4

REACTIONS OF IONS AND MOLECULES IN AQUEOUS SOLUTIONS

The ability of molecules and ions to come into intimate contact when a substance is dissolved in a liquid forms the basis for the chemical reaction that takes place when Alka-Seltzer tablets are dropped into a glass of water. In this chapter we explore a variety of types of chemical reactions that occur in aqueous solutions. *(Gusto Productions/ Photo Researchers, Inc.)*

CHAPTER OUTLINE

THIS CHAPTER IN CONTEXT Ionic compounds are common, and many of them are soluble in water where they break apart into individual ions. Examples of such solutions include seawater and the fluids that surround cells in our bodies. In this chapter our goal is to teach you what happens when ionic substances dissolve in water, the nature of the chemical reactions they undergo, and the products that form.

We will also introduce you to another important class of compounds called acids and bases. These are also common substances that include many household products as well as compounds found in all living creatures. In this chapter we will examine the kinds of substances that are acids and bases and their reactions in aqueous solutions.

In the laboratory, liquid solutions in general (and aqueous solutions in particular) serve as a medium for many chemical reactions. This is because, for a reaction to occur, the particles of the reactants must make physical contact. The particles need freedom of motion, which is made possible when all of the reactants are in one fluid phase. When possible, therefore, solutions of reactants are combined to give a fluid reaction mixture in which chemical changes can occur swiftly and smoothly. To deal quantitatively with such reactions, we will extend the principles of stoichiometry you learned in Chapter 3 to deal with chemical reactions in solution.

4.1 SPECIAL TERMINOLOGY APPLIES TO SOLUTIONS

Before we get to the meat of our subject, we first must define some terms. A **solution** is a homogeneous mixture in which the molecules or ions of the components freely intermingle. When a solution forms, at least two substances are involved. One is the *solvent* and all of the others are *solutes*. The **solvent** is the medium into which the solutes are mixed or dissolved. In this chapter we deal with *aqueous solutions*, so the solvent will be liquid water.[1] A **solute** is any substance dissolved in the solvent. It might be a gas, like the carbon dioxide dissolved in carbonated beverages. Some solutes are liquids, like ethylene glycol dissolved in water to protect a vehicle's radiator against freezing. Solids, of course, can be solutes, like the sugar dissolved in lemonade or the salt dissolved in seawater.

▫ When water is a component of a solution, it is usually considered to be the solvent even when it is present in small amounts.

To describe the composition of a solution, we often specify a **concentration,** which is the *ratio* of the amount of solute either to the amount of solvent or to the amount of solution. A **percentage concentration,** for example, is the number of grams of solute per 100 g of *solution*, a "solute-to-solution" ratio. Thus, the concentration of salt in seawater is often given as 3 g salt/100 g seawater.

The *relative* amounts of solute and solvent are often loosely given without specifying actual quantities. In a **dilute solution** the ratio of solute to solvent is small, for example, a few crystals of salt in a glass of water. In a **concentrated solution,** the ratio of solute to solvent is large. Syrup, for example, is a very concentrated solution of sugar in water.

Concentrated and dilute are relative terms. For example, a solution of 100 g of sugar in 100 mL of water is concentrated compared to one with just 10 g of sugar in 100 mL of water, but the latter solution is more concentrated than one that has 1 g of sugar in 100 mL of water.

Usually there is a limit to the amount of a solute that can dissolve in a given amount of solvent at a given temperature. When this limit is reached, we have a **saturated solution** and any excess solute that's added simply sits at the bottom of the solution. The **solubility** of a solute is the amount required to give a saturated solution, usually expressed as grams dissolved in 100 g of *solvent* at a given temperature. The temperature must be specified because solubilities vary with temperature. A solution having less solute than required for saturation is called an **unsaturated solution.** It is able to dissolve more solute.

In most cases, the solubility of a solute increases with temperature, so more solute can be dissolved by heating a saturated solution in the presence of excess solute. If the temperature of such a warm, saturated solution is subsequently lowered, the additional solute should separate from the solution, and indeed, this tends to happen spontaneously.

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[1] Liquid water is a typical and very common solvent, but the solvent can actually be in any physical state, solid, liquid, or gas.

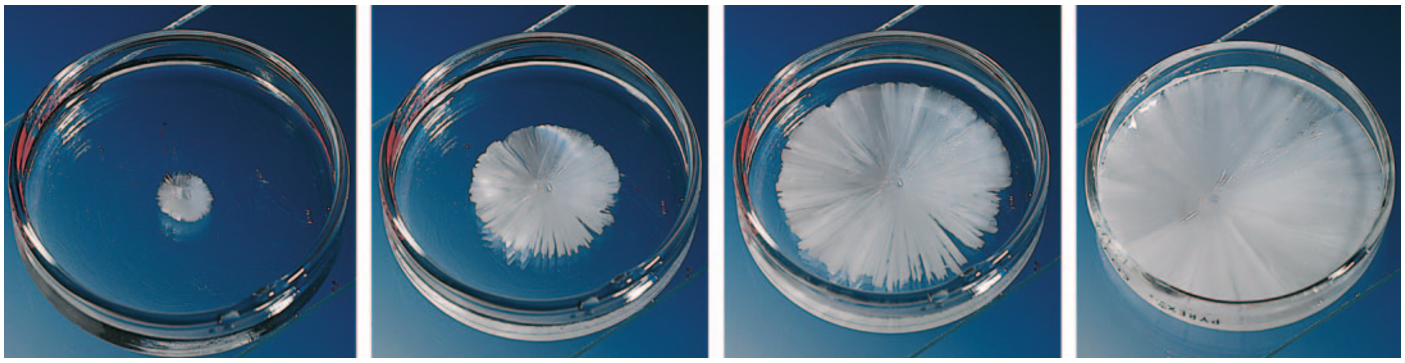


FIG. 4.1 **Crystallization.** When a small seed crystal of sodium acetate is added to a supersaturated solution of the compound, excess solute crystallizes rapidly until the solution is just saturated. The crystallization shown in this sequence took less than 10 seconds! *(Andy Washnik.)*

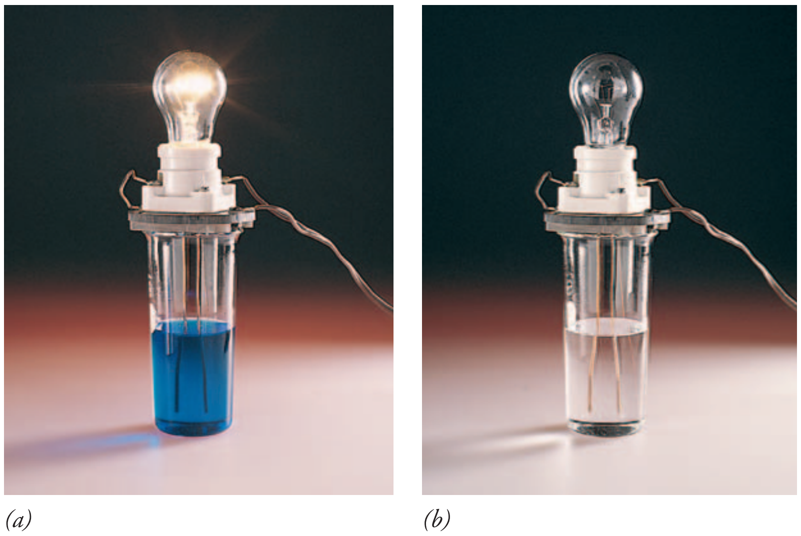
However, sometimes the solute doesn't separate, leaving us with a **supersaturated solution,** a solution that actually contains more solute than required for saturation. Supersaturated solutions are unstable and can only be prepared if there are no traces of undissolved solute. If even a tiny crystal of the solute is present or is added, the extra solute crystallizes (Figure 4.1). A solid that forms in a solution is called a **precipitate,** and a chemical reaction that produces a precipitate is called a **precipitation reaction.**

4.2 IONIC COMPOUNDS CONDUCT ELECTRICITY WHEN DISSOLVED IN WATER

Water itself is a very poor electrical conductor because it consists of electrically neutral molecules that are unable to transport electrical charges. However, as we noted in Chapter 2, when an ionic compound dissolves in water the resulting solution conducts electricity well. This is illustrated in Figure 4.2*a* for a solution of copper sulfate, $CuSO_4$.

