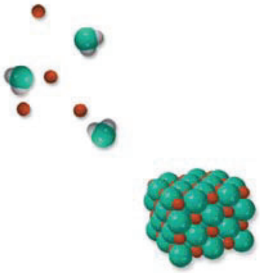
Chapter Outline

A Look Ahead

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

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



4.1 General Properties of Aqueous Solutions

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

Electrolytic Properties

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

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

Comparing the lightbulb's brightness for the same molar amounts of dissolved substances helps us distinguish between strong and weak electrolytes. A characteristic of strong electrolytes is that the solute is assumed to be 100 percent dissociated into ions in solution. (By *dissociation* we mean the breaking up of the compound into cations and anions.) Thus, we can represent sodium chloride dissolving in water as

$$NaCl(s) \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq)$$

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

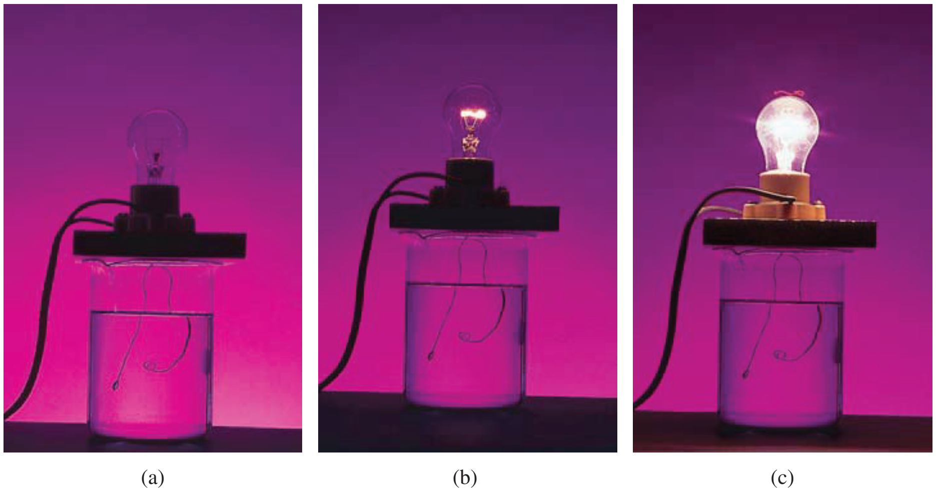

(a) (b) (c)

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

TABLE 4.1 Classification of Solutes in Aqueous Solution

Strong Electrolyte	Weak Electrolyte	Nonelectrolyte
HCl	CH_3COOH	$(NH_2)_2CO$ (urea)
HNO_3	HF	CH_3OH (methanol)
$HClO_4$	HNO_2	C_2H_5OH (ethanol)
H_2SO_4*	NH_3	$C_6H_{12}O_6$ (glucose)
NaOH	H_2O†	$C_{12}H_{22}O_{11}$ (sucrose)
$Ba(OH)_2$		
Ionic compounds		

*H_2SO_4 has two ionizable H^+ ions.
†Pure water is an extremely weak electrolyte.

Table 4.1 lists examples of strong electrolytes, weak electrolytes, and nonelectrolytes. Ionic compounds, such as sodium chloride, potassium iodide (KI), and calcium nitrate [$Ca(NO_3)_2$], are strong electrolytes. It is interesting to note that human body fluids contain many strong and weak electrolytes.

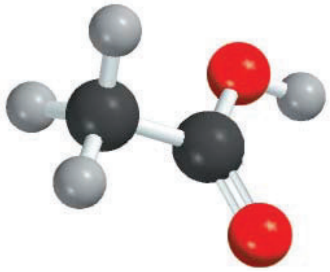
Water is a very effective solvent for ionic compounds. Although water is an electrically neutral molecule, it has a positive region (the H atoms) and a negative region (the O atom), or positive and negative "poles"; for this reason it is a *polar* solvent. When an ionic compound such as sodium chloride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

Acids and bases are also electrolytes. Some acids, including hydrochloric acid (HCl) and nitric acid (HNO_3), are strong electrolytes. These acids are assumed to ionize completely in water; for example, when hydrogen chloride gas dissolves in water, it forms hydrated H^+ and Cl^- ions:

$$HCl(g) \xrightarrow{H_2O} H^+(aq) + Cl^-(aq)$$

In other words, *all* the dissolved HCl molecules separate into hydrated H^+ and Cl^- ions. Thus, when we write HCl(*aq*), it is understood that it is a solution of only $H^+(aq)$ and $Cl^-(aq)$ ions and that there are no hydrated HCl molecules present. On the other hand, certain acids, such as acetic acid (CH_3COOH), which gives vinegar its tart flavor, do not ionize completely and are weak electrolytes. We represent the ionization of acetic acid as

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$



CH_3COOH

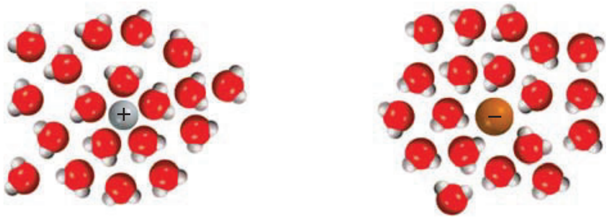


Figure 4.2 *Hydration of Na^+ and Cl^- ions.*

where CH_3COO^- is called the acetate ion. We use the term *ionization* to describe the separation of acids and bases into ions. By writing the formula of acetic acid as CH_3COOH, we indicate that the ionizable proton is in the COOH group.

