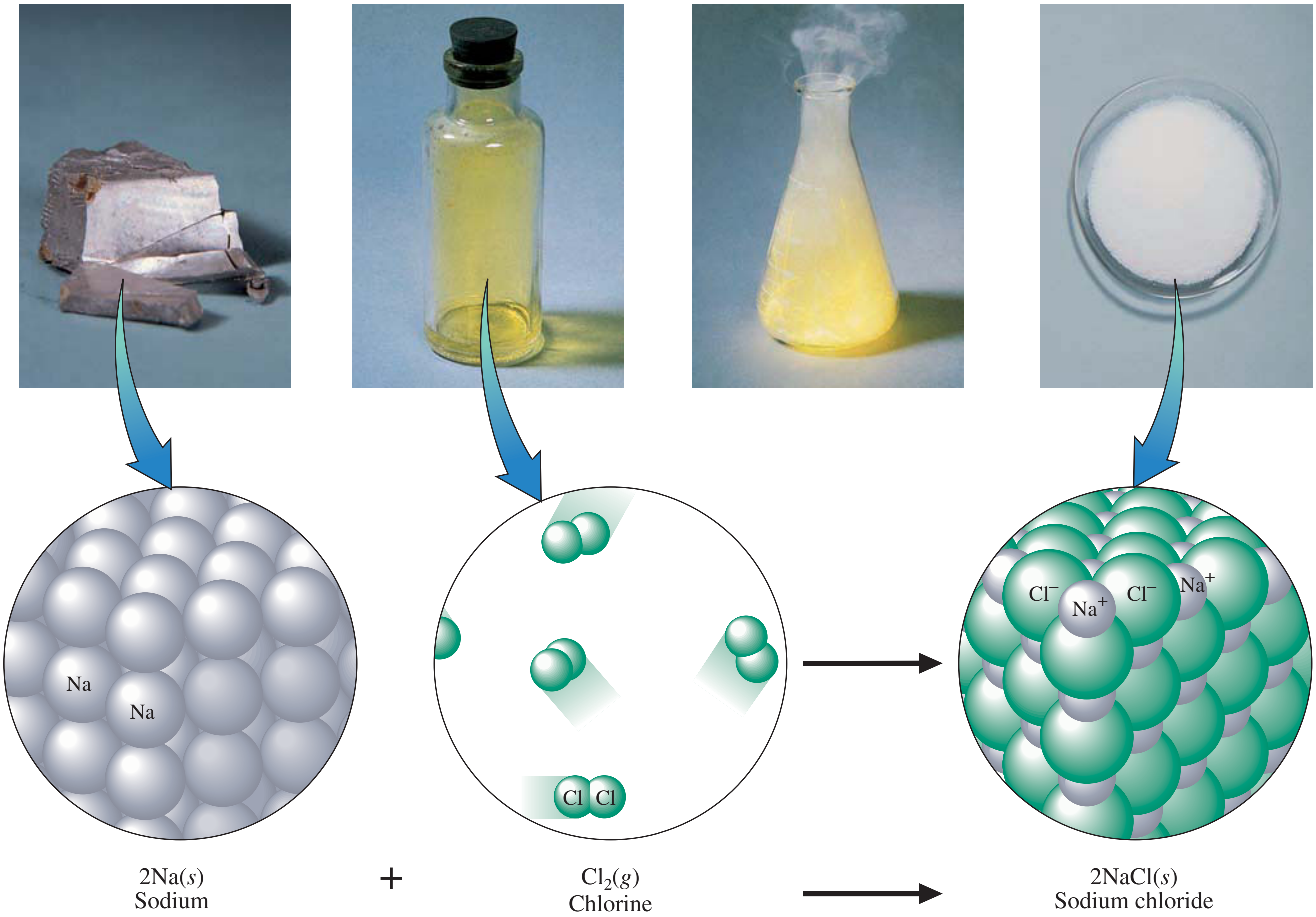


FIGURE 4.19
The reaction of solid sodium and gaseous chlorine to form solid sodium chloride.

Oxidation States

The concept of **oxidation states** (also called *oxidation numbers*) provides a way to keep track of electrons in oxidation–reduction reactions, particularly redox reactions involving covalent substances. Recall that electrons are shared by atoms in covalent bonds. The oxidation states of atoms in covalent compounds are obtained by arbitrarily assigning the electrons (which are actually shared) to particular atoms. We do this as follows: For a covalent bond between two identical atoms, the electrons are split equally between the two. In cases where two different atoms are involved (and the electrons are thus shared unequally), the shared electrons are assigned completely to the atom that has the stronger attraction for electrons. For example, recall from the discussion of the water molecule in Section 4.1 that oxygen has a greater attraction for electrons than does hydrogen. Therefore, in assigning the oxidation state of oxygen and hydrogen in H_2O, we assume that the oxygen atom actually possesses all the electrons. Recall that a hydrogen atom has one electron. Thus, in water, oxygen has formally "taken" the electrons from two hydrogen atoms. This gives the oxygen an *excess* of two electrons (its oxidation state is -2) and leaves each hydrogen with no electrons (the oxidation state of each hydrogen is thus $+1$).

We define the *oxidation states* (or *oxidation numbers*) of the atoms in a covalent compound as the imaginary charges the atoms would have if the shared electrons were divided equally between identical atoms bonded to each other or, for different atoms, were all assigned to the atom in each bond that has the greater attraction for electrons. Of course,

CHEMICAL IMPACT

Iron Zeroes in on Pollution

Treating groundwater contaminated with pollutants is typically very complicated and very expensive. However, chemists have discovered a low-tech, economical method for treating the contaminated groundwater near a former semiconductor manufacturing plant in Sunnyvale, California. They have replaced the elaborate decontamination machinery used at the site for more than a decade with 220 tons of iron filings buried in a giant trough. Because there are no pumps to maintain and no electricity to purchase, this simple system will save approximately $300,000 per year. The property, which was thought to be unusable for the 30-year lifetime of the old clean-up process because of the need for constant monitoring and access, can now be used immediately.

A schematic of the iron treatment method is shown in the accompanying figure. At Sunnyvale, the iron barrier is 40 feet long, 4 feet wide, and 20 feet deep. In the 4 days it takes for contaminated water to seep through the wall of iron, the chlorinated organic contaminants are degraded into products that are then themselves decomposed to simpler substances. According to engineers on the site, the polluted water that seeps through the wall meets Environmental Protection Agency (EPA) standards when it emerges on the other side.

How does iron metal clean up contaminated groundwater? It's a result of the ability of iron metal (oxidation state = 0) to act as a reducing agent toward the chlorine-containing organic pollutant molecules. The reaction can be represented as follows:

$$\mathrm{Fe}(s) + \mathrm{RCl}(aq) + \mathrm{H}^+(aq) \longrightarrow \mathrm{Fe}^{2+}(aq) + \mathrm{RH}(aq) + \mathrm{Cl}^-(aq)$$

where RCl represents a chlorinated organic molecule. The reaction appears to involve a direct reaction between the metal and an RCl molecule adsorbed on the metal surface.

for ionic compounds containing monatomic ions, the oxidation states of the ions are equal to the ion charges.

These considerations lead to a series of rules for assigning oxidation states that are summarized in Table 4.2. Application of these simple rules allows the assignment of oxidation states in most compounds. To apply these rules recognize that *the sum of the oxidation states must be zero for an electrically neutral compound.* For an ion, the sum of the oxidation states must equal the charge of the ion. The principles are illustrated by Sample Exercise 4.16.

Oxidation of copper metal by nitric acid. The copper atoms lose two electrons to form Cu^{2+} ions, which give a deep green color that becomes turquoise when diluted with water.

TABLE 4.2 Rules for Assigning Oxidation States

The Oxidation State of . . .	Summary	Examples
• An atom in an element is zero	Element: 0	$Na(s)$, $O_2(g)$, $O_3(g)$, $Hg(l)$
• A monatomic ion is the same as its charge	Monatomic ion: charge of ion	Na^+, Cl^-
• Fluorine is −1 in its compounds	Fluorine: −1	HF, PF_3
• Oxygen is usually −2 in its compounds Exception: peroxides (containing O_2^{2-}) in which oxygen is −1	Oxygen: −2	H_2O, CO_2
• Hydrogen is +1 in its covalent compounds	Hydrogen: +1	H_2O, HCl, NH_3

In addition to decomposing chlorinated organic contaminants, iron appears to be useful against other pollutants as well. Iron can degrade dye wastes from textile mills and can reduce soluble Cr(VI) compounds to insoluble Cr(III) products, which are much less harmful. Iron's reducing abilities also appear useful in removing radioactive technetium, a common pollutant at nuclear processing facilities. Iron also appears to be effective for removing nitrates from the soil.

Other metals, such as zinc, tin, and palladium, have shown promise for use in groundwater clean-up, too. These metals generally react more quickly than iron but are more expensive and pose their own environmental hazards.

Inexpensive and environmentally benign, iron seems to be the metal of choice for most groundwater clean-up. It's cheap, it's effective, it's almost a miracle!

It is worthwhile to note at this point that the convention is to write actual charges on ions as $n+$ or $n-$, the number being written *before* the plus or minus sign. On the other hand, oxidation states (not actual charges) are written $+n$ or $-n$, the number being written *after* the plus or minus sign.

Sample Exercise 4.16 Assigning Oxidation States

Assign oxidation states to all atoms in the following.

a. CO_2
b. SF_6
c. NO_3^-

Solution

a. Since we have a specific rule for the oxidation state of oxygen, we will assign its value first. The oxidation state of oxygen is -2. The oxidation state of the carbon atom can be determined by recognizing that since CO_2 has no charge, the sum of the oxidation states for oxygen and carbon must be zero. Since each oxygen is -2 and there are two oxygen atoms, the carbon atom must be assigned an oxidation state of $+4$:

$$\underset{+4}{\underset{\nearrow}{\text{C}}}\underset{-2\text{ for each oxygen}}{\underset{\nwarrow}{\text{O}_2}}$$

We can check the assigned oxidation states by noting that when the number of atoms is taken into account, the sum is zero as required:

$$\underset{\substack{\text{No. of C}\\ \text{atoms}}}{\underset{\nearrow}{1}}(+4) + \underset{\substack{\text{No. of O}\\ \text{atoms}}}{\underset{\uparrow}{2}}(-2) = 0$$

b. Since we have no rule for sulfur, we first assign the oxidation state of each fluorine as −1. The sulfur must then be assigned an oxidation state of +6 to balance the total of −6 from the fluorine atoms:

$$\underset{\substack{\nearrow \\ +6}}{S}\;\underset{\substack{\nwarrow \\ -1\text{ for each fluorine}}}{F_6}$$

Reality Check: $+6 + 6(-1) = 0$

c. Oxygen has an oxidation state of −2. Because the sum of the oxidation states of the three oxygens is −6 and the net charge on the NO_3^- ion is 1−, the nitrogen must have an oxidation state of +5:

$$\underset{\substack{\nearrow \\ +5}}{N}\;\underset{\substack{\nwarrow \\ -2\text{ for each oxygen}}}{O_3^-}$$

Reality Check: $+5 + 3(-2) = -1$

Note that in this case the sum must be −1 (the overall charge on the ion).

See Exercises 4.67 through 4.70.

Magnetite is a magnetic ore containing Fe_3O_4. Note that the compass needle points toward the ore.