Solutes such as $CuSO_4$, which yield electrically conducting aqueous solutions, are called **electrolytes.** Their ability to conduct electricity suggests the presence of electrically charged particles that are able to move through the solution. The generally accepted reason is that when an ionic compound dissolves in water, the ions separate from each other and enter the solution as more or less independent particles that are surrounded by molecules of the solvent. This change is called the **dissociation** of the ionic compound, and is

□ Solutions of electrolytes conduct electricity in a way that's different from metals. This is discussed more completely in Chapter 19.



(a) (b)

FIG. 4.2 **Electrical conductivity of solutions of electrolytes versus nonelectrolytes.** *(a)* The copper sulfate solution is a strong conductor of electricity, and $CuSO_4$ is a strong electrolyte. *(b)* Neither sugar nor water is an electrolyte, and this sugar solution is a nonconductor. *(Michael Watson.)*

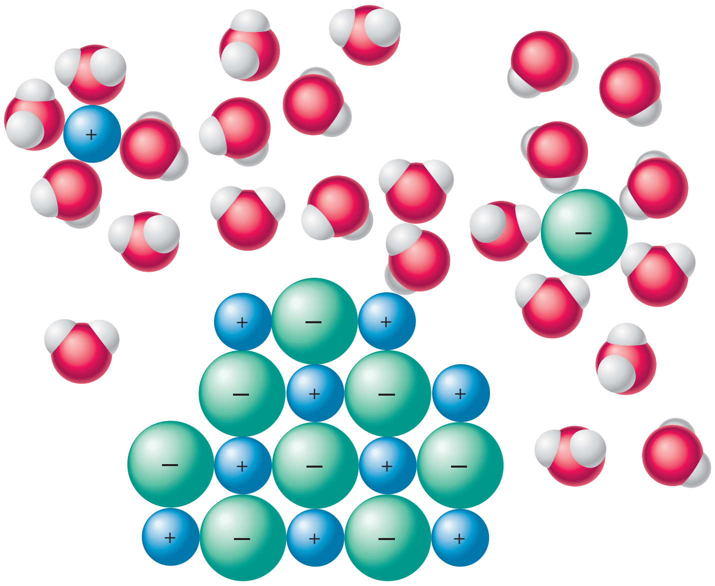


FIG. 4.3 Dissociation of an ionic compound as it dissolves in water. Ions separate from the solid and become surrounded by molecules of water. The ions are said to be hydrated. In the solution, the ions are able to move freely and the solution is able to conduct electricity.

illustrated in Figure 4.3. In general, *we will assume that in water the dissociation of any* ***salt*** *(i.e., ionic compound) is complete* and that the solution contains no undissociated formula units of the salt. Thus, an aqueous solution of $CuSO_4$ is really a solution that contains Cu^{2+} and SO_4^{2-} ions, with virtually no undissociated formula units of $CuSO_4$. Because these solutions contain so many ions, they are strong conductors of electricity, and salts are said to be **strong electrolytes.**

☐ Keep in mind that a strong electrolyte is 100% dissociated in an aqueous solution.

Many ionic compounds have low solubilities in water. An example is AgBr, the light sensitive compound in most photographic film. Although only a tiny amount of this compound dissolves in water, all of it that does dissolve is completely dissociated. However, because of the extremely low solubility, the number of ions in the solution is extremely small and the solution doesn't conduct electricity well. Nevertheless, it is still convenient to think of AgBr as a strong electrolyte because it serves to remind us that salts are completely dissociated in aqueous solution.

Aqueous solutions of most molecular compounds do not conduct electricity, and such solutes are called **nonelectrolytes.** Examples are sugar (Figure 4.2*b*) and ethylene glycol (the solute in antifreeze solutions). Both consist of uncharged molecules that stay intact and simply intermingle with water molecules when they dissolve.

☐ Ethylene glycol, $C_2H_4(OH)_2$, is a type of alcohol. Other alcohols, such as ethanol and methanol, are also nonelectrolytes.

Equations for dissociation reactions show the ions

A convenient way to describe the dissociation of an ionic compound is with a chemical equation. Thus, for the dissociation of calcium chloride in water we write

$$CaCl_2(s) \longrightarrow Ca^{2+}(aq) + 2Cl^-(aq)$$

We use the symbol *aq* after a charged particle to mean that it is surrounded by water molecules in the solution. We say it is **hydrated.** By writing the formulas of the ions separately, we mean that they are essentially independent of each other in the solution. Notice that each formula unit of $CaCl_2(s)$ releases three ions, one $Ca^{2+}(aq)$ and two $Cl^-(aq)$.

Often, when the context is clear that the system is aqueous, the symbols (*s*) and (*aq*) are omitted. They are "understood." You should not be disturbed, therefore, when you see an equation such as

$$CaCl_2 \longrightarrow Ca^{2+} + 2Cl^-$$

Polyatomic ions generally remain intact as dissociation occurs. When copper sulfate dissolves, for example, both Cu^{2+} and SO_4^{2-} ions are released.

$$CuSO_4(s) \longrightarrow Cu^{2+}(aq) + SO_4^{2-}(aq)$$

☐ Be sure you know the formulas and charges on the polyatomic ions listed in Table 2.8 on page 69.

EXAMPLE 4.1

Writing the Equation for the Dissociation of an Ionic Compound

Ammonium sulfate is used as a fertilizer to supply nitrogen to crops. Write the equation for the dissociation of this compound when it dissolves in water.

ANALYSIS: To write the equation correctly, we need to know the formulas of the ions that make up the compound. In this case, the cation is NH_4^+ (ammonium ion) and the anion is SO_4^{2-} (sulfate ion). The correct formula of the compound is therefore $(NH_4)_2SO_4$, which means there are *two* NH_4^+ ions for each SO_4^{2-} ion. We have to be sure to indicate this in the equation.

SOLUTION: We write the formula for the solid on the left of the equation and indicate its state by (*s*). The ions are written on the right side of the equation and are shown to be in aqueous solution by the symbol (*aq*) following their formulas.

$$(NH_4)_2SO_4(s) \longrightarrow 2NH_4^+(aq) + SO_4^{2-}(aq)$$

The subscript 2 becomes the coefficient for NH_4^+.

IS THE ANSWER REASONABLE? There are two things to check when writing equations such as this. First, be sure you have the correct formulas for the ions, including their charges. Second, be sure you've indicated the number of ions of each kind that comes from one formula unit when the compound dissociates. Performing these checks here confirms we've solved the problem correctly.

Practice Exercise 1: Write equations that show the dissociation of the following compounds in water: (a) $FeCl_3$ and (b) potassium phosphate. (Hint: Identify the ions present in each compound.)

Practice Exercise 2: Write equations that show what happens when the following solid ionic compounds dissolve in water: (a) $MgCl_2$, (b) $Al(NO_3)_3$, and (c) sodium carbonate.