The ionization of acetic acid is written with a double arrow to show that it is a ***reversible reaction;*** that is, *the reaction can occur in both directions.* Initially, a number of CH_3COOH molecules break up into CH_3COO^- and H^+ ions. As time goes on, some of the CH_3COO^- and H^+ ions recombine into CH_3COOH molecules. Eventually, a state is reached in which the acid molecules ionize as fast as the ions recombine. Such a chemical state, in which no net change can be observed (although activity is continuous on the molecular level), is called *chemical equilibrium.* Acetic acid, then, is a weak electrolyte because its ionization in water is incomplete. By contrast, in a hydrochloric acid solution the H^+ and Cl^- ions have no tendency to recombine and form molecular HCl. We use a single arrow to represent complete ionizations.

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

4.2 Precipitation Reactions

One common type of reaction that occurs in aqueous solution is the ***precipitation reaction,*** which *results in the formation of an insoluble product, or precipitate.* A ***precipitate*** is *an insoluble solid that separates from the solution.* Precipitation reactions usually involve ionic compounds. For example, when an aqueous solution of lead(II) nitrate [$Pb(NO_3)_2$] is added to an aqueous solution of potassium iodide (KI), a yellow precipitate of lead(II) iodide (PbI_2) is formed:

$$Pb(NO_3)_2(aq) + 2KI(aq) \longrightarrow PbI_2(s) + 2KNO_3(aq)$$

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

The preceding reaction is an example of a ***metathesis reaction*** (also called a double-displacement reaction), *a reaction that involves the exchange of parts between the two compounds.* (In this case, the cations in the two compounds exchange anions, so Pb^{2+} ends up with I^- as PbI_2 and K^+ ends up with NO_3^- as KNO_3.) As we will see, the precipitation reactions discussed in this chapter are examples of metathesis reactions.

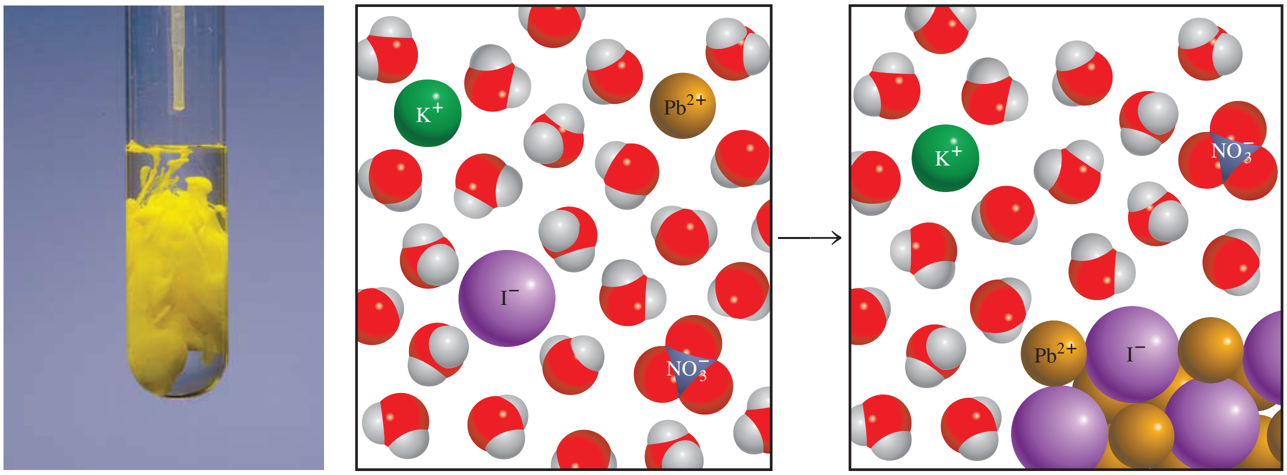


Figure 4.3 *Formation of yellow PbI_2 precipitate as a solution of $Pb(NO_3)_2$ is added to a solution of KI.*