We need to make one more point about oxidation states, and this can be illustrated by the compound Fe_3O_4, which is the main component in magnetite, an iron ore that accounts for the reddish color of many types of rocks and soils. To determine the oxidation states in Fe_3O_4, we first assign each oxygen atom its usual oxidation state of −2. The three iron atoms must yield a total of +8 to balance the total of −8 from the four oxygens. This means that each iron atom has an oxidation state of $+\frac{8}{3}$. A noninteger value for the oxidation state may seem strange because charge is expressed in whole numbers. However, although they are rare, noninteger oxidation states do occur because of the rather arbitrary way that electrons are divided up by the rules in Table 4.2. For Fe_3O_4, for example, the rules assume that all the iron atoms are equal, when in fact this compound can best be viewed as containing four O^{2-} ions, two Fe^{3+} ions, and one Fe^{2+} ion per formula unit. (Note that the "average" charge on iron works out to be $\frac{8}{3}+$, which is equal to the oxidation state we determined above.) Noninteger oxidation states should not intimidate you. They are used in the same way as integer oxidation states—for keeping track of electrons.

The Characteristics of Oxidation–Reduction Reactions

Oxidation–reduction reactions are characterized by a transfer of electrons. In some cases, the transfer occurs in a literal sense to form ions, such as in the reaction

$$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$$

However, sometimes the transfer is less obvious. For example, consider the combustion of methane (the oxidation state for each atom is given):

$$\begin{matrix}\text{Oxidation}\\\text{state}\end{matrix}\quad \underset{\substack{\uparrow\\-4}}{C}\underset{\substack{\nwarrow\\+1\\\text{(each H)}}}{H_4}(g) + 2\underset{\substack{\uparrow\\0}}{O_2}(g) \longrightarrow \underset{\substack{\uparrow\\+4}}{C}\underset{\substack{\nwarrow\\-2\\\text{(each O)}}}{O_2}(g) + 2\underset{\substack{\nwarrow\\+1\\\text{(each H)}}}{H_2}\underset{\substack{\nwarrow\\-2}}{O}(g)$$

Note that the oxidation state for oxygen in O_2 is 0 because it is in elemental form. In this reaction there are no ionic compounds, but we can still describe the process in terms of a transfer of electrons. Note that carbon undergoes a change in oxidation state from −4 in CH_4 to +4 in CO_2. Such a change can be accounted for by a loss of eight electrons (the symbol e^- stands for an electron);

$$\underset{\substack{\uparrow\\-4}}{CH_4} \longrightarrow \underset{\substack{\uparrow\\+4}}{CO_2} + 8e^-$$

CHEMICAL IMPACT

Pearly Whites

People have long been concerned about the "whiteness" of their teeth. In the Middle Ages the local barber-surgeon would whiten teeth using nitric acid—a procedure fraught with dangers, including the fact that nitric acid dissolves tooth enamel, which in turn leads to massive tooth decay. Today many safer procedures are available for keeping teeth sparkling white.

The outer layer of teeth, the enamel, consists of the mineral hydroxyapatite, which contains calcium phosphate. Underneath the enamel is dentin, an off-white mixture of calcium phosphate and collagen that protects the nerves and blood vessels at the center of the tooth.

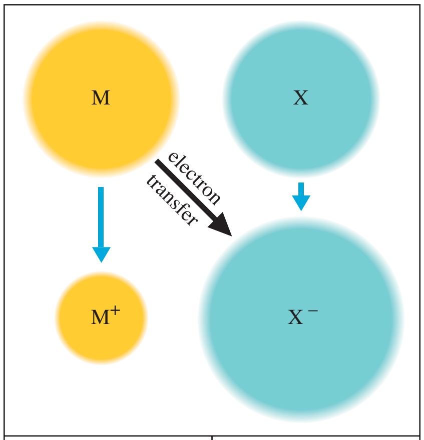
The discoloration of teeth is usually due to colored molecules in our diet from sources such as blueberries, red wine, and coffee. The tar from cigarettes also stains teeth. Aging is another factor. As we get older, chemical changes occur that cause the dentin to become more yellow.

The stains produced when colored molecules are adsorbed to the surfaces of teeth can be removed by brushing. Toothpastes contain abrasives such as tiny particles of silica, aluminum oxide, calcium carbonate, or calcium phosphate to help scrub off adsorbed stains.

Stains due to molecules lying below the surface are usually attacked with an oxidizing agent, hydrogen peroxide (H_2O_2). As H_2O_2 breaks down into water and oxygen, intermediates are produced that react with and decompose the molecules that produce teeth discoloration.

Off-the-shelf teeth whiteners typically contain carbamide peroxide (a 1:1 mixture of urea and hydrogen peroxide), glycerin, stannate and pyrophosphate salts (preservatives), and flavoring agents. These whiteners come in a form that can be brushed directly onto the teeth or are embedded in a plastic strip that can be stuck to the teeth. Because these products have a low strength for safety reasons, it may take several weeks of applying them for full whitening to occur.

Whitening treatments by dentists often involve the application of substances containing more than 30% hydrogen peroxide. These substances must be used with the appropriate protection of the tissues surrounding the teeth. Keeping your teeth white is another example of chemistry in action.



Oxidized	Reduced
loses electrons	*gains* electrons
oxidation state *increases*	oxidation state *decreases*
reducing agent	*oxidizing* agent

FIGURE 4.20
A summary of an oxidation–reduction process, in which M is oxidized and X is reduced.

On the other hand, each oxygen changes from an oxidation state of 0 in O_2 to -2 in H_2O and CO_2, signifying a gain of two electrons per atom. Since four oxygen atoms are involved, this is a gain of eight electrons:

$$\underset{\substack{\uparrow\\0}}{2O_2} + 8e^- \longrightarrow \underbrace{CO_2 + 2H_2O}_{4(-2)\,=\,-8}$$

No change occurs in the oxidation state of hydrogen, and it is not formally involved in the electron-transfer process.

With this background, we can now define some important terms. **Oxidation** is an *increase* in oxidation state (a loss of electrons). **Reduction** is a *decrease* in oxidation state (a gain of electrons). Thus in the reaction

$$\underset{\substack{\uparrow\\0}}{2Na(s)} + \underset{\substack{\uparrow\\0}}{Cl_2(g)} \longrightarrow 2\underset{\substack{\uparrow\\+1}}{Na}\underset{\substack{\nwarrow\\-1}}{Cl}(s)$$

sodium is oxidized and chlorine is reduced. In addition, Cl_2 is called the **oxidizing agent (electron acceptor),** and Na is called the **reducing agent (electron donor).** These terms are summarized in Fig. 4.20.

Concerning the reaction

$$\underset{\substack{\uparrow\\-4}}{C}\underset{\substack{\nwarrow\\+1}}{H_4}(g) + \underset{\substack{\uparrow\\0}}{2O_2(g)} \longrightarrow \underset{\substack{\uparrow\\+4}}{C}\underset{\substack{\nwarrow\\-2}}{O_2}(g) + 2\underset{\substack{\uparrow\\+1}}{H_2}\underset{\substack{\nwarrow\\-2}}{O}(g)$$

CHEMICAL IMPACT

Aging: Does It Involve Oxidation?

Although aging is supposed to bring wisdom, almost no one wants to get old. Along with wisdom, aging brings wrinkles, loss of physical strength, and greater susceptibility to disease.

Why do we age? No one knows for certain, but many scientists think that oxidation plays a major role. The oxygen molecule and other oxidizing agents in the body apparently can extract single electrons from the large molecules that make up cell membranes, thus making them very reactive. Subsequently, these activated molecules can link up, changing the properties of the cell membrane. At some point, enough of these reactions have occurred that the body's immune system comes to view the changed cell as an "enemy" and destroys it. This is particularly detrimental to the organism when the cells involved are irreplaceable. Nerve cells, for example, fall into this category. They rarely regenerate in an adult.

The body has defenses against oxidation, such as vitamin E, a well-known antioxidant. Studies have shown that red blood cells age much faster than normal when they are deficient in vitamin E. Based on studies such as these, some have suggested large doses of vitamin E as a preventive measure against aging, but there is no solid evidence that this practice has any impact on aging.

Another protective antioxidant found in our bodies is superoxide dismutase (SOD), which protects us from the superoxide ion O_2^-, a powerful oxidizing agent that is particularly damaging to vital enzymes. The importance of SOD in opposing the aging process is indicated from the results of a study by Dr. Richard Cutler at the Gerontology Research

Oxidation is an increase in oxidation state. *Reduction* is a decrease in oxidation state.

A helpful mnemonic device is OIL RIG (**O**xidation **I**nvolves **L**oss; **R**eduction **I**nvolves **G**ain). Another common mnemonic is LEO says GER. (**L**oss of **E**lectrons, **O**xidation; **G**ain of **E**lectrons, **R**eduction).

An oxidizing agent is reduced and a reducing agent is oxidized in a redox reaction.

we can say the following:

> Carbon is oxidized because there has been an increase in its oxidation state (carbon has formally lost electrons).
>
> Oxygen is reduced because there has been a decrease in its oxidation state (oxygen has formally gained electrons).
>
> CH_4 is the reducing agent.
>
> O_2 is the oxidizing agent.

Note that when the oxidizing or reducing agent is named, the *whole compound* is specified, not just the element that undergoes the change in oxidation state.

Sample Exercise 4.17 Oxidation–Reduction Reactions I

Finely ground aluminum and iodine are mixed and react vigorously to form aluminum iodide after a drop of water is added. The purple cloud is excess iodine vaporized by the heat of the reaction.

When powdered aluminum metal is mixed with pulverized iodine crystals and a drop of water is added to help the reaction get started, the resulting reaction produces a great deal of energy. The mixture bursts into flames, and a purple smoke of I_2 vapor is produced from the excess iodine. The equation for the reaction is

$$2\text{Al}(s) + 3\text{I}_2(s) \longrightarrow 2\text{AlI}_3(s)$$

For this reaction, identify the atoms that are oxidized and reduced, and specify the oxidizing and reducing agents.

Solution

The first step is to assign oxidation states:

$$\underset{\substack{\uparrow\\ 0}}{2\text{Al}(s)} + \underset{\substack{\uparrow\\ 0}}{3\text{I}_2(s)} \longrightarrow 2\underset{\substack{\uparrow\\ +3}}{\text{Al}}\underset{\substack{\nwarrow\\ -1\ (\text{each I})}}{\text{I}_3}(s)$$

Free elements

$AlI_3(s)$ is a salt that contains Al^{3+} and I^- ions

Center of the National Institutes of Health in Baltimore that showed a strong correlation between the life spans of a dozen mammalian species and their levels of SOD. Human SOD is now being produced by the techniques of biotechnology in amounts that will enable scientists to carefully study its effects on aging and on various diseases such as rheumatoid arthritis and muscular dystrophy. Although SOD is available in health food stores in forms to be taken orally, this practice is useless because the SOD is digested (broken down into simpler substances) before it can reach the bloodstream.

Research does indicate that consuming certain foods may retard the aging process. For example, a recent study of 8000 male Harvard graduates found that chocolate and candy eaters live almost a year longer than those who abstain. Although the researchers from Harvard School of Public Health are not certain of the mechanism for this effect, they suggest that the antioxidants present in chocolate may provide the health benefits. For example, chocolate contains phenols, antioxidants that are also present in wine, another substance that seems to promote good health if used in moderation.

Oxidation is only one possible cause for aging. Research continues on many fronts to try to discover why we get "older" as time passes.

Can eating chocolate slow down the aging process?

Since each aluminum atom changes its oxidation state from 0 to +3 (an increase in oxidation state), aluminum is *oxidized.* On the other hand, the oxidation state of each iodine atom decreases from 0 to −1, and iodine is *reduced.* Since Al furnishes electrons for the reduction of iodine, it is the *reducing agent;* I_2 is the *oxidizing agent.*

See Exercises 4.71 and 4.72.