Equations for ionic reactions can be written in different ways

Often, ionic compounds react with each other when their aqueous solutions are combined. For example, when solutions of lead nitrate, $Pb(NO_3)_2$, and potassium iodide, KI, are mixed, a bright yellow precipitate of lead iodide, PbI_2, forms (Figure 4.4). The chemical equation for the reaction is

$$Pb(NO_3)_2(aq) + 2KI(aq) \longrightarrow PbI_2(s) + 2KNO_3(aq) \qquad (4.1)$$

where we have noted the insolubility of PbI_2 by writing (*s*) following its formula. This is called a **molecular equation** because all the formulas are written with the ions together, as if the substances in solution consist of neutral "molecules." Equation 4.1 is fine for performing stoichiometric calculations, but let's look at other ways that we might write the chemical equation.

Soluble ionic compounds are fully dissociated in solution, so $Pb(NO_3)_2$, KI, and KNO_3 are not present in the solution as intact units or "molecules." To show this, we can write the formulas of all soluble strong electrolytes in "dissociated" form to give the **ionic equation** for the reaction.

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

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

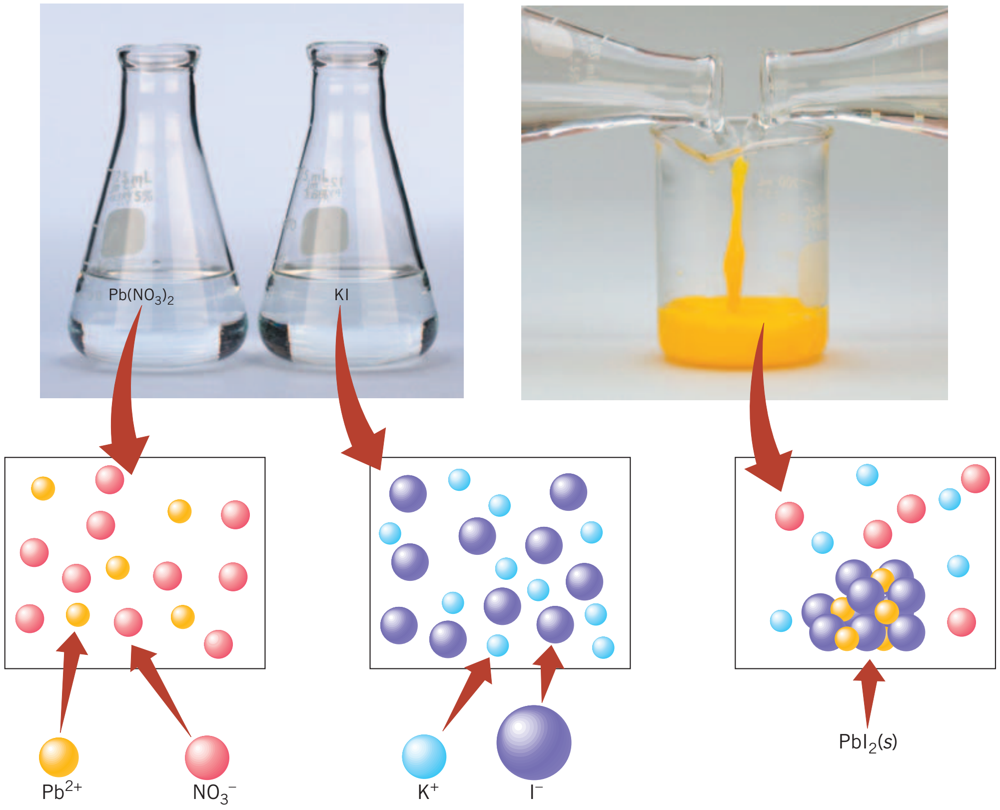


FIG. 4.4 **The reaction of $Pb(NO_3)_2$ with KI.** On the left are flasks containing solutions of lead nitrate and potassium iodide. These solutes exist as separated ions in their respective solutions. On the right, we observe that when the solutions of the ions are combined, there is an immediate reaction as the Pb^{2+} ions join with the I^- ions to give a precipitate of small crystals of solid, yellow PbI_2. The reaction is so rapid that the yellow color develops where the two streams of liquid come together. If the $Pb(NO_3)_2$ and KI are combined in a 1-to-2 mole ratio, the solution would now contain only K^+ and NO_3^- ions (the ions of KNO_3). *(Andy Washnik.)*

Notice that we have *not* separated PbI_2 into its ions in this equation. This is because PbI_2 has an extremely low solubility in water; it is essentially insoluble. When the Pb^{2+} and I^- ions meet in the solution, insoluble PbI_2 forms and separates as a precipitate. Therefore, after the reaction is over, the Pb^{2+} and I^- ions are no longer able to move independently. They are trapped in the insoluble product.

The ionic equation gives a clearer picture of what is actually going on in the solution during the reaction. The Pb^{2+} and I^- ions come together to form the product, while the other ions, K^+ and NO_3^-, are unchanged by the reaction. *Ions that do not actually take part in a reaction are sometimes called* **spectator ions;** in a sense, they just "stand by and watch the action."

To emphasize the actual reaction that occurs, we can write the **net ionic equation,** *which is obtained by eliminating spectator ions from the ionic equation*. Let's cross out the spectator ions, K^+ and NO_3^-.

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

What remains is the net ionic equation,

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

Notice how it calls our attention to the ions that are actually participating in the reaction as well as the change that occurs.

FACETS OF CHEMISTRY 4.1

Boiler Scale and Hard Water

Precipitation reactions occur around us all the time and we hardly ever take notice until they cause a problem. One common problem is caused by **hard water**—groundwater that contains the "hardness ions," Ca^{2+}, Mg^{2+}, Fe^{2+}, or Fe^{3+}, in concentrations high enough to form precipitates with ordinary soap. Soap normally consists of the sodium salts of organic acids derived from animal fats or oils (so-called *fatty acids*). An example is sodium stearate, $NaC_{18}H_{35}O_2$. The negative ion of the soap forms an insoluble "scum" with hardness ions, which reduces the effectiveness of the soap for removing dirt and grease.

Hardness ions can be removed from water in a number of ways. One way is to add hydrated sodium carbonate, $Na_2CO_3 \cdot 10H_2O$, often called washing soda, to the water. The carbonate ion forms insoluble precipitates with the hardness ions; an example is $CaCO_3$.

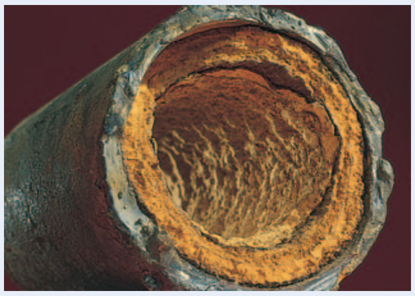
$$Ca^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow CaCO_3(s)$$

Once precipitated, the hardness ions are not available to interfere with the soap.

Another problem when the hard water of a particular locality is rich in bicarbonate ion is the precipitation of insoluble carbonates on the inner walls of hot pipes. When solutions containing HCO_3^- are heated, the ion decomposes as follows.

$$2HCO_3^-(aq) \longrightarrow H_2O + CO_2(g) + CO_3^{2-}(aq)$$

Like most gases, carbon dioxide becomes less soluble as the temperature is raised, so CO_2 is driven from the hot solution and the HCO_3^- is gradually converted to CO_3^{2-}. As the carbonate ions form, they are able to precipitate the hardness ions. This precipitate, which sticks to the inner walls of pipes and hot water boilers, is called *boiler scale*. In locations that have high concentrations of Ca^{2+} and HCO_3^- in the water supply, boiler scale is a very serious problem, as illustrated in the accompanying photograph.