Solubility

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

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

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

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

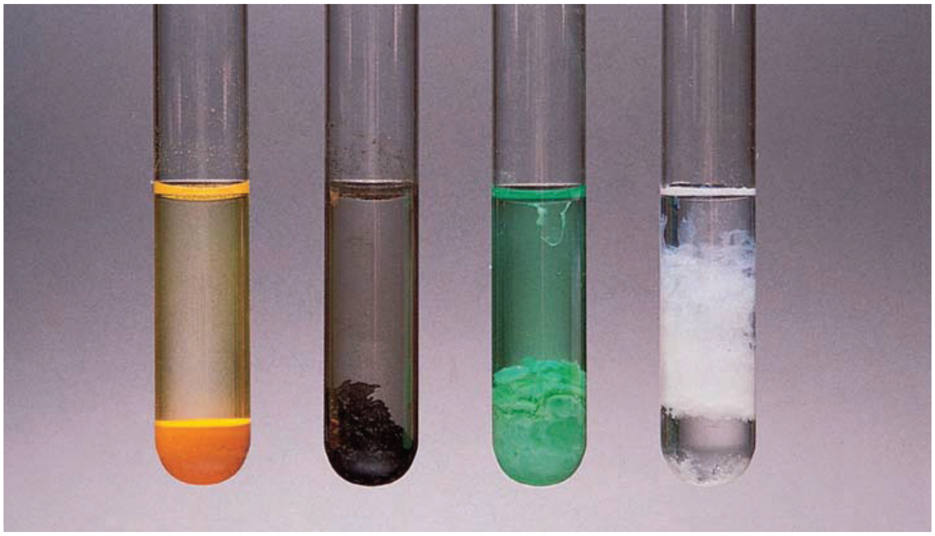


Figure 4.4 *Appearance of several precipitates. From left to right: CdS, PbS, Ni(OH)$_2$, and Al(OH)$_3$.*

Example 4.1 applies the solubility rules in Table 4.2.

EXAMPLE 4.1

Classify the following ionic compounds as soluble or insoluble: (a) silver sulfate (Ag_2SO_4), (b) calcium carbonate ($CaCO_3$), (c) sodium phosphate (Na_3PO_4).

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

Solution (a) According to Table 4.2, Ag_2SO_4 is insoluble.

(b) This is a carbonate and Ca is a Group 2A metal. Therefore, $CaCO_3$ is insoluble.

(c) Sodium is an alkali metal (Group 1A) so Na_3PO_4 is soluble.

Practice Exercise Classify the following ionic compounds as soluble or insoluble: (a) CuS, (b) $Ca(OH)_2$, (c) $Zn(NO_3)_2$.

Molecular Equations, Ionic Equations, and Net Ionic Equations

The equation describing the precipitation of lead(II) iodide on page 124 is called a ***molecular equation*** because *the formulas of the compounds are written as though all species existed as molecules or whole units.* A molecular equation is useful because it identifies the reagents [that is, lead(II) nitrate and potassium iodide]. If we wanted to bring about this reaction in the laboratory, we would use the molecular equation. However, a molecular equation does not describe in detail what actually is happening in solution.

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

$$Pb^{2+}(aq) + 2NO_3^-(aq) + 2K^+(aq) + 2I^-(aq) \longrightarrow PbI_2(s) + 2K^+(aq) + 2NO_3^-(aq)$$

The preceding equation is an example of an ***ionic equation,*** which *shows dissolved species as free ions.* To see whether a precipitate might form from this solution, we first combine the cation and anion from different compounds; that is, PbI_2 and KNO_3. Referring to Table 4.2, we see that PbI_2 is an insoluble compound and KNO_3 is soluble. Therefore, the dissolved KNO_3 remains in solution as separate K^+ and NO_3^- ions, which are called ***spectator ions,*** or *ions that are not involved in the overall reaction.* Because spectator ions appear on both sides of an equation, they can be eliminated from the ionic equation

$$Pb^{2+}(aq) + \cancel{2NO_3^-(aq)} + \cancel{2K^+(aq)} + 2I^-(aq) \longrightarrow PbI_2(s) + \cancel{2K^+(aq)} + \cancel{2NO_3^-(aq)}$$

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

$$Pb^{2+}(aq) + 2I^-(aq) \longrightarrow PbI_2(s)$$

Figure 4.5 *Formation of $BaSO_4$ precipitate.*

Looking at another example, we find that when an aqueous solution of barium chloride ($BaCl_2$) is added to an aqueous solution of sodium sulfate (Na_2SO_4), a white precipitate is formed (Figure 4.5). Treating this as a metathesis reaction, the products are $BaSO_4$ and NaCl. From Table 4.2 we see that only $BaSO_4$ is insoluble. Therefore, we write the molecular equation as

$$BaCl_2(aq) + Na_2SO_4(aq) \longrightarrow BaSO_4(s) + 2NaCl(aq)$$

The ionic equation for the reaction is

$$Ba^{2+}(aq) + 2Cl^-(aq) + 2Na^+(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s) + 2Na^+(aq) + 2Cl^-(aq)$$

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

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$$

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

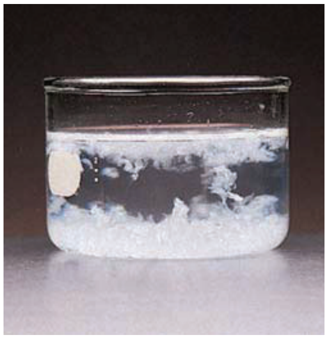
1. Write a balanced molecular equation for the reaction, using the correct formulas for the reactant and product ionic compounds. Refer to Table 4.2 to decide which of the products is insoluble and therefore will appear as a precipitate.
2. Write the ionic equation for the reaction. The compound that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

These steps are applied in Example 4.2.