Sample Exercise 4.18

Oxidation–Reduction Reactions II

Metallurgy, the process of producing a metal from its ore, always involves oxidation–reduction reactions. In the metallurgy of galena (PbS), the principal lead-containing ore, the first step is the conversion of lead sulfide to its oxide (a process called *roasting*):

$$2\text{PbS}(s) + 3\text{O}_2(g) \longrightarrow 2\text{PbO}(s) + 2\text{SO}_2(g)$$

The oxide is then treated with carbon monoxide to produce the free metal:

$$\text{PbO}(s) + \text{CO}(g) \longrightarrow \text{Pb}(s) + \text{CO}_2(g)$$

For each reaction, identify the atoms that are oxidized and reduced, and specify the oxidizing and reducing agents.

Solution

For the first reaction, we can assign the following oxidation states:

$$2\underset{\overset{\nearrow}{+2}}{\text{Pb}}\underset{\overset{\uparrow}{-2}}{\text{S}}(s) + 3\underset{\overset{\uparrow}{0}}{\text{O}_2}(g) \longrightarrow 2\underset{\overset{\uparrow}{+2}}{\text{Pb}}\underset{\overset{\nwarrow}{-2}}{\text{O}}(s) + 2\underset{\overset{\uparrow}{+4}}{\text{S}}\underset{\overset{\nwarrow}{-2\text{ (each O)}}}{\text{O}_2}(g)$$

The oxidation state for the sulfur atom increases from −2 to +4. Thus sulfur is oxidized. The oxidation state for each oxygen atom decreases from 0 to −2. Oxygen is reduced. The oxidizing agent (that accepts the electrons) is O_2, and the reducing agent (that donates electrons) is PbS.

For the second reaction we have

$$\underset{\substack{\uparrow\quad\nwarrow\\ +2\quad -2}}{\mathrm{PbO}(s)} + \underset{\substack{\uparrow\quad\nwarrow\\ +2\quad -2}}{\mathrm{CO}(g)} \longrightarrow \underset{\substack{\uparrow\\ 0}}{\mathrm{Pb}(s)} + \underset{\substack{\uparrow\quad\nwarrow\\ +4\quad -2\ \text{(each O)}}}{\mathrm{CO_2}(g)}$$

Lead is reduced (its oxidation state decreases from +2 to 0), and carbon is oxidized (its oxidation state increases from +2 to +4). PbO is the oxidizing agent, and CO is the reducing agent.

See Exercises 4.71 and 4.72.

4.10 Balancing Oxidation–Reduction Equations

Oxidation–reduction reactions in aqueous solutions are often complicated, which means that it can be difficult to balance their equations by simple inspection. In this section we will discuss a special technique for balancing the equations of redox reactions that occur in aqueous solutions. It is called the *half-reaction method.*

The Half-Reaction Method for Balancing Oxidation–Reduction Reactions in Aqueous Solutions

For oxidation–reduction reactions that occur in aqueous solution, it is useful to separate the reaction into two **half-reactions:** one involving oxidation and the other involving reduction. For example, consider the unbalanced equation for the oxidation–reduction reaction between cerium(IV) ion and tin(II) ion:

$$\mathrm{Ce^{4+}}(aq) + \mathrm{Sn^{2+}}(aq) \longrightarrow \mathrm{Ce^{3+}}(aq) + \mathrm{Sn^{4+}}(aq)$$

This reaction can be separated into a half-reaction involving the substance being *reduced,*

$$\mathrm{Ce^{4+}}(aq) \longrightarrow \mathrm{Ce^{3+}}(aq)$$

and one involving the substance being *oxidized,*

$$\mathrm{Sn^{2+}}(aq) \longrightarrow \mathrm{Sn^{4+}}(aq)$$

The general procedure is to balance the equations for the half-reactions separately and then to add them to obtain the overall balanced equation. The half-reaction method for balancing oxidation–reduction equations differs slightly depending on whether the reaction takes place in acidic or basic solution.

The Half-Reaction Method for Balancing Equations for Oxidation–Reduction Reactions Occurring in Acidic Solution

1. **Write separate equations for the oxidation and reduction half-reactions.**
2. **For each half-reaction,**
   a. **Balance all the elements except hydrogen and oxygen.**
   b. **Balance oxygen using H_2O.**

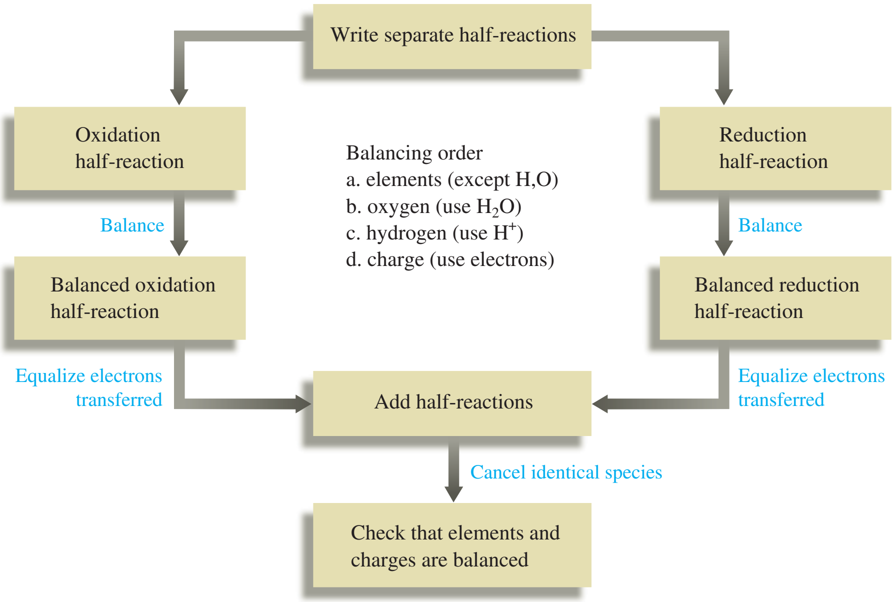
c. Balance hydrogen using H^+.
d. Balance the charge using electrons.

3 If necessary, multiply one or both balanced half-reactions by an integer to equalize the number of electrons transferred in the two half-reactions.

4 Add the half-reactions, and cancel identical species.

5 Check that the elements and charges are balanced.

These steps are summarized by the following flowchart:



We will illustrate this method by balancing the equation for the reaction between permanganate and iron(II) ions in acidic solution:

$$MnO_4^-(aq) + Fe^{2+}(aq) \xrightarrow{\text{Acid}} Fe^{3+}(aq) + Mn^{2+}(aq)$$

This reaction can be used to analyze iron ore for its iron content.

1 *Identify and write equations for the half-reactions.* The oxidation states for the half-reaction involving the permanganate ion show that manganese is reduced:

$$\underset{+7}{\underset{\nearrow}{Mn}}\underset{-2\,(\text{each O})}{\underset{\uparrow}{O_4^-}} \longrightarrow \underset{+2}{\underset{\uparrow}{Mn^{2+}}}$$

This is the *reduction half-reaction.* The other half-reaction involves the oxidation of iron(II) to iron(III) ion and is the *oxidation half-reaction:*

$$\underset{+2}{\underset{\uparrow}{Fe^{2+}}} \longrightarrow \underset{+3}{\underset{\uparrow}{Fe^{3+}}}$$

➥ **2** *Balance each half-reaction.* For the reduction reaction, we have

$$\mathrm{MnO_4}^-(aq) \longrightarrow \mathrm{Mn}^{2+}(aq)$$

a. The manganese is balanced.
b. We balance oxygen by adding $4H_2O$ to the right side of the equation:

$$\mathrm{MnO_4}^-(aq) \longrightarrow \mathrm{Mn}^{2+}(aq) + 4\mathrm{H_2O}(l)$$

c. Next, we balance hydrogen by adding $8H^+$ to the left side:

$$8\mathrm{H}^+(aq) + \mathrm{MnO_4}^-(aq) \longrightarrow \mathrm{Mn}^{2+}(aq) + 4\mathrm{H_2O}(l)$$

d. All the elements have been balanced, but we need to balance the charge using electrons. At this point we have the following overall charges for reactants and products in the reduction half-reaction:

$$\underbrace{\overset{}{\underset{8+}{8\mathrm{H}^+(aq)}} \underset{+}{+} \underset{1-}{\mathrm{MnO_4}^-(aq)}}_{7+} \longrightarrow \underbrace{\underset{2+}{\mathrm{Mn}^{2+}(aq)} \underset{+}{+} \underset{0}{4\mathrm{H_2O}(l)}}_{2+}$$

We can equalize the charges by adding five electrons to the left side:

$$\underbrace{5e^- + 8\mathrm{H}^+(aq) + \mathrm{MnO_4}^-(aq)}_{2+} \longrightarrow \underbrace{\mathrm{Mn}^{2+}(aq) + 4\mathrm{H_2O}(l)}_{2+}$$

Both the *elements* and the *charges* are now balanced, so this represents the balanced reduction half-reaction. The fact that five electrons appear on the reactant side of the equation makes sense, since five electrons are required to reduce $\mathrm{MnO_4}^-$ (Mn has an oxidation state of +7) to Mn^{2+} (Mn has an oxidation state of +2).

For the oxidation reaction

$$\mathrm{Fe}^{2+}(aq) \longrightarrow \mathrm{Fe}^{3+}(aq)$$

the elements are balanced, and we must simply balance the charge:

$$\underbrace{\mathrm{Fe}^{2+}(aq)}_{2+} \longrightarrow \underbrace{\mathrm{Fe}^{3+}(aq)}_{3+}$$

One electron is needed on the right side to give a net 2+ charge on both sides:

$$\underbrace{\mathrm{Fe}^{2+}(aq)}_{2+} \longrightarrow \underbrace{\mathrm{Fe}^{3+}(aq) + e^-}_{2+}$$

The number of electrons gained in the reduction half-reaction must equal the number of electrons lost in the oxidation half-reaction.

➥ **3** *Equalize the electron transfer in the two half-reactions.* Since the reduction half-reaction involves a transfer of five electrons and the oxidation half-reaction involves a transfer of only one electron, the oxidation half-reaction must be multiplied by 5:

$$5\mathrm{Fe}^{2+}(aq) \longrightarrow 5\mathrm{Fe}^{3+}(aq) + 5e^-$$

➥ **4** *Add the half-reactions.* The half-reactions are added to give

$$5e^- + 5\mathrm{Fe}^{2+}(aq) + \mathrm{MnO_4}^-(aq) + 8\mathrm{H}^+(aq) \longrightarrow$$
$$5\mathrm{Fe}^{3+}(aq) + \mathrm{Mn}^{2+}(aq) + 4\mathrm{H_2O}(l) + 5e^-$$

Note that the electrons cancel (as they must) to give the final balanced equation:

$$5\mathrm{Fe}^{2+}(aq) + \mathrm{MnO_4}^-(aq) + 8\mathrm{H}^+(aq) \longrightarrow 5\mathrm{Fe}^{3+}(aq) + \mathrm{Mn}^{2+}(aq) + 4\mathrm{H_2O}(l)$$

➥ **5** *Check that elements and charges are balanced.*

Elements balance: 5Fe, 1Mn, 4O, 8H ⟶ 5Fe, 1Mn, 4O, 8H

Charges balance: $5(2+) + (1-) + 8(1+) = 17+ \longrightarrow 5(3+) + (2+) + 0 = 17+$

The equation is balanced.

Sample Exercise 4.19 Balancing Oxidation–Reduction Reactions (Acidic)

Potassium dichromate ($K_2Cr_2O_7$) is a bright orange compound that can be reduced to a blue-violet solution of Cr^{3+} ions. Under certain conditions, $K_2Cr_2O_7$ reacts with ethyl alcohol (C_2H_5OH) as follows:

$$H^+(aq) + Cr_2O_7^{2-}(aq) + C_2H_5OH(l) \longrightarrow Cr^{3+}(aq) + CO_2(g) + H_2O(l)$$

Balance this equation using the half-reaction method.