Boiler scale built up on the inside of a water pipe. *(Courtesy of Betz Company.)*

The net ionic equation is especially useful because it permits us to *generalize*. It tells us that if we combine *any* solution that contains Pb^{2+} with *any* other solution that contains I^-, we ought to expect a precipitate of PbI_2. And this is exactly what happens if we mix aqueous solutions of lead acetate, $Pb(C_2H_3O_2)_2$, and sodium iodide, NaI. A yellow precipitate of PbI_2 forms immediately (Figure 4.5). Example 4.2 demonstrates how we construct the molecular, ionic, and net ionic equations for the reaction.

FIG. 4.5 Another reaction that forms lead iodide. The net ionic equation tells us that any soluble lead compound will react with any soluble iodide compound to give lead iodide. This prediction is borne out here as a precipitate of lead iodide is formed when a solution of sodium iodide is added to a solution of lead acetate. *(Andy Washnik.)*

EXAMPLE 4.2
Writing Molecular, Ionic, and Net Ionic Equations

Write the molecular, ionic, and net ionic equations for the reaction of aqueous solutions of lead acetate and sodium iodide, which yields a precipitate of lead iodide and leaves the compound sodium acetate in solution.

If necessary, review Section 2.9, which discusses naming ionic compounds.

ANALYSIS: To write a chemical equation, we must begin with the correct formulas of the reactants and products. If only the names of the reactants and products are given, we have to translate them into chemical formulas. Following the rules we discussed in Chapter 2, we have

Reactants		*Products*	
lead acetate	$Pb(C_2H_3O_2)_2$	lead iodide	PbI_2
sodium iodide	NaI	sodium acetate	$NaC_2H_3O_2$

We arrange the formulas to form the molecular equation, which we then balance. To obtain the ionic equation, we write soluble ionic compounds in dissociated form and the formula of the precipitate in "molecular" form. Finally, we look for spectator ions and eliminate them from the ionic equation to obtain the net ionic equation.

SOLUTION:

The Molecular Equation We assemble the chemical formulas into the molecular equation.

$$Pb(C_2H_3O_2)_2(aq) + 2NaI(aq) \longrightarrow PbI_2(s) + 2NaC_2H_3O_2(aq)$$

Notice that we've indicated which substances are in solution and which is a precipitate, and we've balanced the equation. This is the *balanced molecular equation.*

The Ionic Equation To write the ionic equation, we write the formulas of all soluble salts in dissociated form and the formulas of precipitates in "molecular" form. We are careful to use the subscripts and coefficients in the molecular equation to properly obtain the coefficients of the ions in the ionic equation.

$$\begin{tikzcd}[column sep=tiny]
 & Pb(C_2H_3O_2)_2(aq) \arrow[dl] \arrow[dr] & & & & 2NaI(aq) \arrow[dl] \arrow[dr] & & & & & & 2NaC_2H_3O_2(aq) \arrow[dl] \arrow[dr] & \\
Pb^{2+}(aq) & + & 2C_2H_3O_2^-(aq) & + & 2Na^+(aq) & + & 2I^-(aq) & \longrightarrow & PbI_2(s) & + & 2Na^+(aq) & + & 2C_2H_3O_2^-(aq)
\end{tikzcd}$$

This is the *balanced ionic equation*. Notice that to properly write the ionic equation it is necessary to know both the formulas and charges of the ions.

The Net Ionic Equation We obtain the net ionic equation from the ionic equation by eliminating spectator ions, which are Na^+ and $C_2H_3O_2^-$ (they're the same on both sides of the arrow). Let's cross them out.

$$Pb^{2+}(aq) + \cancel{2C_2H_3O_2^-(aq)} + \cancel{2Na^+(aq)} + 2I^-(aq) \longrightarrow$$
$$PbI_2(s) + \cancel{2Na^+(aq)} + \cancel{2C_2H_3O_2^-(aq)}$$

What's left is the *net ionic equation.*

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

Notice this is the same net ionic equation as in the reaction of lead nitrate with potassium iodide.

ARE THE ANSWERS REASONABLE? When you look back over a problem such as this, things to ask yourself are (1) "Have I written the correct formulas for the reactants and products?", (2) "Is the molecular equation balanced correctly?", (3) "Have I divided the soluble ionic compounds into their ions correctly, being careful to properly apply the subscripts of the ions and the coefficients in the molecular equation?", and (4) "Have I identified and eliminated the correct ions from the ionic equation to obtain the net ionic equation?" If each of these questions can be answered in the affirmative, as they can here, the problem has been solved correctly.

Practice Exercise 3: When solutions of $(NH_4)_2SO_4$ and $Ba(NO_3)_2$ are mixed, a precipitate of $BaSO_4$ forms, leaving soluble NH_4NO_3 in the solution. Write the molecular, ionic, and net ionic equations for the reaction. (Hint: Remember that polyatomic ions do not break apart when ionic compounds dissolve in water.)

Practice Exercise 4: Write molecular, ionic, and net ionic equations for the reaction of aqueous solutions of cadmium chloride and sodium sulfide to give a precipitate of cadmium sulfide and a solution of sodium chloride.

FIG. 4.6 **An acid–base indicator.** Litmus paper, a strip of paper impregnated with the dye litmus, becomes blue in aqueous ammonia (a base) and pink in lemon juice (which contains citric acid). *(Ken Karp.)*

In a balanced ionic or net ionic equation, both atoms and charge must balance

In the ionic and net ionic equations we've written, not only are the atoms in balance, but so is the net electrical charge, which is the same on both sides of the equation. Thus, in the ionic equation for the reaction of lead nitrate with potassium iodide, the sum of the charges of the ions on the left (Pb^{2+}, $2NO_3^-$, $2K^+$, and $2I^-$) is zero, which matches the sum of the charges on all of the formulas of the products (PbI_2, $2K^+$, and $2NO_3^-$).[2] In the net ionic equation the charges on both sides are also the same: on the left we have Pb^{2+} and $2I^-$, with a net charge of zero, and on the right we have PbI_2, also with a charge of zero. We now have an additional requirement for an ionic equation or net ionic equation to be balanced: *the net electrical charge on both sides of the equation must be the same.*

Criteria for Balanced Ionic and Net Ionic Equations

1. **Material balance.** There must be the same number of atoms of each kind on both sides of the arrow.
2. **Electrical balance.** The *net* electrical charge on the left must equal the *net* electrical charge on the right (although this charge does not necessarily have to be zero).

TOOLS
Criteria for a balanced ionic equation

4.3 ACIDS AND BASES ARE CLASSES OF COMPOUNDS WITH SPECIAL PROPERTIES

Acids and bases constitute a class of compounds that include some of our most familiar chemicals and important laboratory reagents. Vinegar, lemon juice, and the liquid in an automobile battery contain acids. The white crystals of lye in some drain cleaners, the white substance that makes milk of magnesia opaque, and household ammonia are all bases.

There are some general properties that are common to aqueous solutions of acids and bases. For example, **acids** generally have a tart (sour) taste, whereas **bases** have a somewhat bitter taste and have a soapy "feel." (However, taste is ***never*** used as a laboratory test for acids or bases; some are extremely corrosive to animal tissue. ***Never taste chemicals in the laboratory!***)

Acids and bases also affect the colors of certain dyes we call **acid–base indicators.** An example is litmus (Figure 4.6), which has a pink or red color in an acidic solution and a blue color in a basic solution.[3]

One of the most important properties of acids and bases is their reaction with each other, a reaction referred to as **neutralization.** For example, when solutions of hydrochloric acid, HCl(*aq*), and the base sodium hydroxide, NaOH(*aq*), are mixed the following reaction occurs.

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O$$

Acids and bases should be treated with respect because of their potential for causing bodily injury if spilled on the skin. If you spill an acid or base on yourself in the lab, be sure to wash it off immediately and notify your instructor at once.