EXAMPLE 4.2

Predict what happens when a potassium phosphate (K_3PO_4) solution is mixed with a calcium nitrate [$Ca(NO_3)_2$] solution. Write a net ionic equation for the reaction.

(Continued)



Precipitate formed by the reaction between $K_3PO_4(aq)$ and $Ca(NO_3)_2(aq)$.

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

$$K_3PO_4(aq) + Ca(NO_3)_2(aq) \longrightarrow ?$$

What happens when ionic compounds dissolve in water? What ions are formed from the dissociation of K_3PO_4 and $Ca(NO_3)_2$? What happens when the cations encounter the anions in solution?

Solution In solution, K_3PO_4 dissociates into K^+ and PO_4^{3-} ions and $Ca(NO_3)_2$ dissociates into Ca^{2+} and NO_3^- ions. According to Table 4.2, calcium ions (Ca^{2+}) and phosphate ions (PO_4^{3-}) will form an insoluble compound, calcium phosphate [$Ca_3(PO_4)_2$], while the other product, KNO_3, is soluble and remains in solution. Therefore, this is a precipitation reaction. We follow the stepwise procedure just outlined.

Step 1: The balanced molecular equation for this reaction is

$$2K_3PO_4(aq) + 3Ca(NO_3)_2(aq) \longrightarrow Ca_3(PO_4)_2(s) + 6KNO_3(aq)$$

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

$$6K^+(aq) + 2PO_4^{3-}(aq) + 3Ca^{2+}(aq) + 6NO_3^-(aq) \longrightarrow 6K^+(aq) + 6NO_3^-(aq) + Ca_3(PO_4)_2(s)$$

Step 3: Canceling the spectator ions (K^+ and NO_3^-) on each side of the equation, we obtain the net ionic equation:

$$3Ca^{2+}(aq) + 2PO_4^{3-}(aq) \longrightarrow Ca_3(PO_4)_2(s)$$

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

Practice Exercise Predict the precipitate produced by mixing an $Al(NO_3)_3$ solution with a NaOH solution. Write the net ionic equation for the reaction.

4.3 Acid-Base Reactions

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

General Properties of Acids and Bases

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

Svante Arrhenius[†] to classify substances whose properties in aqueous solutions were well known.

Figure 4.6 *A piece of blackboard chalk, which is mostly $CaCO_3$, reacts with hydrochloric acid.*

Acids

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

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

- Acids react with carbonates and bicarbonates, such as Na_2CO_3, $CaCO_3$, and $NaHCO_3$, to produce carbon dioxide gas (Figure 4.6). For example,

$$2HCl(aq) + CaCO_3(s) \longrightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$
$$HCl(aq) + NaHCO_3(s) \longrightarrow NaCl(aq) + H_2O(l) + CO_2(g)$$

- Aqueous acid solutions conduct electricity.

Bases

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

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

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

Acid-Base Neutralization

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

$$\text{acid} + \text{base} \longrightarrow \text{salt} + \text{water}$$

The substance we know as table salt, NaCl, is a product of the acid-base reaction

$$\text{HCl}(aq) + \text{NaOH}(aq) \longrightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$$

Acid-base reactions generally go to completion.

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

$$\text{H}^+(aq) + \text{Cl}^-(aq) + \text{Na}^+(aq) + \text{OH}^-(aq) \longrightarrow \text{Na}^+(aq) + \text{Cl}^-(aq) + \text{H}_2\text{O}(l)$$

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

$$\text{H}^+(aq) + \text{OH}^-(aq) \longrightarrow \text{H}_2\text{O}(l)$$

Both Na^+ and Cl^- are spectator ions.

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

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

$$\text{HCN}(aq) + \text{NaOH}(aq) \longrightarrow \text{NaCN}(aq) + \text{H}_2\text{O}(l)$$

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

$$\text{HCN}(aq) + \text{Na}^+(aq) + \text{OH}^-(aq) \longrightarrow \text{Na}^+(aq) + \text{CN}^-(aq) + \text{H}_2\text{O}(l)$$

and the net ionic equation is

$$\mathrm{HCN}(aq) + \mathrm{OH}^-(aq) \longrightarrow \mathrm{CN}^-(aq) + \mathrm{H_2O}(l)$$

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

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

$$\mathrm{HF}(aq) + \mathrm{KOH}(aq) \longrightarrow \mathrm{KF}(aq) + \mathrm{H_2O}(l)$$
$$\mathrm{H_2SO_4}(aq) + 2\mathrm{NaOH}(aq) \longrightarrow \mathrm{Na_2SO_4}(aq) + 2\mathrm{H_2O}(l)$$