Solution

➥ **1** The reduction half-reaction is

$$Cr_2O_7^{2-}(aq) \longrightarrow Cr^{3+}(aq)$$

Chromium is reduced from an oxidation state of $+6$ in $Cr_2O_7^{2-}$ to one of $+3$ in Cr^{3+}.

The oxidation half-reaction is

$$C_2H_5OH(l) \longrightarrow CO_2(g)$$

Carbon is oxidized from an oxidation state of -2 in C_2H_5OH to $+4$ in CO_2.

➥ **2** Balancing all elements except hydrogen and oxygen in the first half-reaction, we have

$$Cr_2O_7^{2-}(aq) \longrightarrow 2Cr^{3+}(aq)$$

Balancing oxygen using H_2O, we have

$$Cr_2O_7^{2-}(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

Balancing hydrogen using H^+, we have

$$14H^+(aq) + Cr_2O_7^{2-}(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

Balancing the charge using electrons, we have

$$6e^- + 14H^+(aq) + Cr_2O_7^{2-}(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

When potassium dichromate reacts with ethanol, a blue-violet solution containing Cr^{3+} is formed.

Next, we turn to the oxidation half-reaction

$$C_2H_5OH(l) \longrightarrow CO_2(g)$$

Balancing carbon, we have

$$C_2H_5OH(l) \longrightarrow 2CO_2(g)$$

Balancing oxygen using H_2O, we have

$$C_2H_5OH(l) + 3H_2O(l) \longrightarrow 2CO_2(g)$$

Balancing hydrogen using H^+, we have

$$C_2H_5OH(l) + 3H_2O(l) \longrightarrow 2CO_2(g) + 12H^+(aq)$$

We then balance the charge by adding $12e^-$ to the right side:

$$C_2H_5OH(l) + 3H_2O(l) \longrightarrow 2CO_2(g) + 12H^+(aq) + 12e^-$$

➥ 3 In the reduction half-reaction there are 6 electrons on the left-hand side, and there are 12 electrons on the right-hand side of the oxidation half-reaction. Thus we multiply the reduction half-reaction by 2 to give

$$12e^- + 28H^+(aq) + 2Cr_2O_7^{2-}(aq) \longrightarrow 4Cr^{3+}(aq) + 14H_2O(l)$$

➥ 4 Adding the half-reactions and canceling identical species, we have

$$\begin{array}{lr}
\textbf{Reduction Half-Reaction:} & 12e^- + 28H^+(aq) + 2Cr_2O_7^{2-}(aq) \longrightarrow 4Cr^{3+}(aq) + 14H_2O(l) \\
\textbf{Oxidation Half-Reaction:} & C_2H_5OH(l) + 3H_2O(l) \longrightarrow 2CO_2(g) + 12H^+(aq) + 12e^- \\
\cline{2-2}
\textbf{Complete Reaction:} & 16H^+(aq) + 2Cr_2O_7^{2-}(aq) + C_2H_5OH(l) \longrightarrow 4Cr^{3+} + 11H_2O(l) + 2CO_2(g)
\end{array}$$

➥ 5 Check that elements and charges are balanced.

Elements balance: $22H, 4Cr, 15O, 2C \longrightarrow 22H, 4Cr, 15O, 2C$

Charges balance: $+16 + 2(-2) + 0 = +12 \longrightarrow 4(+3) + 0 + 0 = +12$

See Exercises 4.73 and 4.74.

Oxidation–reduction reactions can occur in basic solutions (the reactions involve OH^- ions) as well as in acidic solution (the reactions involve H^+ ions). The half-reaction method for balancing equations is slightly different for the two cases.

The Half-Reaction Method for Balancing Equations for Oxidation–Reduction Reactions Occurring in Basic Solution

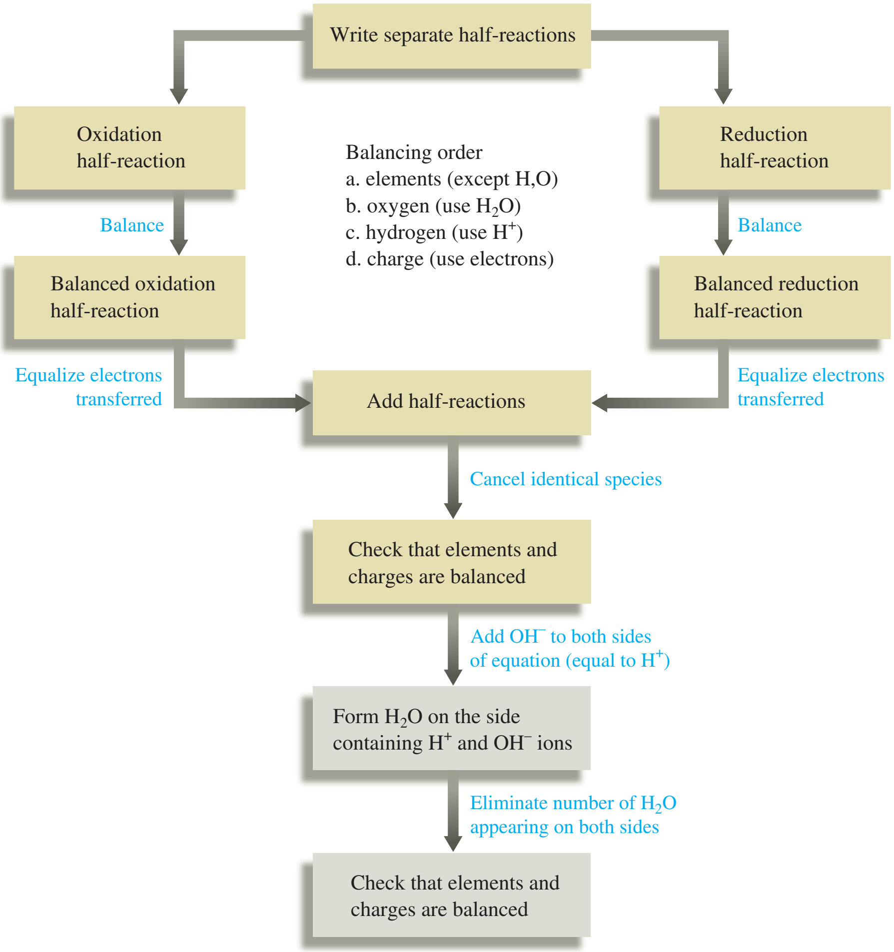
➥ 1 **Use the half-reaction method as specified for acidic solutions to obtain the final balanced equation *as if H^+ ions were present.***

➥ 2 **To both sides of the equation obtained above, add a number of OH^- ions that is equal to the number of H^+ ions. (We want to eliminate H^+ by forming H_2O.)**

➥ 3 **Form H_2O on the side containing both H^+ and OH^- ions, and eliminate the number of H_2O molecules that appear on both sides of the equation.**

➥ 4 **Check that elements and charges are balanced.**

This method is summarized by the following flowchart:



We will illustrate how this method is applied in Sample Exercise 4.20.

Sample Exercise 4.20

Balancing Oxidation–Reduction Reactions (Basic)

Silver is sometimes found in nature as large nuggets; more often it is found mixed with other metals and their ores. An aqueous solution containing cyanide ion is often used to extract the silver using the following reaction that occurs in basic solution:

$$\mathrm{Ag}(s) + \mathrm{CN}^-(aq) + \mathrm{O}_2(g) \xrightarrow{\text{Basic}} \mathrm{Ag(CN)}_2^-(aq)$$

Balance this equation using the half-reaction method.

Solution

➥ **1** Balance the equation as if H^+ ions were present. Balance the oxidation half-reaction:

$$\mathrm{CN}^-(aq) + \mathrm{Ag}(s) \longrightarrow \mathrm{Ag(CN)}_2^-(aq)$$

Balance carbon and nitrogen:

$$2\mathrm{CN}^-(aq) + \mathrm{Ag}(s) \longrightarrow \mathrm{Ag(CN)}_2^-(aq)$$

Balance the charge:

$$2\mathrm{CN}^-(aq) + \mathrm{Ag}(s) \longrightarrow \mathrm{Ag(CN)}_2^-(aq) + \mathrm{e}^-$$

Balance the reduction half-reaction:

$$O_2(g) \longrightarrow$$

Balance oxygen:

$$O_2(g) \longrightarrow 2H_2O(l)$$

Balance hydrogen:

$$O_2(g) + 4H^+(aq) \longrightarrow 2H_2O(l)$$

Balance the charge:

$$4e^- + O_2(g) + 4H^+(aq) \longrightarrow 2H_2O(l)$$

Multiply the balanced oxidation half-reaction by 4:

$$8CN^-(aq) + 4Ag(s) \longrightarrow 4Ag(CN)_2^-(aq) + 4e^-$$

Add the half-reactions, and cancel identical species:

Oxidation Half-Reaction: $8CN^-(aq) + 4Ag(s) \longrightarrow 4Ag(CN)_2^-(aq) + 4e^-$

Reduction Half-Reaction: $4e^- + O_2(g) + 4H^+(aq) \longrightarrow 2H_2O(l)$

Complete Reaction: $8CN^-(aq) + 4Ag(s) + O_2(g) + 4H^+(aq) \longrightarrow 4Ag(CN)_2^-(aq) + 2H_2O(l)$

➥ **2** Add OH^- ions to both sides of the balanced equation to eliminate the H^+ ions. We need to add $4OH^-$ to each side:

$$8CN^-(aq) + 4Ag(s) + O_2(g) + \underbrace{4H^+(aq) + 4OH^-(aq)}_{4H_2O(l)} \longrightarrow 4Ag(CN)_2^-(aq) + 2H_2O(l) + 4OH^-(aq)$$

➥ **3** Eliminate as many H_2O molecules as possible:

$$8CN^-(aq) + 4Ag(s) + O_2(g) + 2H_2O(l) \longrightarrow 4Ag(CN)_2^-(aq) + 4OH^-(aq)$$

➥ **4** Check that elements and charges are balanced.

Elements balance: 8C, 8N, 4Ag, 4O, 4H $\longrightarrow$ 8C, 8N, 4Ag, 4O, 4H

Charges balance: $8(1-) + 0 + 0 + 0 = 8- \longrightarrow 4(1-) + 4(1-) = 8-$

See Exercises 4.75 and 4.76.

Key Terms

aqueous solution

Section 4.1
polar molecule
hydration
solubility

Section 4.2
solute
solvent
electrical conductivity
strong electrolyte
weak electrolyte
nonelectrolyte
acid
strong acid
strong base
weak acid
weak base

For Review

Chemical reactions in solution are very important in everyday life.

Water is a polar solvent that dissolves many ionic and polar substances.