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[2] There is no charge written for the formula of a compound such as PbI_2, so as we add up charges, we take the charge on PbI_2 to be zero.

[3] Litmus paper, commonly found among the items in a locker in the general chemistry lab, consists of strips of absorbent paper that have been soaked in a solution of litmus and dried. Red litmus paper is used to test if a solution is basic. A basic solution turns red litmus blue. To test if the solution is acidic, blue litmus paper is used. Acidic solutions turn blue litmus red.

When the reactants are combined in a 1-to-1 ratio by moles, the acidic and basic properties of the solutes disappear and the resulting solution is neither acidic nor basic. We say an *acid–base neutralization* has occurred. Svante Arrhenius,[4] a Swedish chemist, was the first to suggest that an acid–base neutralization is simply the combination of a hydrogen ion with a hydroxide ion to produce a water molecule, thus making H^+ ions and OH^- ions disappear.

Today we know that in aqueous solutions hydrogen ions, H^+, attach themselves to water molecules to form **hydronium ions,** H_3O^+. However, for the sake of convenience, we often use the term *hydrogen ion* as a substitute for *hydronium ion*, and in many equations, we use $H^+(aq)$ to stand for $H_3O^+(aq)$. In fact, whenever you see the symbol $H^+(aq)$, you should realize that we are actually referring to $H_3O^+(aq)$.

▫ Even the formula H_3O^+ is something of a simplification. In water the H^+ ion is associated with more than one molecule of water, but we use the formula H_3O^+ as a simple representation.

For most purposes, we find that the following modified versions of Arrhenius' definitions work satisfactorily when we deal with aqueous solutions.

Arrhenius Definition of Acids and Bases

An **acid** is a substance that reacts with water to produce hydronium ion, H_3O^+.

A **base** is a substance that produces hydroxide ion in water.

In general, the reaction of an acid with a base produces an ionic compound as one of the products. In the reaction of $HCl(aq)$ with $NaOH(aq)$, the compound is sodium chloride, or salt. This reaction is so general, in fact, that *we use the word* **salt** *to mean any ionic compound that doesn't contain either hydroxide ion,* OH^-*, or oxide ion,* O^{2-}. (Ionic compounds that contain OH^- or O^{2-} are bases, as described below.)

In aqueous solutions, acids give H_3O^+

In general, **acids** are molecular substances that react with water to produce ions, one of which is the hydronium ion, H_3O^+. Thus, when gaseous molecular HCl dissolves in water, a hydrogen ion (H^+) transfers from the HCl molecule to a water molecule. The reaction is depicted in Figure 4.7 using space-filling models, and is represented by the chemical equation

$$HCl(g) + H_2O \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

▫ If gaseous HCl is cooled to about −85 °C, it condenses to a liquid that doesn't conduct electricity. No ions are present in pure liquid HCl.

This is an **ionization reaction** because ions form where none existed before. Because the solution contains ions, it conducts electricity, so acids are electrolytes.

Sometimes acids also contain hydrogen atoms that are not able to form H_3O^+. An example is acetic acid, $HC_2H_3O_2$, the acid that gives vinegar its sour taste. This acid reacts with water as follows.

$$HC_2H_3O_2(aq) + H_2O \longrightarrow H_3O^+(aq) + C_2H_3O_2^-(aq)$$

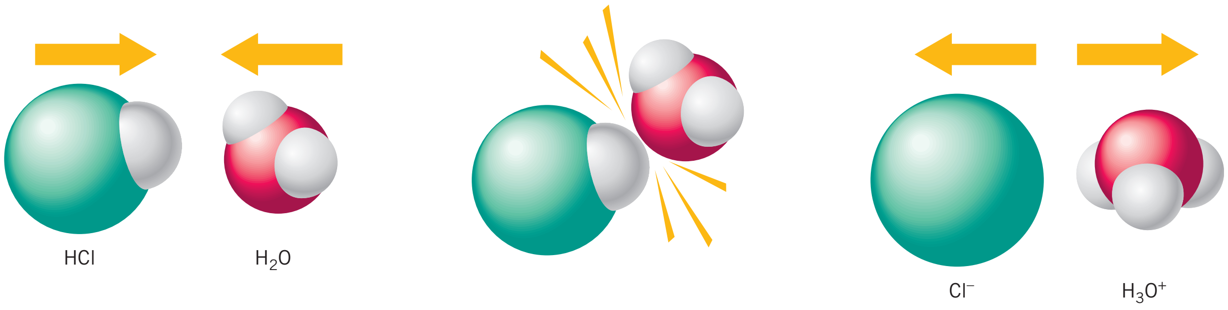

FIG. 4.7 **Ionization of HCl in water.** Collisions between HCl molecules and water molecules lead to a transfer of H^+ from HCl to H_2O, giving Cl^- and H_3O^+ as products.

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[4] Arrhenius proposed his theory of acids and bases in 1884 in his Ph.D. thesis. He won the Nobel Prize in Chemistry for his work in 1903.

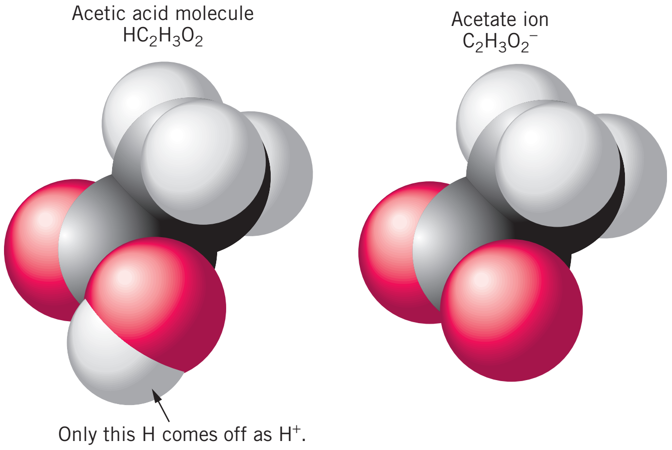

FIG. 4.8 **Acetic acid and acetate ion.** The structures of acetic acid and acetate ion are illustrated here. In acetic acid, only the hydrogen attached to an oxygen can come off as H^+.

Notice that only the hydrogen written first in the formula is able to transfer to H_2O to give hydronium ions. The structures of the acetic acid molecule and the acetate ion are shown in Figure 4.8, with the hydrogen that can be lost by the acetic acid molecule indicated.

As noted earlier, the "active ingredient" in the hydronium ion is H^+, which is why $H^+(aq)$ is often used in place of $H_3O^+(aq)$ in equations. Using this simplification, the ionization of HCl and $HC_2H_3O_2$ in water can be represented as

◻ Hydrogens that are able to be transferred to water molecules to form hydronium ions are usually written first in the formula for the acid.

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

and

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

In the ionization reactions of HCl and $HC_2H_3O_2$, an anion is formed when the acid transfers an H^+ to the water molecule. If we represent the acid molecule by the general formula HA, we might represent the ionization of an acid in general terms by the equation

$$HA + H_2O \longrightarrow H_3O^+ + A^- \tag{4.2}$$

TOOLS *Ionization of an acid in water*

The molecules HCl and $HC_2H_3O_2$ are said to be **monoprotic acids** because they are capable of furnishing only *one* H^+ per molecule of acid. **Polyprotic acids** can furnish more than one H^+ per molecule. They undergo reactions similar to those of HCl and $HC_2H_3O_2$, except that the loss of H^+ by the acid occurs in two or more steps. Thus, the ionization of sulfuric acid, a **diprotic acid,** takes place by two successive steps.

$$H_2SO_4(aq) + H_2O \longrightarrow H_3O^+(aq) + HSO_4^-(aq)$$

$$HSO_4^-(aq) + H_2O \longrightarrow H_3O^+(aq) + SO_4^{2-}(aq)$$

Triprotic acids ionize in three steps, as illustrated in Example 4.3.