Acid-Base Reactions Leading to Gas Formation

Certain salts like carbonates (containing the $\mathrm{CO_3^{2-}}$ ion), bicarbonates (containing the $\mathrm{HCO_3^-}$ ion), sulfites (containing the $\mathrm{SO_3^{2-}}$ ion), and sulfides (containing the $\mathrm{S^{2-}}$ ion) react with acids to form gaseous products. For example, the molecular equation for the reaction between sodium carbonate ($\mathrm{Na_2CO_3}$) and $\mathrm{HCl}(aq)$ is (see Figure 4.6)

$$\mathrm{Na_2CO_3}(aq) + 2\mathrm{HCl}(aq) \longrightarrow 2\mathrm{NaCl}(aq) + \mathrm{H_2CO_3}(aq)$$

Carbonic acid is unstable and if present in solution in sufficient concentrations decom-poses as follows:

$$\mathrm{H_2CO_3}(aq) \longrightarrow \mathrm{H_2O}(l) + \mathrm{CO_2}(g)$$

Similar reactions involving other mentioned salts are

$$\mathrm{NaHCO_3}(aq) + \mathrm{HCl}(aq) \longrightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l) + \mathrm{CO_2}(g)$$

4.5 Concentration of Solutions

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

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

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}} \tag{4.1}$$

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

Equation (4.1) can also be expressed algebraically as

$$M = \frac{n}{V} \tag{4.2}$$

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

A 1.46 molar glucose ($C_6H_{12}O_6$) solution, written as 1.46 M $C_6H_{12}O_6$, contains 1.46 moles of the solute ($C_6H_{12}O_6$) in 1 L of the solution. Of course, we do not always work with solution volumes of 1 L. Thus, a 500-mL solution containing 0.730 mole of $C_6H_{12}O_6$ also has a concentration of 1.46 M:

$$\text{molarity} = \frac{0.730\text{ mol } C_6H_{12}O_6}{500\ \cancel{\text{mL soln}}} \times \frac{1000\ \cancel{\text{mL soln}}}{1\text{ L soln}} = 1.46\ M\ C_6H_{12}O_6$$

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

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

$$\text{KCl}(s) \xrightarrow{H_2O} \text{K}^+(aq) + \text{Cl}^-(aq)$$

Because KCl is a strong electrolyte, it undergoes complete dissociation in solution. Thus, a 1 M KCl solution contains 1 mole of K^+ ions and 1 mole of Cl^- ions, and no KCl units are present. The concentrations of the ions can be expressed as $[K^+] = 1\ M$ and $[Cl^-] = 1\ M$, where the square brackets [ ] indicate that the concentration is expressed in molarity. Similarly, in a 1 M barium nitrate [$Ba(NO_3)_2$] solution

$$\text{Ba(NO}_3)_2(s) \xrightarrow{H_2O} \text{Ba}^{2+}(aq) + 2\text{NO}_3^-(aq)$$

we have $[Ba^{2+}] = 1\ M$ and $[NO_3^-] = 2\ M$ and no $Ba(NO_3)_2$ units at all.

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

Animation
Making a Solution

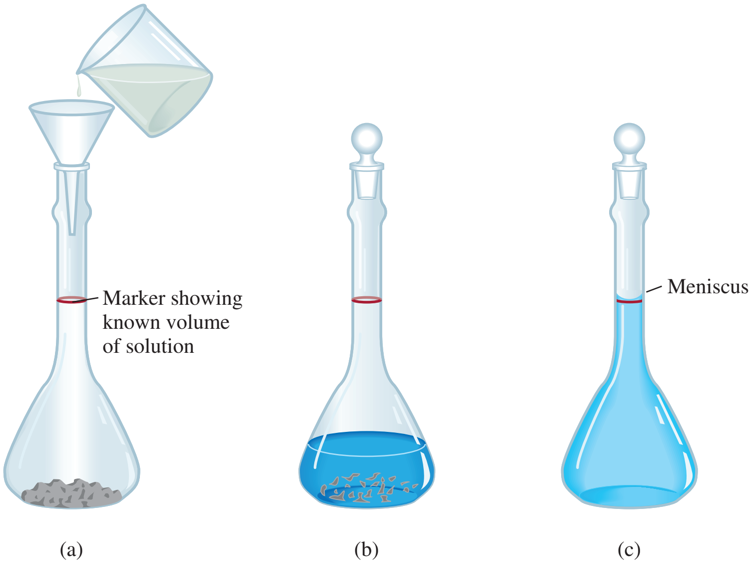


Figure 4.18 *Preparing a solution of known molarity. (a) A known amount of a solid solute is transferred into the volumetric flask; then water is added through a funnel. (b) The solid is slowly dissolved by gently swirling the flask. (c) After the solid has completely dissolved, more water is added to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

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

Examples 4.6 and 4.7 illustrate the applications of Equations (4.1) and (4.2).

A $K_2Cr_2O_7$ solution.

EXAMPLE 4.6

How many grams of potassium dichromate ($K_2Cr_2O_7$) are required to prepare a 250-mL solution whose concentration is 2.16 *M*?