Electrolytes

- Strong electrolyte: 100% dissociated to produce separate ions; strongly conducts an electric current
- Weak electrolyte: Only a small percentage of dissolved molecules produce ions; weakly conducts an electric current
- Nonelectrolyte: Dissolved substance produces no ions; does not conduct an electric current

Acids and bases

- Arrhenius model
  - Acid: produces H^+
  - Base: produces OH^-

Section 4.3

molarity
standard solution
dilution

Section 4.5

precipitation reaction
precipitate

Section 4.6

formula equation
complete ionic equation
spectator ions
net ionic equation

Section 4.8

acid
base
neutralization reaction
volumetric analysis
titration
stoichiometric (equivalence) point
indicator
endpoint

Section 4.9

oxidation–reduction (redox) reaction
oxidation state
oxidation
reduction
oxidizing agent (electron acceptor)
reducing agent (electron donor)

Section 4.10

half-reactions

- Brønsted–Lowry model
  - Acid: proton donor
  - Base: proton acceptor
- Strong acid: completely dissociates into separated H^+ and anions
- Weak acid: dissociates to a slight extent

Molarity

- One way to describe solution composition

$$\text{Molarity } (M) = \frac{\text{moles of solute}}{\text{volume of solution (L)}}$$

- Moles solute = volume of solution (L) × molarity
- Standard solution: molarity is accurately known

Dilution

- Solvent is added to reduce the molarity
- Moles of solute after dilution = moles of solute before dilution

$$M_1V_1 = M_2V_2$$

Types of equations that describe solution reactions

- Formula equation: all reactants and products are written as complete formulas
- Complete ionic equation: all reactants and products that are strong electrolytes are written as separated ions
- Net ionic equation: only those compounds that undergo a change are written; spectator ions are not included

Solubility rules

- Based on experiment observation
- Help predict the outcomes of precipitation reactions

Important types of solution reactions

- Acid–base reactions: involve a transfer of H^+ ions
- Precipitation reactions: formation of a solid occurs
- Oxidation–reduction reactions: involve electron transfer

Titrations

- Measures the volume of a standard solution (titrant) needed to react with a substance in solution
- Stoichiometric (equivalence) point: the point at which the required amount of titrant has been added to exactly react with the substance being analyzed
- Endpoint: the point at which a chemical indicator changes color

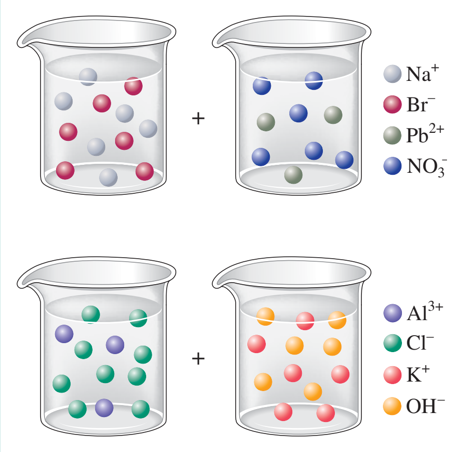
Oxidation–reduction reactions

- Oxidation states are assigned using a set of rules to keep track of electron flow
- Oxidation: increase in oxidation state (a loss of electrons)
- Reduction: decrease in oxidation state (a gain of electrons)
- Oxidizing agent: gains electrons (is reduced)
- Reducing agent: loses electrons (is oxidized)
- Equations for oxidation–reduction reactions are usually balanced by the half-reaction method

REVIEW QUESTIONS

1. The (*aq*) designation listed after a solute indicates the process of hydration. Using $KBr(aq)$ and $C_2H_5OH(aq)$ as your examples, explain the process of hydration for soluble ionic compounds and for soluble covalent compounds.
2. Characterize strong electrolytes versus weak electrolytes versus nonelectrolytes. Give examples of each. How do you experimentally determine whether a soluble substance is a strong electrolyte, weak electrolyte, or nonelectrolyte?

3. Distinguish between the terms *slightly soluble* and *weak electrolyte.*
4. Molarity is a conversion factor relating moles of solute in solution to the volume of the solution. How does one use molarity as a conversion factor to convert from moles of solute to volume of solution, and from volume of solution to moles of solute present?
5. What is a dilution? What stays constant in a dilution? Explain why the equation $M_1V_1 = M_2V_2$ works for dilution problems.
6. When the following beakers are mixed, draw a molecular-level representation of the product mixture (see Fig. 4.17).



7. Differentiate between the formula equation, the complete ionic equation, and the net ionic equation. For each reaction in Question 6, write all three balanced equations.
8. What is an acid–base reaction? Strong bases are soluble ionic compounds that contain the hydroxide ion. List the strong bases. When a strong base reacts with an acid, what is always produced? Explain the terms *titration, stoichiometric point, neutralization,* and *standardization.*
9. Define the terms *oxidation, reduction, oxidizing agent,* and *reducing agent.* Given a chemical reaction, how can you tell if it is a redox reaction?
10. What is a half-reaction? Why must the number of electrons lost in the oxidation equal the number of electrons gained in a reduction? Summarize briefly the steps in the half-reaction method for balancing redox reactions. What two items must be balanced in a redox reaction (or any reaction)?

Active Learning Questions

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

1. Assume you have a highly magnified view of a solution of HCl that allows you to "see" the HCl. Draw this magnified view. If you dropped in a piece of magnesium, the magnesium would disappear and hydrogen gas would be released. Represent this change using symbols for the elements, and write out the balanced equation.

2. You have a solution of table salt in water. What happens to the salt concentration (increases, decreases, or stays the same) as the solution boils? Draw pictures to explain your answer.

3. You have a sugar solution (solution *A*) with concentration *x*. You pour one-fourth of this solution into a beaker, and add an equivalent volume of water (solution *B*).
   - **a.** What is the ratio of sugar in solutions *A* and *B*?
   - **b.** Compare the volumes of solutions *A* and *B*.
   - **c.** What is the ratio of the concentrations of sugar in solutions *A* and *B*?

4. You add an aqueous solution of lead nitrate to an aqueous solution of potassium iodide. Draw highly magnified views of each solution individually, and the mixed solution including any product that forms. Write the balanced equation for the reaction.

5. Order the following molecules from lowest to highest oxidation state of the nitrogen atom: HNO_3, NH_4Cl, N_2O, NO_2, $NaNO_2$.

6. Why is it that when something gains electrons, it is said to be *reduced?* What is being reduced?

7. Consider separate aqueous solutions of HCl and H_2SO_4 with the same molar concentrations. You wish to neutralize an aqueous solution of NaOH. For which acid solution would you need to add more volume (in milliliters) to neutralize the base?

- **a.** the HCl solution
- **b.** the H_2SO_4 solution
- **c.** You need to know the acid concentrations to answer this question.
- **d.** You need to know the volume and concentration of the NaOH solution to answer this question.
- **e.** c and d

Explain.

8. Draw molecular-level pictures to differentiate between concentrated and dilute solutions.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide.*

Questions

9. Differentiate between what happens when the following are dissolved in water.

- **a.** polar solute versus nonpolar solute
- **b.** KF versus $C_6H_{12}O_6$
- **c.** RbCl versus AgCl
- **d.** HNO_3 versus CO

10. A student wants to prepare 1.00 L of a 1.00 *M* solution of NaOH (molar mass = 40.00 g/mol). If solid NaOH is available, how would the student prepare this solution? If 2.00 *M* NaOH is available, how would the student prepare the solution? To help insure three significant figures in the NaOH molarity, to how many significant figures should the volumes and mass be determined?

11. List the formulas of three soluble bromide salts and three insoluble bromide salts. Do the same exercise for sulfate salts, hydroxide salts, and phosphate salts (list three soluble salts and three insoluble salts). List the formulas for six insoluble Pb^{2+} salts and one soluble Pb^{2+} salt.

12. When 1.0 mol of solid lead nitrate is added to 2.0 mol of aqueous potassium iodide, a yellow precipitate forms. After the precipitate settles to the bottom, does the solution above the precipitate conduct electricity? Explain. Write the complete ionic equation to help you answer this question.

13. What is an acid and what is a base? An acid–base reaction is sometimes called a proton-transfer reaction. Explain.

14. A student had 1.00 L of a 1.00 *M* acid solution. Much to the surprise of the student, it took 2.00 L of 1.00 *M* NaOH solution to react completely with the acid. Explain why it took twice as much NaOH to react with all of the acid.

In a different experiment, a student had 10.0 mL of 0.020 *M* HCl. Again, much to the surprise of the student, it took only 5.00 mL of 0.020 *M* strong base to react completely with the HCl. Explain why it took only half as much strong base to react with all of the HCl.

15. Differentiate between the following terms.

- **a.** species reduced versus the reducing agent
- **b.** species oxidized versus the oxidizing agent
- **c.** oxidation state versus actual charge

16. When balancing reactions in Chapter 3, we did not mention that reactions must be charge balanced as well as mass balanced. What do *charge balanced* and *mass balanced* mean? How are redox reactions charge balanced?

Exercises

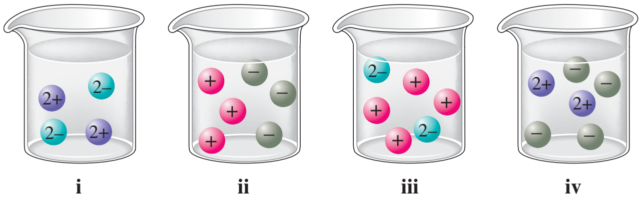
In this section similar exercises are paired.

Aqueous Solutions: Strong and Weak Electrolytes

17. Show how each of the following strong electrolytes "breaks up" into its component ions upon dissolving in water by drawing molecular-level pictures.

a. NaBr	**f.** $FeSO_4$
b. $MgCl_2$	**g.** $KMnO_4$
c. $Al(NO_3)_3$	**h.** $HClO_4$
d. $(NH_4)_2SO_4$	**i.** $NH_4C_2H_3O_2$ (ammonium acetate)
e. NaOH	

18. Match each name below with the following microscopic pictures of that compound in aqueous solution.



a. barium nitrate	**c.** potassium carbonate
b. sodium chloride	**d.** magnesium sulfate

Which picture best represents $HNO_3(aq)$? Why aren't any of the pictures a good representation of $HC_2H_3O_2(aq)$?

19. Calcium chloride is a strong electrolyte and is used to "salt" streets in the winter to melt ice and snow. Write a reaction to show how this substance breaks apart when it dissolves in water.

20. Commercial cold packs and hot packs are available for treating athletic injuries. Both types contain a pouch of water and a dry chemical. When the pack is struck, the pouch of water breaks, dissolving the chemical, and the solution becomes either hot or cold. Many hot packs use magnesium sulfate, and many cold packs use ammonium nitrate. Write reactions to show how these strong electrolytes break apart when they dissolve in water.

Solution Concentration: Molarity

21. Calculate the molarity of each of these solutions.

- **a.** A 5.623-g sample of $NaHCO_3$ is dissolved in enough water to make 250.0 mL of solution.
- **b.** A 184.6-mg sample of $K_2Cr_2O_7$ is dissolved in enough water to make 500.0 mL of solution.
- **c.** A 0.1025-g sample of copper metal is dissolved in 35 mL of concentrated HNO_3 to form Cu^{2+} ions and then water is added to make a total volume of 200.0 mL. (Calculate the molarity of Cu^{2+}.)

22. A solution of ethanol (C_2H_5OH) in water is prepared by dissolving 75.0 mL of ethanol (density = 0.79 g/cm^3) in enough water to make 250.0 mL of solution. What is the molarity of the ethanol in this solution?

23. Calculate the concentration of all ions present in each of the following solutions of strong electrolytes.
a. 0.100 mol of $Ca(NO_3)_2$ in 100.0 mL of solution
b. 2.5 mol of Na_2SO_4 in 1.25 L of solution
c. 5.00 g of NH_4Cl in 500.0 mL of solution
d. 1.00 g K_3PO_4 in 250.0 mL of solution

24. Calculate the concentration of all ions present in each of the following solutions of strong electrolytes.
a. 0.0200 mol of sodium phosphate in 10.0 mL of solution
b. 0.300 mol of barium nitrate in 600.0 mL of solution
c. 1.00 g of potassium chloride in 0.500 L of solution
d. 132 g of ammonium sulfate in 1.50 L of solution

25. Which of the following solutions of strong electrolytes contains the largest number of moles of chloride ions: 100.0 mL of 0.30 *M* $AlCl_3$, 50.0 mL of 0.60 *M* $MgCl_2$, or 200.0 mL of 0.40 *M* NaCl?

26. Which of the following solutions of strong electrolytes contains the largest number of ions: 100.0 mL of 0.100 *M* NaOH, 50.0 mL of 0.200 *M* $BaCl_2$, or 75.0 mL of 0.150 *M* Na_3PO_4?