EXAMPLE 4.3
Writing Equations for Ionization Reactions of Acids

Phosphoric acid, H_3PO_4, is a triprotic acid found in some soft drinks such as Coca-Cola where it adds a touch of tartness to the beverage. Write equations for its stepwise ionization in water.

ANALYSIS: We are told that H_3PO_4 is a triprotic acid, which is also indicated by the three hydrogens at the beginning of the formula. Because there are three hydrogens to come off the molecule, we expect there to be three steps in the ionization. Each step removes one H^+, and we can use that knowledge to deduce the formulas of the products. Let's line them up so we can see the progression.

$$H_3PO_4 \xrightarrow{-H^+} H_2PO_4^- \xrightarrow{-H^+} HPO_4^{2-} \xrightarrow{-H^+} PO_4^{3-}$$

Notice that loss of H^+ decreases the number of hydrogens by one and increases the negative charge by one unit. Also, the product of one step serves as the reactant in the next step. We'll use Equation 4.2 for the ionization of an acid as a tool in writing the chemical equation for each step.

SOLUTION: The first step is the reaction of H_3PO_4 with water to give H_3O^+ and $H_2PO_4^-$.

$$H_3PO_4(aq) + H_2O \longrightarrow H_3O^+(aq) + H_2PO_4^-(aq)$$

The second and third steps are similar to the first.

$$H_2PO_4^-(aq) + H_2O \longrightarrow H_3O^+(aq) + HPO_4^{2-}(aq)$$
$$HPO_4^{2-}(aq) + H_2O \longrightarrow H_3O^+(aq) + PO_4^{3-}(aq)$$

IS THE ANSWER REASONABLE? Check to see whether the equations are balanced in terms of atoms and charge. If any mistakes were made, something would be out of balance and we would discover the error. In this case, all the equations are balanced, so we can feel confident we've written them correctly.

Practice Exercise 5: Write the equation for the ionization of $HCHO_2$ (formic acid) in water. Formic acid is used industrially to remove hair from animal skins prior to tanning. (Hint: Formic acid and acetic acid are both examples of organic acids.)

Practice Exercise 6: Write equations for the stepwise ionization in water of citric acid, $H_3C_6H_5O_7$, the acid in citrus fruits.

Nonmetal oxides can be acids

The acids we've discussed so far have been molecules containing hydrogen atoms that can be transferred to water molecules. Nonmetal oxides form another class of compounds that yield acidic solutions in water. Examples are SO_3, CO_2, and N_2O_5 whose aqueous solutions contain H_3O^+ and turn litmus red. These oxides are called **acidic anhydrides,** where *anhydride* means "without water." They react with water to form molecular acids containing hydrogen, which are then able to undergo reaction with water to yield H_3O^+.

$$SO_3(g) + H_2O \longrightarrow H_2SO_4(aq) \qquad \text{sulfuric acid}$$
$$N_2O_5(g) + H_2O \longrightarrow 2HNO_3(aq) \qquad \text{nitric acid}$$
$$CO_2(g) + H_2O \longrightarrow H_2CO_3(aq) \qquad \text{carbonic acid}$$

Although carbonic acid is too unstable to be isolated as a pure compound, its solutions in water are quite common. Carbon dioxide from the atmosphere dissolves in rainwater and the waters of lakes and streams where it exists partly as carbonic acid and its ions (HCO_3^- and CO_3^{2-}). This makes these waters naturally slightly acidic. Carbonic acid is also present in carbonated beverages.

Not all nonmetal oxides are acidic anhydrides, only those that are able to react with water. For example, carbon monoxide doesn't react with water, so its solutions in water are not acidic; carbon monoxide, therefore, is not classified as an acidic anhydride.

Bases are substances that give OH^- in water

Bases fall into two categories: ionic compounds that contain OH^- or O^{2-}, and molecular compounds that react with water to give hydroxide ions. Because solutions of bases contain ions, they conduct electricity. Therefore, bases are electrolytes.

Ionic bases are metal hydroxides and oxides

Ionic bases include metal hydroxides, such as NaOH and $Ca(OH)_2$. When dissolved in water, they dissociate just like other soluble ionic compounds.

$$\mathrm{NaOH}(s) \longrightarrow \mathrm{Na}^+(aq) + \mathrm{OH}^-(aq)$$
$$\mathrm{Ca(OH)_2}(s) \longrightarrow \mathrm{Ca}^{2+}(aq) + 2\mathrm{OH}^-(aq)$$

Soluble metal oxides are **basic anhydrides** because they react with water to form the hydroxide ion as one of the products. Calcium oxide is typical.

$$\mathrm{CaO}(s) + \mathrm{H_2O} \longrightarrow \mathrm{Ca(OH)_2}(aq)$$

This reaction occurs when water is added to dry cement or concrete because calcium oxide or "quicklime" is an ingredient in those materials. In this case it is the oxide ion, O^{2-}, that actually forms the OH^-.

$$\mathrm{O}^{2-} + \mathrm{H_2O} \longrightarrow 2\mathrm{OH}^-$$

☐ Continual contact of your hands with fresh Portland cement can lead to irritation because the mixture is quite basic.

Even insoluble metal hydroxides and oxides are basic because they are able to neutralize acids. We will study these reactions in Section 4.5.

Many nitrogen compounds are molecular bases

The most common molecular base is the gas ammonia, NH_3, which dissolves in water and reacts to give a basic solution by an ionization reaction.

$$\mathrm{NH_3}(aq) + \mathrm{H_2O} \longrightarrow \mathrm{NH_4}^+(aq) + \mathrm{OH}^-(aq)$$

Organic compounds called amines, in which fragments of hydrocarbons are attached to nitrogen in place of hydrogen, are similar to ammonia in their behavior toward water. An example is methylamine, CH_3NH_2, in which a **methyl group,** CH_3, replaces a hydrogen in ammonia.

$$\mathrm{CH_3NH_2}(aq) + \mathrm{H_2O} \longrightarrow \mathrm{CH_3NH_3}^+(aq) + \mathrm{OH}^-(aq)$$

The hydrogen taken from the H_2O molecule becomes attached to the nitrogen atom of the amine. This is how nitrogen-containing bases behave, which is why we've included the H^+ with the other two hydrogens on the nitrogen.

Notice that when a molecular base reacts with water, an H^+ is lost by the water molecule and gained by the base. (See Figure 4.9.) One product is a cation that has one more H and one more positive charge than the reactant base. Loss of H^+ by the water gives the other product, the OH^- ion, which is why the solution is basic. We might represent this by the general equation

$$\mathrm{base} + \mathrm{H_2O} \longrightarrow \mathrm{baseH}^+ + \mathrm{OH}^-$$

If we signify the base by the symbol *B*, this becomes

$$\boxed{B + \mathrm{H_2O} \longrightarrow B\mathrm{H}^+ + \mathrm{OH}^-} \qquad (4.3)$$

TOOLS *Ionization of a base in water*

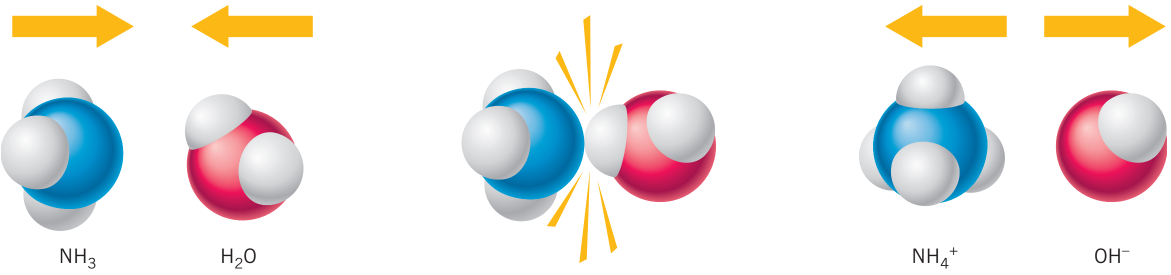

FIG. 4.9 **Ionization of ammonia in water.** Collisions between NH_3 molecules and water molecules lead to a transfer of H^+ from H_2O to NH_3, giving NH_4^+ and OH^- ions.