Strategy How many moles of $K_2Cr_2O_7$ does a 1-L (or 1000 mL) 2.16 *M* $K_2Cr_2O_7$ solution contain? A 250-mL solution? How would you convert moles to grams?

Solution The first step is to determine the number of moles of $K_2Cr_2O_7$ in 250 mL or 0.250 L of a 2.16 *M* solution. Rearranging Equation (4.1) gives

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

Thus,

$$\begin{aligned}\text{moles of } K_2Cr_2O_7 &= \frac{2.16 \text{ mol } K_2Cr_2O_7}{1 \cancel{\text{ L soln}}} \times 0.250 \cancel{\text{ L soln}} \\ &= 0.540 \text{ mol } K_2Cr_2O_7\end{aligned}$$

The molar mass of $K_2Cr_2O_7$ is 294.2 g, so we write

$$\begin{aligned}\text{grams of } K_2Cr_2O_7 \text{ needed} &= 0.540 \cancel{\text{ mol } K_2Cr_2O_7} \times \frac{294.2 \text{ g } K_2Cr_2O_7}{1 \cancel{\text{ mol } K_2Cr_2O_7}} \\ &= \boxed{159 \text{ g } K_2Cr_2O_7}\end{aligned}$$

(Continued)

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

Practice Exercise What is the molarity of an 85.0-mL ethanol (C_2H_5OH) solution containing 1.77 g of ethanol?

EXAMPLE 4.7

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

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

Solution From the molar mass of glucose, we write

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

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

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

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

Check One liter of the solution contains 2.53 moles of $C_6H_{12}O_6$. Therefore, the number of moles in 8.36 mL or 8.36×10^{-3} L is (2.53 mol $\times 8.36 \times 10^{-3}$) or 2.12×10^{-2} mol. The small difference is due to the different ways of rounding off.

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

Dilution of Solutions

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

Suppose that we want to prepare 1 L of a 0.400 *M* $KMnO_4$ solution from a solution of 1.00 *M* $KMnO_4$. For this purpose we need 0.400 mole of $KMnO_4$. Because there is 1.00 mole of $KMnO_4$ in 1 L of a 1.00 *M* $KMnO_4$ solution, there is 0.400 mole of $KMnO_4$ in 0.400 L of the same solution:

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

Therefore, we must withdraw 400 mL from the 1.00 *M* $KMnO_4$ solution and dilute it to 1000 mL by adding water (in a 1-L volumetric flask). This method gives us 1 L of the desired solution of 0.400 *M* $KMnO_4$.

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

Two $KMnO_4$ solutions of different concentrations.

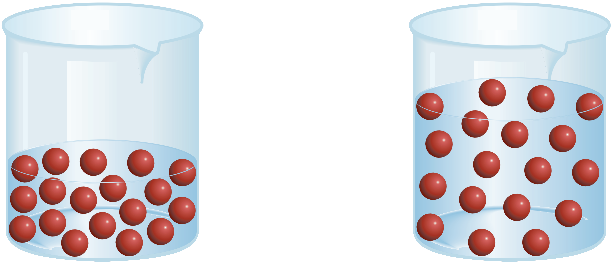

(a) (b)

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

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

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

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

$$\underbrace{\frac{\text{moles of solute}}{\text{liters of soln}}}_{M} \times \underbrace{\text{volume of soln (in liters)}}_{V} = \underbrace{\text{moles of solute}}_{n}$$

or

$$MV = n$$

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

$$\underset{\substack{\text{moles of solute}\\\text{before dilution}}}{M_iV_i} = \underset{\substack{\text{moles of solute}\\\text{after dilution}}}{M_fV_f} \qquad (4.3)$$

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

We apply Equation (4.3) in Example 4.8.

EXAMPLE 4.8

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

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

Solution We prepare for the calculation by tabulating our data:

$$M_i = 8.61\ M \qquad M_f = 1.75\ M$$
$$V_i = ? \qquad V_f = 5.00 \times 10^2\ \text{mL}$$

(Continued)

Substituting in Equation (4.3),

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

Thus, we must dilute 102 mL of the 8.61 M H_2SO_4 solution with sufficient water to give a final volume of 5.00×10^2 mL in a 500-mL volumetric flask to obtain the desired concentration.

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

Practice Exercise How would you prepare 2.00×10^2 mL of a 0.866 M NaOH solution, starting with a 5.07 M stock solution?