27. What mass of NaOH is contained in 250.0 mL of a 0.400 *M* sodium hydroxide solution?

28. If 10. g of $AgNO_3$ is available, what volume of 0.25 *M* $AgNO_3$ solution can be prepared?

29. Describe how you would prepare 2.00 L of each of the following solutions.
a. 0.250 *M* NaOH from solid NaOH
b. 0.250 *M* NaOH from 1.00 *M* NaOH stock solution
c. 0.100 *M* K_2CrO_4 from solid K_2CrO_4
d. 0.100 *M* K_2CrO_4 from 1.75 *M* K_2CrO_4 stock solution

30. How would you prepare 1.00 L of a 0.50 *M* solution of each of the following?
a. H_2SO_4 from "concentrated" (18 *M*) sulfuric acid
b. HCl from "concentrated" (12 *M*) reagent
c. $NiCl_2$ from the salt $NiCl_2 \cdot 6H_2O$
d. HNO_3 from "concentrated" (16 *M*) reagent
e. Sodium carbonate from the pure solid

31. A solution is prepared by dissolving 10.8 g ammonium sulfate in enough water to make 100.0 mL of stock solution. A 10.00-mL sample of this stock solution is added to 50.00 mL of water. Calculate the concentration of ammonium ions and sulfate ions in the final solution.

32. Calculate the sodium ion concentration when 70.0 mL of 3.0 *M* sodium carbonate is added to 30.0 mL of 1.0 *M* sodium bicarbonate.

33. A standard solution is prepared for the analysis of fluoxymesterone ($C_{20}H_{29}FO_3$), an anabolic steroid. A stock solution is first prepared by dissolving 10.0 mg of fluoxymesterone in enough water to give a total volume of 500.0 mL. A 100.0-μL aliquot (portion) of this solution is diluted to a final volume of 100.0 mL. Calculate the concentration of the final solution in terms of molarity.

34. A stock solution containing Mn^{2+} ions was prepared by dissolving 1.584 g pure manganese metal in nitric acid and diluting to a final volume of 1.000 L. The following solutions were then prepared by dilution:

For solution *A*, 50.00 mL of stock solution was diluted to 1000.0 mL.
For solution *B*, 10.00 mL of solution *A* was diluted to 250.0 mL.
For solution *C*, 10.00 mL of solution *B* was diluted to 500.0 mL.

Calculate the concentrations of the stock solution and solutions *A*, *B*, and *C*.

Precipitation Reactions

35. On the basis of the general solubility rules given in Table 4.1, predict which of the following substances are likely to be soluble in water.
a. aluminum nitrate
b. magnesium chloride
c. rubidium sulfate
d. nickel(II) hydroxide
e. lead(II) sulfide
f. magnesium hydroxide
g. iron(III) phosphate

36. On the basis of the general solubility rules given in Table 4.1, predict which of the following substances are likely to be soluble in water.
a. zinc chloride
b. lead(II) nitrate
c. lead(II) sulfate
d. sodium iodide
e. cobalt(III) sulfide
f. chromium(III) hydroxide
g. magnesium carbonate
h. ammonium carbonate

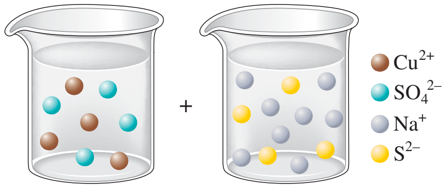
37. When the following solutions are mixed together, what precipitate (if any) will form?
a. $FeSO_4(aq) + KCl(aq)$
b. $Al(NO_3)_3(aq) + Ba(OH)_2(aq)$
c. $CaCl_2(aq) + Na_2SO_4(aq)$
d. $K_2S(aq) + Ni(NO_3)_2(aq)$

38. When the following solutions are mixed together, what precipitate (if any) will form?
a. $Hg_2(NO_3)_2(aq) + CuSO_4(aq)$
b. $Ni(NO_3)_2(aq) + CaCl_2(aq)$
c. $K_2CO_3(aq) + MgI_2(aq)$
d. $Na_2CrO_4(aq) + AlBr_3(aq)$

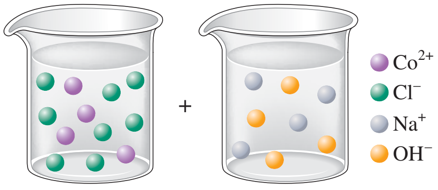
39. For the reactions in Exercise 37, write the balanced formula equation, complete ionic equation, and net ionic equation. If no precipitate forms, write "No reaction."

40. For the reactions in Exercise 38, write the balanced formula equation, complete ionic equation, and net ionic equation. If no precipitate forms, write "No reaction."

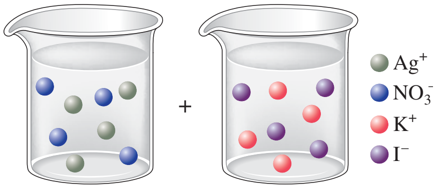
41. Write the balanced formula and net ionic equation for the reaction that occurs when the contents of the two beakers are added together. What colors represent the spectator ions in each reaction?



a.



b.



c.

42. Give an example how each of the following insoluble ionic compounds could be produced using a precipitation reaction. Write the balanced formula equation for each reaction.

a. $Fe(OH)_3(s)$
c. $PbSO_4(s)$
b. $Hg_2Cl_2(s)$
d. $BaCrO_4(s)$

43. Write net ionic equations for the reaction, if any, that occurs when aqueous solutions of the following are mixed.

a. ammonium sulfate and barium nitrate
b. lead(II) nitrate and sodium chloride
c. sodium phosphate and potassium nitrate
d. sodium bromide and rubidium chloride
e. copper(II) chloride and sodium hydroxide

44. Write net ionic equations for the reaction, if any, that occurs when aqueous solutions of the following are mixed.

a. chromium(III) chloride and sodium hydroxide
b. silver nitrate and ammonium carbonate
c. copper(II) sulfate and mercury(I) nitrate
d. strontium nitrate and potassium iodide

45. Separate samples of a solution of an unknown soluble ionic compound are treated with KCl, Na_2SO_4, and NaOH. A precipitate forms only when Na_2SO_4 is added. Which cations could be present in the unknown soluble ionic compound?

46. A sample may contain any or all of the following ions: Hg_2^{2+}, Ba^{2+}, and Mn^{2+}.

a. No precipitate formed when an aqueous solution of NaCl was added to the sample solution.
b. No precipitate formed when an aqueous solution of Na_2SO_4 was added to the sample solution.
c. A precipitate formed when the sample solution was made basic with NaOH.

Which ion or ions are present in the sample solution?

47. What mass of Na_2CrO_4 is required to precipitate all of the silver ions from 75.0 mL of a 0.100 *M* solution of $AgNO_3$?

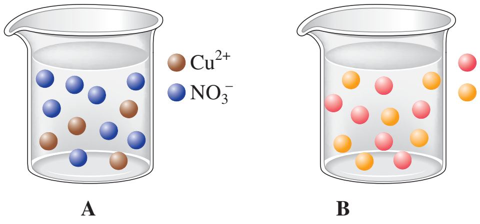
48. What volume of 0.100 *M* Na_3PO_4 is required to precipitate all the lead(II) ions from 150.0 mL of 0.250 *M* $Pb(NO_3)_2$?

49. What mass of solid aluminum hydroxide can be produced when 50.0 mL of 0.200 *M* $Al(NO_3)_3$ is added to 200.0 mL of 0.100 *M* KOH?

50. What mass of barium sulfate can be produced when 100.0 mL of a 0.100 *M* solution of barium chloride is mixed with 100.0 mL of a 0.100 *M* solution of iron(III) sulfate?

51. How many grams of silver chloride can be prepared by the reaction of 100.0 mL of 0.20 *M* silver nitrate with 100.0 mL of 0.15 *M* calcium chloride? Calculate the concentrations of each ion remaining in solution after precipitation is complete.

52. The drawings below represent aqueous solutions. Solution A is 2.00 L of a 2.00 *M* aqueous solution of copper(II) nitrate. Solution B is 2.00 L of a 3.00 *M* aqueous solution of potassium hydroxide.



a. Draw a picture of the solution made by mixing solutions A and B together after the precipitation reaction takes place. Make sure this picture shows the correct relative volume compared to solutions A and B, and the correct relative number of ions, along with the correct relative amount of solid formed.
b. Determine the concentrations (in *M*) of all ions left in solution (from part a) and the mass of solid formed.

53. A 1.42-g sample of a pure compound, with formula M_2SO_4, was dissolved in water and treated with an excess of aqueous calcium chloride, resulting in the precipitation of all the sulfate ions as calcium sulfate. The precipitate was collected, dried, and found to weigh 1.36 g. Determine the atomic mass of M, and identify M.

54. You are given a 1.50-g mixture of sodium nitrate and sodium chloride. You dissolve this mixture into 100 mL of water and then add an excess of 0.500 *M* silver nitrate solution. You produce a white solid, which you then collect, dry, and measure. The white solid has a mass of 0.641 g.

a. If you had an extremely magnified view of the solution (to the atomic-molecular level), list the species you would see (include charges, if any).
b. Write the balanced net ionic equation for the reaction that produces the solid. Include phases and charges.
c. Calculate the percent sodium chloride in the original unknown mixture.

Acid–Base Reactions

55. Write the balanced formula, complete ionic, and net ionic equations for each of the following acid–base reactions.

a. $HClO_4(aq) + Mg(OH)_2(s) \rightarrow$
b. $HCN(aq) + NaOH(aq) \rightarrow$
c. $HCl(aq) + NaOH(aq) \rightarrow$

56. Write the balanced formula, complete ionic, and net ionic equations for each of the following acid–base reactions.

a. $HNO_3(aq) + Al(OH)_3(s) \rightarrow$
b. $HC_2H_3O_2(aq) + KOH(aq) \rightarrow$
c. $Ca(OH)_2(aq) + HCl(aq) \rightarrow$

57. Write the balanced formula, complete ionic, and net ionic equations for the reactions that occur when the following are mixed.

a. potassium hydroxide (aqueous) and nitric acid
b. barium hydroxide (aqueous) and hydrochloric acid
c. perchloric acid [$HClO_4(aq)$] and solid iron(III) hydroxide

58. Write the balanced formula, complete ionic, and net ionic equations for the reactions that occur when the following are mixed.
a. solid silver hydroxide and hydrobromic acid
b. aqueous strontium hydroxide and hydroiodic acid
c. solid chromium(III) hydroxide and nitric acid

59. What volume of each of the following acids will react completely with 50.00 mL of 0.200 *M* NaOH?
a. 0.100 *M* HCl
b. 0.150 *M* HNO_3
c. 0.200 *M* $HC_2H_3O_2$ (1 acidic hydrogen)

60. What volume of each of the following bases will react completely with 25.00 mL of 0.200 *M* HCl?
a. 0.100 *M* NaOH
b. 0.0500 *M* $Ba(OH)_2$
c. 0.250 *M* KOH

61. Hydrochloric acid (75.0 mL of 0.250 *M*) is added to 225.0 mL of 0.0550 *M* $Ba(OH)_2$ solution. What is the concentration of the excess H^+ or OH^- ions left in this solution?

62. A student mixes four reagents together, thinking that the solutions will neutralize each other. The solutions mixed together are 50.0 mL of 0.100 *M* hydrochloric acid, 100.0 mL of 0.200 *M* of nitric acid, 500.0 mL of 0.0100 *M* calcium hydroxide, and 200.0 mL of 0.100 *M* rubidium hydroxide. Is the resulting solution neutral? If not, calculate the concentration of excess H^+ or OH^- ions left in solution.

63. A 25.00-mL sample of hydrochloric acid solution requires 24.16 mL of 0.106 *M* sodium hydroxide for complete neutralization. What is the concentration of the original hydrochloric acid solution?