EXAMPLE 4.4

Writing the Equation for the Ionization of a Base

Dimethylamine, $(CH_3)_2NH$, is used as an attractant for boll weevils so they can be destroyed. This insect has caused more than a \$14 billion loss to the yield of cotton in the United States since it arrived from Mexico in 1892. The compound is a base in water. Write an equation for its ionization.

ANALYSIS: The reactants in the equation are $(CH_3)_2NH$ and H_2O. To write the equation, we need to know the formulas of the products. We've been told that $(CH_3)_2NH$ is a base, so Equation 4.3 is the tool we will use to write the chemical equation.

SOLUTION: When a base reacts with water, it takes an H^+ from H_2O, leaving OH^- behind. Therefore, when an H^+ is picked up by $(CH_3)_2NH$, the product will be $(CH_3)_2NH_2^+$. The equation for the reaction is

$$(CH_3)_2NH(aq) + H_2O \longrightarrow (CH_3)_2NH_2^+(aq) + OH^-(aq)$$

IS THE ANSWER REASONABLE? Compare the equation we've written with the general equation for reaction of a base with water. Notice that the formula for the product has one more H and a positive charge, and that the H^+ has been added to the nitrogen. Also, notice that the water has become OH^- when it loses H^+. The equation is therefore correct.

Practice Exercise 7: Triethylamine, $(C_2H_5)_3N$, is a base in water. Write an equation for its reaction with the solvent. (Hint: How do nitrogen-containing bases react toward water?)

Practice Exercise 8: Hydroxylamine, $HONH_2$, is a base in water. Write an equation for its reaction with the solvent.

Acids and bases are classified as strong or weak

Ionic compounds such as NaCl and $CaCl_2$ break up essentially 100% into ions in water. No "molecules" of either NaCl or $CaCl_2$ are detectable in their aqueous solutions. Because these solutions contain so many ions, they are strong conductors of electricity, so ionic compounds are said to be **strong electrolytes.**

□ All strong acids are strong electrolytes.

Hydrochloric acid is also a strong electrolyte. Its ionization in water is essentially complete; its solutions are strongly acidic, and it is said to be a *strong acid*. In general, *acids that are strong electrolytes are called* **strong acids.** There are relatively few strong acids; the most common ones are listed below.

TOOLS *List of strong acids*

Strong Acids

$HClO_4(aq)$	perchloric acid
$HCl(aq)$	hydrochloric acid
$HBr(aq)$	hydrobromic acid
$HI(aq)$	hydroiodic acid[5]
$HNO_3(aq)$	nitric acid
$H_2SO_4(aq)$	sulfuric acid

Metal hydroxides are ionic compounds, so they are also strong electrolytes. Those that are soluble are the hydroxides of Group IA and the hydroxides of calcium, strontium, and barium of Group IIA. Solutions of these compounds are strongly basic, so these substances are considered to be **strong bases.** The hydroxides of other metals have very low solubilities in water. They are strong electrolytes in the sense that the small amounts of them that dissolve in solution are completely dissociated. However, because of their low solubility in water, their solutions are very weakly basic.

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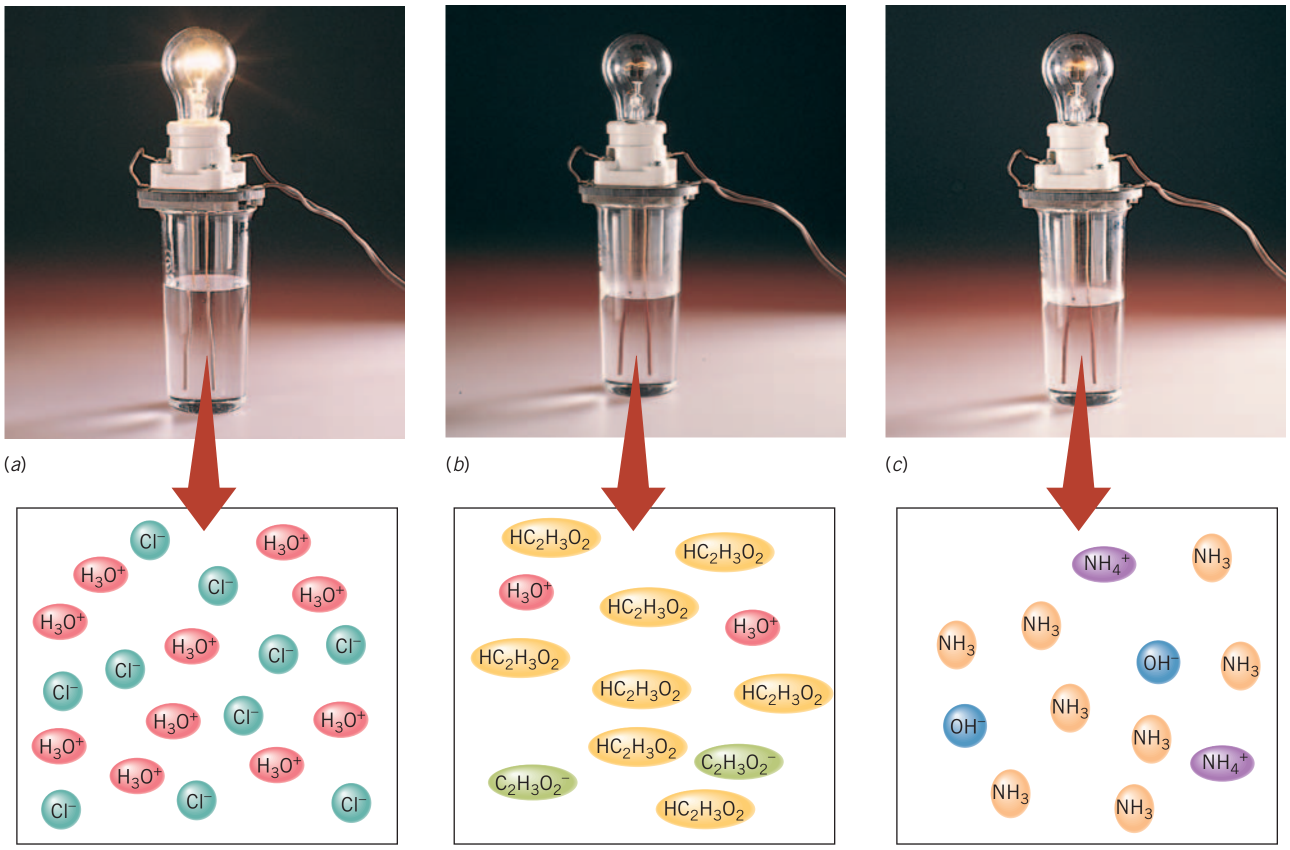
[5] Sometimes the first "o" in the name of $HI(aq)$ is dropped for ease of pronunciation to give *hydriodic acid*.



All the HCl is ionized in the solution, so there are many ions present.

Only a small fraction of the acetic acid is ionized, so there are few ions to conduct electricity. Most of the acetic acid is present as neutral molecules of $HC_2H_3O_2$.

Only a small fraction of the ammonia is ionized, so few ions are present to conduct electricity. Most of the ammonia is present as neutral molecules of NH_3.