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

4.6 Gravimetric Analysis

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

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

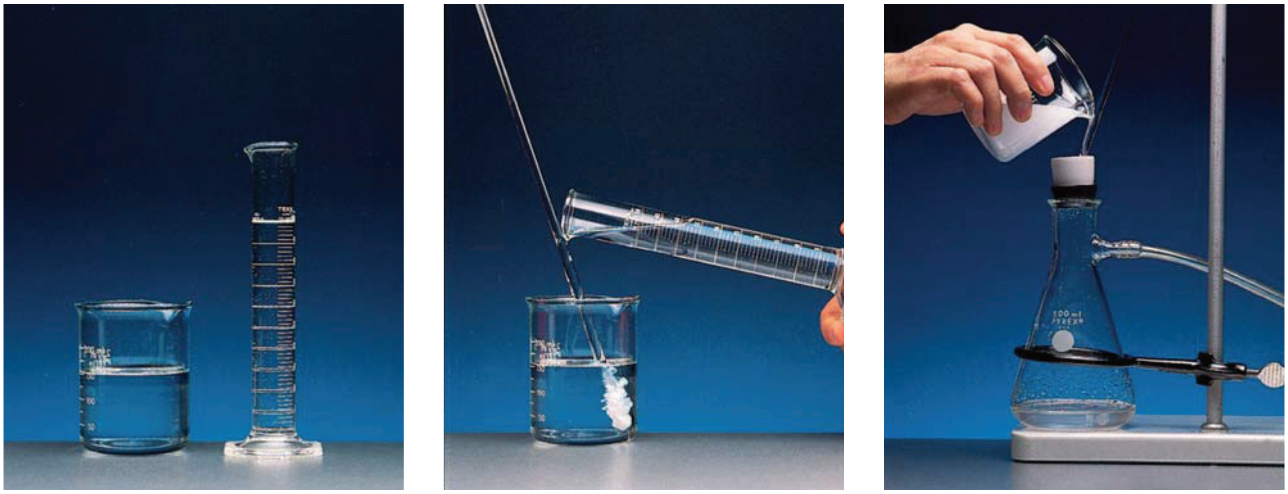
$$AgNO_3(aq) + NaCl(aq) \longrightarrow NaNO_3(aq) + AgCl(s)$$

The net ionic equation is

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

The precipitate is silver chloride (see Table 4.2). As an example, let us say that we wanted to determine *experimentally* the percent by mass of Cl in NaCl. First, we would accurately weigh out a sample of NaCl and dissolve it in water. Next, we would add enough $AgNO_3$ solution to the NaCl solution to cause the precipitation of all the

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



(a) (b) (c)

Figure 4.20 *Basic steps for gravimetric analysis. (a) A solution containing a known amount of NaCl in a beaker. (b) The precipitation of AgCl upon the addition of $AgNO_3$ solution from a measuring cylinder. In this reaction, $AgNO_3$ is the excess reagent and NaCl is the limiting reagent. (c) The solution containing the AgCl precipitate is filtered through a preweighed sintered-disk crucible, which allows the liquid (but not the precipitate) to pass through. The crucible is then removed from the apparatus, dried in an oven, and weighed again. The difference between this mass and that of the empty crucible gives the mass of the AgCl precipitate.*

Cl^- ions present in solution as AgCl. In this procedure, NaCl is the limiting reagent and $AgNO_3$ the excess reagent. The AgCl precipitate is separated from the solution by filtration, dried, and weighed. From the measured mass of AgCl, we can calculate the mass of Cl using the percent by mass of Cl in AgCl. Because this same amount of Cl was present in the original NaCl sample, we can calculate the percent by mass of Cl in NaCl. Figure 4.20 shows how this procedure is performed.

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

Example 4.9 shows the calculations involved in a gravimetric experiment.

EXAMPLE 4.9

A 0.5662-g sample of an ionic compound containing chloride ions and an unknown metal is dissolved in water and treated with an excess of $AgNO_3$. If 1.0882 g of AgCl precipitate forms, what is the percent by mass of Cl in the original compound?

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

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

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

(Continued)

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

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

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

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

Because the original compound also contained this amount of Cl^- ions, the percent by mass of Cl in the compound is

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

Practice Exercise A sample of 0.3220 g of an ionic compound containing the bromide ion (Br^-) is dissolved in water and treated with an excess of $AgNO_3$. If the mass of the AgBr precipitate that forms is 0.6964 g, what is the percent by mass of Br in the original compound?

Note that gravimetric analysis does not establish the whole identity of the unknown. Thus, in Example 4.9 we still do not know what the cation is. However, knowing the per-cent by mass of Cl greatly helps us to narrow the possibilities. Because no two compounds containing the same anion (or cation) have the same percent composition by mass, com-parison of the percent by mass obtained from gravimetric analysis with that calculated f

From the equation for the neutralization reaction just shown, we see that 1 mole of H_2SO_4 neutralizes 2 moles of NaOH. How many moles of H_2SO_4 are contained in 20.0 mL of a 0.245 *M* H_2SO_4 solution? How many moles of NaOH would this quantity of H_2SO_4 neutralize?

Solution First we calculate the number of moles of H_2SO_4 in a 20.0 mL solution:

$$\begin{aligned}\text{moles } H_2SO_4 &= \frac{0.245 \text{ mol } H_2SO_4}{1000 \cancel{\text{mL soln}}} \times 20.0 \cancel{\text{mL soln}} \\ &= 4.90 \times 10^{-3} \text{ mol } H_2SO_4\end{aligned}$$

From the stoichiometry we see that 1 mol $H_2SO_4 \bumpeq$ 2 mol NaOH. Therefore, the number of moles of NaOH reacted must be $2 \times 4.90 \times 10^{-3}$ mole, or 9.80×10^{-3} mole. From the definition of molarity [see Equation (4.1)], we have

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

or

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

Practice Exercise How many milliliters of a 1.28 *M* H_2SO_4 solution are needed to neutralize 60.2 mL of a 0.427 *M* KOH solution?