64. What volume of 0.0200 *M* calcium hydroxide is required to neutralize 35.00 mL of 0.0500 *M* nitric acid?

65. A student titrates an unknown amount of potassium hydrogen phthalate ($KHC_8H_4O_4$, often abbreviated KHP) with 20.46 mL of a 0.1000 *M* NaOH solution. KHP (molar mass = 204.22 g/mol) has one acidic hydrogen. What mass of KHP was titrated (reacted completely) by the sodium hydroxide solution?

66. The concentration of a certain sodium hydroxide solution was determined by using the solution to titrate a sample of potassium hydrogen phthalate (abbreviated as KHP). KHP is an acid with one acidic hydrogen and a molar mass of 204.22 g/mol. In the titration, 34.67 mL of the sodium hydroxide solution was required to react with 0.1082 g KHP. Calculate the molarity of the sodium hydroxide.

Oxidation–Reduction Reactions

67. Assign oxidation states for all atoms in each of the following compounds.
a. $KMnO_4$
b. NiO_2
c. $Na_4Fe(OH)_6$
d. $(NH_4)_2HPO_4$
e. P_4O_6
f. Fe_3O_4
g. $XeOF_4$
h. SF_4
i. CO
j. $C_6H_{12}O_6$

68. Assign oxidation states for all atoms in each of the following compounds.
a. UO_2^{2+}
b. As_2O_3
c. $NaBiO_3$
d. As_4
e. $HAsO_2$
f. $Mg_2P_2O_7$
g. $Na_2S_2O_3$
h. Hg_2Cl_2
i. $Ca(NO_3)_2$

69. Assign the oxidation state for nitrogen in each of the following.
a. Li_3N
b. NH_3
c. N_2H_4
d. NO
e. N_2O
f. NO_2
g. NO_2^-
h. NO_3^-
i. N_2

70. Assign oxidation numbers to all the atoms in each of the following.
a. $SrCr_2O_7$
b. $CuCl_2$
c. O_2
d. H_2O_2
e. $MgCO_3$
f. Ag
g. $PbSO_3$
h. PbO_2
i. $Na_2C_2O_4$
j. CO_2
k. $(NH_4)_2Ce(SO_4)_3$
l. Cr_2O_3

71. Specify which of the following are oxidation–reduction reactions, and identify the oxidizing agent, the reducing agent, the substance being oxidized, and the substance being reduced.
a. $Cu(s) + 2Ag^+(aq) \rightarrow 2Ag(s) + Cu^{2+}(aq)$
b. $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$
c. $SiCl_4(l) + 2H_2O(l) \rightarrow 4HCl(aq) + SiO_2(s)$
d. $SiCl_4(l) + 2Mg(s) \rightarrow 2MgCl_2(s) + Si(s)$
e. $Al(OH)_4^-(aq) \rightarrow AlO_2^-(aq) + 2H_2O(l)$

72. Specify which of the following equations represent oxidation–reduction reactions, and indicate the oxidizing agent, the reducing agent, the species being oxidized, and the species being reduced.
a. $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$
b. $2AgNO_3(aq) + Cu(s) \rightarrow Cu(NO_3)_2(aq) + 2Ag(s)$
c. $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$
d. $2H^+(aq) + 2CrO_4^{2-}(aq) \rightarrow Cr_2O_7^{2-}(aq) + H_2O(l)$

73. Balance the following oxidation–reduction reactions that occur in acidic solution.
a. $Zn(s) + HCl(aq) \rightarrow Zn^{2+}(aq) + H_2(g) + Cl^-(aq)$
b. $I^-(aq) + ClO^-(aq) \rightarrow I_3^-(aq) + Cl^-(aq)$
c. $As_2O_3(s) + NO_3^-(aq) \rightarrow H_3AsO_4(aq) + NO(g)$
d. $Br^-(aq) + MnO_4^-(aq) \rightarrow Br_2(l) + Mn^{2+}(aq)$
e. $CH_3OH(aq) + Cr_2O_7^{2-}(aq) \rightarrow CH_2O(aq) + Cr^{3+}(aq)$

74. Balance the following oxidation–reduction reactions that occur in acidic solution using the half-reaction method.
a. $Cu(s) + NO_3^-(aq) \rightarrow Cu^{2+}(aq) + NO(g)$
b. $Cr_2O_7^{2-}(aq) + Cl^-(aq) \rightarrow Cr^{3+}(aq) + Cl_2(g)$
c. $Pb(s) + PbO_2(s) + H_2SO_4(aq) \rightarrow PbSO_4(s)$
d. $Mn^{2+}(aq) + NaBiO_3(s) \rightarrow Bi^{3+}(aq) + MnO_4^-(aq)$
e. $H_3AsO_4(aq) + Zn(s) \rightarrow AsH_3(g) + Zn^{2+}(aq)$

75. Balance the following oxidation–reduction reactions that occur in basic solution.
a. $Al(s) + MnO_4^-(aq) \rightarrow MnO_2(s) + Al(OH)_4^-(aq)$
b. $Cl_2(g) \rightarrow Cl^-(aq) + OCl^-(aq)$
c. $NO_2^-(aq) + Al(s) \rightarrow NH_3(g) + AlO_2^-(aq)$

76. Balance the following oxidation–reduction reactions that occur in basic solution.

a. $Cr(s) + CrO_4^{2-}(aq) \rightarrow Cr(OH)_3(s)$
b. $MnO_4^-(aq) + S^{2-}(aq) \rightarrow MnS(s) + S(s)$
c. $CN^-(aq) + MnO_4^-(aq) \rightarrow CNO^-(aq) + MnO_2(s)$

77. Chlorine gas was first prepared in 1774 by C. W. Scheele by oxidizing sodium chloride with manganese(IV) oxide. The reaction is

$$NaCl(aq) + H_2SO_4(aq) + MnO_2(s) \longrightarrow Na_2SO_4(aq) + MnCl_2(aq) + H_2O(l) + Cl_2(g)$$

Balance this equation.

78. Gold metal will not dissolve in either concentrated nitric acid or concentrated hydrochloric acid. It will dissolve, however, in aqua regia, a mixture of the two concentrated acids. The products of the reaction are the $AuCl_4^-$ ion and gaseous NO. Write a balanced equation for the dissolution of gold in aqua regia.

Additional Exercises

79. Which of the following statements is (are) true? For the false statements, correct them.

a. A concentrated solution in water will always contain a strong or weak electrolyte.
b. A strong electrolyte will break up into ions when dissolved in water.
c. An acid is a strong electrolyte.
d. All ionic compounds are strong electrolytes in water.

80. A 230.-mL sample of a 0.275 *M* $CaCl_2$ solution is left on a hot plate overnight; the following morning, the solution is 1.10 *M*. What volume of water evaporated from the 0.275 *M* $CaCl_2$ solution?

81. Using the general solubility rules given in Table 4.1, name three reagents that would form precipitates with each of the following ions in aqueous solution. Write the net ionic equation for each of your suggestions.

a. chloride ion
b. calcium ion
c. iron(III) ion
d. sulfate ion
e. mercury(I) ion, Hg_2^{2+}
f. silver ion

82. Consider a 1.50-g mixture of magnesium nitrate and magnesium chloride. After dissolving this mixture in water, 0.500 *M* silver nitrate is added dropwise until precipitate formation is complete. The mass of the white precipitate formed is 0.641 g.

a. Calculate the mass percent of magnesium chloride in the mixture.
b. Determine the minimum volume of silver nitrate that must have been added to ensure complete formation of the precipitate.

83. A 1.00-g sample of an alkaline earth metal chloride is treated with excess silver nitrate. All of the chloride is recovered as 1.38 g of silver chloride. Identify the metal.

84. A mixture contains only NaCl and $Al_2(SO_4)_3$. A 1.45-g sample of the mixture is dissolved in water and an excess of NaOH is added, producing a precipitate of $Al(OH)_3$. The precipitate is filtered, dried, and weighed. The mass of the precipitate is 0.107 g. What is the mass percent of $Al_2(SO_4)_3$ in the sample?

85. Saccharin ($C_7H_5NO_3S$) is sometimes dispensed in tablet form. Ten tablets with a total mass of 0.5894 g were dissolved in water. They were oxidized to convert all the sulfur to sulfate ion, which was precipitated by adding an excess of barium chloride solution. The mass of $BaSO_4$ obtained was 0.5032 g. What is the average mass of saccharin per tablet? What is the average mass percent of saccharin in the tablets?

86. A mixture contains only NaCl and $Fe(NO_3)_3$. A 0.456-g sample of the mixture is dissolved in water, and an excess of NaOH is added, producing a precipitate of $Fe(OH)_3$. The precipitate is filtered, dried, and weighed. Its mass is 0.107 g. Calculate the following.

a. the mass of iron in the sample
b. the mass of $Fe(NO_3)_3$ in the sample
c. the mass percent of $Fe(NO_3)_3$ in the sample

87. A student added 50.0 mL of an NaOH solution to 100.0 mL of 0.400 *M* HCl. The solution was then treated with an excess of aqueous chromium(III) nitrate, resulting in formation of 2.06 g of precipitate. Determine the concentration of the NaOH solution.

88. What acid and what strong base would react in aqueous solution to produce the following salts in the formula equation? Write the balanced formula equation for each reaction.

a. potassium perchlorate
b. cesium nitrate
c. calcium iodide

89. A 10.00-mL sample of vinegar, an aqueous solution of acetic acid ($HC_2H_3O_2$), is titrated with 0.5062 *M* NaOH, and 16.58 mL is required to reach the equivalence point.

a. What is the molarity of the acetic acid?
b. If the density of the vinegar is 1.006 g/cm^3, what is the mass percent of acetic acid in the vinegar?

90. When hydrochloric acid reacts with magnesium metal, hydrogen gas and aqueous magnesium chloride are produced. What volume of 5.0 *M* HCl is required to react completely with 3.00 g of magnesium?

91. A 2.20-g sample of an unknown acid (empirical formula = $C_3H_4O_3$) is dissolved in 1.0 L of water. A titration required 25.0 mL of 0.500 *M* NaOH to react completely with all the acid present. Assuming the unknown acid has one acidic proton per molecule, what is the molecular formula of the unknown acid?

92. Carminic acid, a naturally occurring red pigment extracted from the cochineal insect, contains only carbon, hydrogen, and oxygen. It was commonly used as a dye in the first half of the nineteenth century. It is 53.66% C and 4.09% H by mass. A titration required 18.02 mL of 0.0406 *M* NaOH to neutralize 0.3602 g carminic acid. Assuming that there is only one acidic hydrogen per molecule, what is the molecular formula of carminic acid?

93. A 30.0-mL sample of an unknown strong base is neutralized after the addition of 12.0 mL of a 0.150 *M* HNO_3 solution. If the unknown base concentration is 0.0300 *M*, give some possible identities for the unknown base.

94. Many oxidation–reduction reactions can be balanced by inspection. Try to balance the following reactions by inspection. In each reaction, identify the substance reduced and the substance oxidized.

a. $Al(s) + HCl(aq) \rightarrow AlCl_3(aq) + H_2(g)$
b. $CH_4(g) + S(s) \rightarrow CS_2(l) + H_2S(g)$
c. $C_3H_8(g) + O_2(g) \rightarrow CO_2(g) + H_2O(l)$
d. $Cu(s) + Ag^+(aq) \rightarrow Ag(s) + Cu^{2+}(aq)$

95. One of the classical methods for the determination of the manganese content in steel is to convert all the manganese to the deeply colored permanganate ion and then to measure the absorption of light. The steel is dissolved in nitric acid, producing the manganese(II) ion and nitrogen dioxide gas. This solution is then reacted with an acidic solution containing periodate ion; the products are the permanganate and iodate ions. Write balanced chemical equations for both these steps.

Challenge Problems

96. The units of parts per million (ppm) and parts per billion (ppb) are commonly used by environmental chemists. In general, 1 ppm means 1 part of solute for every 10^6 parts of solution. Mathematically, by mass:

$$\text{ppm} = \frac{\mu\text{g solute}}{\text{g solution}} = \frac{\text{mg solute}}{\text{kg solution}}$$

In the case of very dilute aqueous solutions, a concentration of 1.0 ppm is equal to 1.0 μg of solute per 1.0 mL, which equals 1.0 g solution. Parts per billion is defined in a similar fashion. Calculate the molarity of each of the following aqueous solutions.

a. 5.0 ppb Hg in H_2O
b. 1.0 ppb $CHCl_3$ in H_2O
c. 10.0 ppm As in H_2O
d. 0.10 ppm DDT ($C_{14}H_9Cl_5$) in H_2O

97. In most of its ionic compounds, cobalt is either Co(II) or Co(III). One such compound, containing chloride ion and waters of hydration, was analyzed, and the following results were obtained. A 0.256-g sample of the compound was dissolved in water, and excess silver nitrate was added. The silver chloride was filtered, dried, and weighed, and it had a mass of 0.308 g. A second sample of 0.416 g of the compound was dissolved in water, and an excess of sodium hydroxide was added. The hydroxide salt was filtered and heated in a flame, forming cobalt(III) oxide. The mass of cobalt(III) oxide formed was 0.145 g.

a. What is the percent composition, by mass, of the compound?
b. Assuming the compound contains one cobalt atom per formula unit, what is the molecular formula?
c. Write balanced equations for the three reactions described.

98. Polychlorinated biphenyls (PCBs) have been used extensively as dielectric materials in electrical transformers. Because PCBs have been shown to be potentially harmful, analysis for their presence in the environment has become very important. PCBs are manufactured according to the following generic reaction:

$$C_{12}H_{10} + nCl_2 \rightarrow C_{12}H_{10-n}Cl_n + nHCl$$

This reaction results in a mixture of PCB products. The mixture is analyzed by decomposing the PCBs and then precipitating the resulting Cl^- as AgCl.

a. Develop a general equation that relates the average value of n to the mass of a given mixture of PCBs and the mass of AgCl produced.
b. A 0.1947-g sample of a commercial PCB yielded 0.4791 g of AgCl. What is the average value of n for this sample?

99. You have two 500.0 mL aqueous solutions. Solution A is a solution of silver nitrate, and solution B is a solution of potassium chromate. The masses of the solutes in each of the solutions are the same. When the solutions are added together, a blood-red precipitate forms. After the reaction has gone to completion, you dry the solid and find that it has a mass of 331.8 g.

a. Calculate the concentration of the potassium ions in the original potassium chromate solution.
b. Calculate the concentration of the chromate ions in the final solution.

100. A sample is a mixture of KCl and KBr. When 0.1024 g of the sample is dissolved in water and reacted with excess silver nitrate, 0.1889 g solid is obtained. What is the composition by mass percent of the original mixture?

101. You are given a solid that is a mixture of Na_2SO_4 and K_2SO_4. A 0.205-g sample of the mixture is dissolved in water. An excess of an aqueous solution of $BaCl_2$ is added. The $BaSO_4$ that is formed is filtered, dried, and weighed. Its mass is 0.298 g. What mass of SO_4^{2-} ion is in the sample? What is the mass percent of SO_4^{2-} ion in the sample? What are the percent compositions by mass of Na_2SO_4 and K_2SO_4 in the sample?

102. Zinc and magnesium metal each react with hydrochloric acid according to the following equations:

$$Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$$
$$Mg(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$$

A 10.00-g mixture of zinc and magnesium is reacted with the stoichiometric amount of hydrochloric acid. The reaction mixture is then reacted with 156 mL of 3.00 M silver nitrate to produce the maximum possible amount of silver chloride.

a. Determine the percent magnesium by mass in the original mixture.
b. If 78.0 mL of HCl was added, what was the concentration of the HCl?

103. You made 100.0 mL of a lead(II) nitrate solution for lab but forgot to cap it. The next lab session you noticed that there was only 80.0 mL left (the rest had evaporated). In addition, you forgot the initial concentration of the solution. You decide to take 2.00 mL of the solution and add an excess of a concentrated sodium chloride solution. You obtain a solid with a mass of 3.407 g. What was the concentration of the original lead(II) nitrate solution?

104. Consider reacting copper(II) sulfate with iron. Two possible reactions can occur, as represented by the following equations.

$$\text{copper(II) sulfate}(aq) + \text{iron}(s) \longrightarrow \text{copper}(s) + \text{iron(II) sulfate}(aq)$$
$$\text{copper(II) sulfate}(aq) + \text{iron}(s) \longrightarrow \text{copper}(s) + \text{iron(III) sulfate}(aq)$$

You place 87.7 mL of a 0.500 M solution of copper(II) sulfate in a beaker. You then add 2.00 g of iron filings to the copper(II) sulfate solution. After one of the above reactions occurs, you isolate 2.27 g of copper. Which equation above describes the reaction that occurred? Support your answer.

105. Consider an experiment in which two burets, Y and Z, are simultaneously draining into a beaker that initially contained 275.0 mL of 0.300 M HCl. Buret Y contains 0.150 M NaOH and buret Z contains 0.250 M KOH. The stoichiometric point in the titration is reached 60.65 minutes after Y and Z were started simultaneously. The total volume in the beaker at the stoichiometric point is 655 mL. Calculate the flow rates of burets Y and Z. Assume the flow rates remain constant during the experiment.

106. Complete and balance each acid–base reaction.
  a. $H_3PO_4(aq) + NaOH(aq) \rightarrow$
  Contains three acidic hydrogens
  b. $H_2SO_4(aq) + Al(OH)_3(s) \rightarrow$
  Contains two acidic hydrogens
  c. $H_2Se(aq) + Ba(OH)_2(aq) \rightarrow$
  Contains two acidic hydrogens
  d. $H_2C_2O_4(aq) + NaOH(aq) \rightarrow$
  Contains two acidic hydrogens

107. What volume of 0.0521 *M* $Ba(OH)_2$ is required to neutralize exactly 14.20 mL of 0.141 *M* H_3PO_4? Phosphoric acid contains three acidic hydrogens.

108. A 10.00-mL sample of sulfuric acid from an automobile battery requires 35.08 mL of 2.12 *M* sodium hydroxide solution for complete neutralization. What is the molarity of the sulfuric acid? Sulfuric acid contains two acidic hydrogens.

109. Some of the substances commonly used in stomach antacids are MgO, $Mg(OH)_2$, and $Al(OH)_3$.
  a. Write a balanced equation for the neutralization of hydrochloric acid by each of these substances.
  b. Which of these substances will neutralize the greatest amount of 0.10 *M* HCl per gram?

110. A 6.50-g sample of a diprotic acid requires 137.5 mL of a 0.750 *M* NaOH solution for complete reaction. Determine the molar mass of the acid.

111. Citric acid, which can be obtained from lemon juice, has the molecular formula $C_6H_8O_7$. A 0.250-g sample of citric acid dissolved in 25.0 mL of water requires 37.2 mL of 0.105 *M* NaOH for complete neutralization. What number of acidic hydrogens per molecule does citric acid have?

112. Balance the following equations by the half-reaction method.
  a. $Fe(s) + HCl(aq) \rightarrow HFeCl_4(aq) + H_2(g)$
  b. $IO_3^-(aq) + I^-(aq) \xrightarrow{\text{Acid}} I_3^-(aq)$
  c. $Cr(NCS)_6^{4-}(aq) + Ce^{4+}(aq) \xrightarrow{\text{Acid}}$
  $Cr^{3+}(aq) + Ce^{3+}(aq) + NO_3^-(aq) + CO_2(g) + SO_4^{2-}(aq)$
  d. $CrI_3(s) + Cl_2(g) \xrightarrow{\text{Base}} CrO_4^{2-}(aq) + IO_4^-(aq) + Cl^-(aq)$
  e. $Fe(CN)_6^{4-}(aq) + Ce^{4+}(aq) \xrightarrow{\text{Base}}$
  $Ce(OH)_3(s) + Fe(OH)_3(s) + CO_3^{2-}(aq) + NO_3^-(aq)$
  f. $Fe(OH)_2(s) + H_2O_2(aq) \xrightarrow{\text{Base}} Fe(OH)_3(s)$

113. It took 25.06 ±0.05 mL of a sodium hydroxide solution to titrate a 0.4016-g sample of KHP (see Exercise 65). Calculate the concentration and uncertainty in the concentration of the sodium hydroxide solution. (See Appendix 1.5.) Neglect any uncertainty in the mass.

Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

114. Tris(pentafluorophenyl)borane, commonly known by its acronym BARF, is frequently used to initiate polymerization of ethylene or propylene in the presence of a catalytic transition metal compound. It is composed solely of C, F, and B; it is 42.23% C by mass and 55.66% F by mass.
  a. What is the empirical formula of BARF?
  b. A 2.251-g sample of BARF dissolved in 347.0 mL of solution produces a 0.01267 *M* solution. What is the molecular formula of BARF?

115. In a 1-L beaker, 203 mL of 0.307 *M* ammonium chromate was mixed with 137 mL of 0.269 *M* chromium(III) nitrite to produce ammonium nitrite and chromium(III) chromate. Write the balanced chemical reaction occurring here. If the percent yield of the reaction was 88.0%, how much chromium(III) chromate was isolated?

116. The vanadium in a sample of ore is converted to VO^{2+}. The VO^{2+} ion is subsequently titrated with MnO_4^- in acidic solution to form $V(OH)_4^+$ and manganese(II) ion. To titrate the solution, 26.45 mL of 0.02250 *M* MnO_4^- was required. If the mass percent of vanadium in the ore was 58.1%, what was the mass of the ore sample? Which of the four transition metal ions in this titration has the highest oxidation state?

117. The unknown acid H_2X can be neutralized completely by OH^- according to the following (unbalanced) equation:

$$H_2X(aq) + OH^- \longrightarrow X^{2-} + H_2O$$

The ion formed as a product, X^{2-}, was shown to have 36 total electrons. What is element X? Propose a name for H_2X? To completely neutralize a sample of H_2X, 35.6 mL of 0.175 *M* OH^- solution was required. What was the mass of the H_2X sample used?

Marathon Problems

These problems are designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

118. Three students were asked to find the identity of the metal in a particular sulfate salt. They dissolved a 0.1472-g sample of the salt in water and treated it with excess barium chloride, resulting in the precipitation of barium sulfate. After the precipitate had been filtered and dried, it weighed 0.2327 g.

Each student analyzed the data independently and came to different conclusions. Pat decided that the metal was titanium. Chris thought it was sodium. Randy reported that it was gallium. What formula did each student assign to the sulfate salt?

Look for information on the sulfates of gallium, sodium, and titanium in this text and reference books such as the *CRC Handbook of Chemistry and Physics.* What further tests would you suggest to determine which student is most likely correct?

119. You have two 500.0-mL aqueous solutions. Solution A is a solution of a metal nitrate that is 8.246% nitrogen by mass. The ionic compound in solution B consists of potassium, chromium, and oxygen; chromium has an oxidation state of +6 and there are 2 potassiums and 1 chromium in the formula. The masses of the solutes in each of the solutions are the same. When the solutions are added together, a blood-red precipitate forms. After the reaction has gone to completion, you dry the solid and find that it has a mass of 331.8 g.
  a. Identify the ionic compounds in solution A and solution B.
  b. Identify the blood-red precipitate.
  c. Calculate the concentration (molarity) of all ions in the original solutions.
  d. Calculate the concentration (molarity) of all ions in the final solution.

Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at **college.hmco.com/PIC/zumdahl7e.**