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

Key Equations

$\text{molarity} = \dfrac{\text{moles of solute}}{\text{liters of solution}}$ (4.1)	Calculating molarity
$M = \dfrac{n}{V}$ (4.2)	Calculating molarity
$M_iV_i = M_fV_f$ (4.3)	Dilution of solution

Summary of Facts and Concepts

1. Aqueous solutions are electrically conducting if the solutes are electrolytes. If the solutes are nonelectrolytes, the solutions do not conduct electricity.
2. Three major categories of chemical reactions that take place in aqueous solution are precipitation reactions, acid-base reactions, and oxidation-reduction reactions.
3. From general rules about solubilities of ionic compounds, we can predict whether a precipitate will form in a reaction.
4. Arrhenius acids ionize in water to give H^+ ions, and Arrhenius bases ionize in water to give OH^- ions. Brønsted acids donate protons, and Brønsted bases accept protons.
5. The reaction of an acid and a base is called neutralization.
6. In redox reactions, oxidation and reduction always occur simultaneously. Oxidation is characterized by the loss of electrons, reduction by the gain of electrons.
7. Oxidation numbers help us keep track of charge distribution and are assigned to all atoms in a compound or ion according to specific rules. Oxidation can be defined as an increase in oxidation number; reduction can be defined as a decrease in oxidation number.
8. Many redox reactions can be subclassified as combination, decomposition, combustion, displacement, or disproportionation reactions.
9. The concentration of a solution is the amount of solute present in a given amount of solution. Molarity expresses concentration as the number of moles of solute in 1 L of solution.
10. Adding a solvent to a solution, a process known as dilution, decreases the concentration (molarity) of the solution without changing the total number of moles of solute present in the solution.

11. Gravimetric analysis is a technique for determining the identity of a compound and/or the concentration of a solution by measuring mass. Gravimetric experiments often involve precipitation reactions.
12. In acid-base titration, a solution of known concentration (say, a base) is added gradually to a solution of unknown concentration (say, an acid) with the goal of determining the unknown concentration. The point at which the reaction in the titration is complete, as shown by the change in the indicator's color, is called the equivalence point.
13. Redox titrations are similar to acid-base titrations. The point at which the oxidation-reduction reaction is complete is called the equivalence point.

Key Words

Activity series, p. 142
Aqueous solution, p. 122
Brønsted acid, p. 130
Brønsted base, p. 130
Combination reaction, p. 139
Combustion reaction, p. 141
Concentration of a solution, p. 147
Decomposition reaction, p. 141
Dilution, p. 149
Diprotic acid, p. 131
Displacement reaction, p. 141
Disproportionation reaction, p. 144
Electrolyte, p. 122
Equivalence point, p. 154
Gravimetric analysis, p. 151
Half-reaction, p. 135
Hydration, p. 123
Hydronium ion, p. 131
Indicator, p. 154
Ionic equation, p. 127
Metathesis reaction, p. 124
Molar concentration, p. 147
Molarity (*M*), p. 147
Molecular equation, p. 126
Monoprotic acid, p. 131
Net ionic equation, p. 127
Neutralization reaction, p. 133
Nonelectrolyte, p. 122
Oxidation number, p. 136
Oxidation state, p. 136
Oxidation reaction, p. 136
Oxidation-reduction reaction, p. 135
Oxidizing agent, p. 136
Precipitate, p. 124
Precipitation reaction, p. 124
Quantitative analysis, p. 151
Redox reaction, p. 135
Reducing agent, p. 136
Reduction reaction, p. 136
Reversible reaction, p. 124
Salt, p. 133
Solubility, p. 125
Solute, p. 122
Solution, p. 122
Solvent, p. 122
Spectator ion, p. 127
Standard solution, p. 153
Titration, p. 153
Triprotic acid, p. 131

Answers to Practice Exercises

4.1 (a) Insoluble, (b) insoluble, (c) soluble. **4.2** $Al^{3+}(aq) + 3OH^{-}(aq) \longrightarrow Al(OH)_3(s)$. **4.3** (a)Brønstedbase, (b) Brønsted acid. **4.4** (a) P: $+3$, F: -1; (b) Mn: $+7$, O: -2. **4.5** (a) Hydrogen displacement reaction, (b) combination reaction, (c) disproportionation reaction, (d) metal displacement reaction. **4.6** 0.452 *M*. **4.7** 494 mL. **4.8** Dilute 34.2 mL of the stock solution to 200 mL. **4.9** 92.02%. **4.10** 0.3822g. **4.11** 10.1mL. **4.12** 204 mL.