FIG. 4.10 **Electrical conductivity of solutions of strong and weak acids and bases at equal concentrations.** *(a)* HCl is 100% ionized and is a strong conductor, enabling the light to glow brightly. *(b)* $HC_2H_3O_2$ is a weaker conductor than HCl because the extent of its ionization is far less, so the light is dimmer. *(c)* NH_3 also is a weaker conductor than HCl because the extent of its ionization is low, and the light remains dim. *(Michael Watson.)*

Weak acids and bases are weak electrolytes

Most acids are not completely ionized in water. For instance, a solution of acetic acid, $HC_2H_3O_2$, is a relatively poor conductor of electricity compared to a solution of HCl with the same concentration (Figure 4.10), so acetic acid is classified as a **weak electrolyte** and is a **weak acid.**

The reason an acetic acid solution is a poor conductor is because in the solution only a small fraction of the acid exists as H_3O^+ and $C_2H_3O_2^-$ ions. The rest is present as molecules of $HC_2H_3O_2$. This is because $C_2H_3O_2^-$ ions have a strong tendency to react with H_3O^+ when the ions meet in the solution. As a result, there are two opposing reactions occurring simultaneously (Figure 4.11). One involves the formation of the ions,

$$HC_2H_3O_2(aq) + H_2O \longrightarrow H_3O^+(aq) + C_2H_3O_2^-(aq)$$

and the other removes ions

$$H_3O^+(aq) + C_2H_3O_2^-(aq) \longrightarrow HC_2H_3O_2(aq) + H_2O$$

A balance is reached when ions form and disappear at the same rate, and for acetic acid this happens when only a small percentage of the $HC_2H_3O_2$ is ionized.

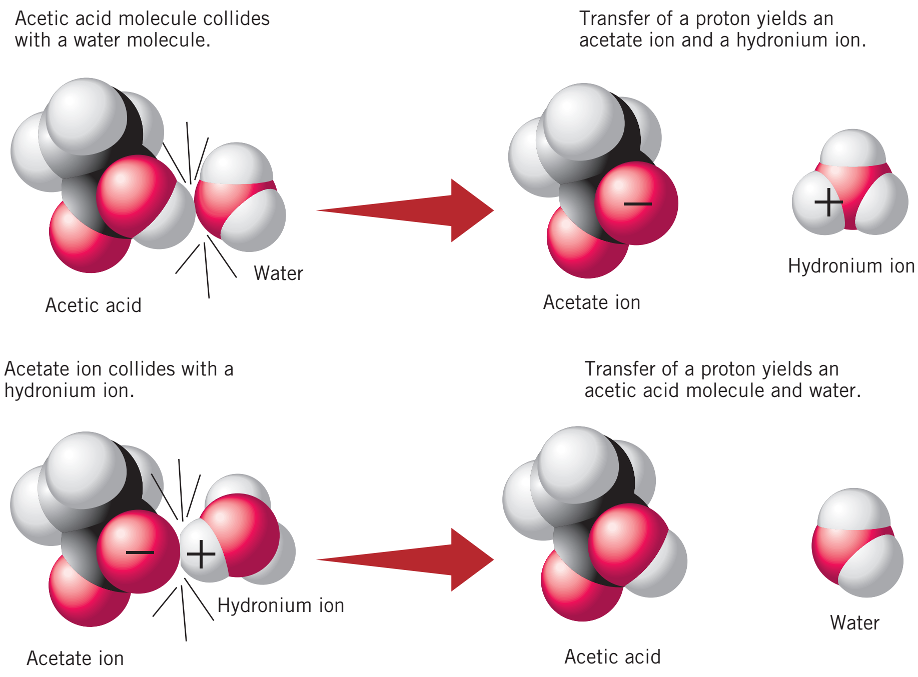


FIG. 4.11 Equilibrium in a solution of acetic acid. Two opposing reactions take place simultaneously in a solution of acetic acid. Molecules of acid collide with molecules of water and form acetate ions and H_3O^+ ions. Meanwhile, acetate ions collide with H_3O^+ ions to give acetic acid molecules and water molecules. (The usual colors are used: white = H, red = O, black = C.)

The condition we've just described, with two opposing reactions occurring at the same rate, is called a **chemical equilibrium** or **dynamic equilibrium.** It is an *equilibrium* because the concentrations of the substances present in the solution do not change with time; it is *dynamic* because the opposing reactions continue endlessly.

The two opposing processes in a dynamic equilibrium are usually represented in a single equation by using double arrows, $\rightleftharpoons$. For acetic acid, we write

$$HC_2H_3O_2(aq) + H_2O \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$$

The **forward reaction** (read from left to right) forms the ions; the **reverse reaction** (from right to left) removes them from the solution.

Molecular bases, such as ammonia and methylamine, are also weak electrolytes and have a low percentage ionization. They are classified as **weak bases.** (See Figure 4.10*c*.) In a solution of ammonia, only a small fraction of the solute is ionized to give NH_4^+ and OH^- because the ions have a strong tendency to react with each other. This leads to the dynamic equilibrium (Figure 4.12)

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

in which most of the base is present as NH_3 molecules.

Let's briefly summarize the results of our discussion.

Weak acids and weak bases are weak electrolytes.

Strong acids and strong bases are strong electrolytes.

In describing equilibria such as those above, we will often talk about the **position of equilibrium.** By this we mean the extent to which the forward reaction proceeds toward completion. If very little of the products are present at equilibrium, the forward reaction has not gone far toward completion and we say "the position of equilibrium lies to the left," toward the reactants. On the other hand, if large amounts of the products are present at equilibrium, we say "the position of equilibrium lies to the right."

For any weak electrolyte, only a small percentage of the solute is actually ionized at any instant after equilibrium is reached, so the position of equilibrium lies to the left. To call acetic acid a *weak* acid, for example, is just another way of saying that the forward reaction in this equilibrium is far from completion.

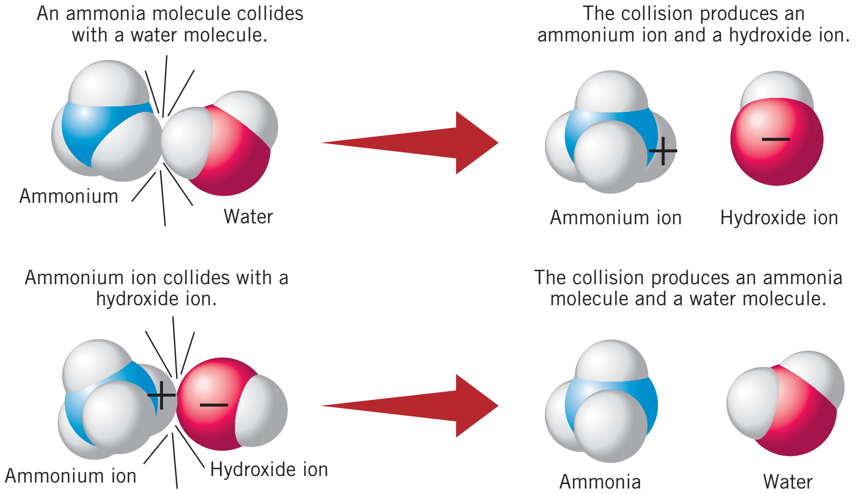


FIG. 4.12 **Equilibrium in a solution of the weak base ammonia.** Collisions between water and ammonia molecules produce ammonium and hydroxide ions. The reverse process, which involves collisions between ammonium ions and hydroxide ions, removes ions from the solution and forms ammonia and water molecules.

Strong acids do not participate in equilibria because they are fully ionized

With molecular compounds that are strong electrolytes, the tendency of the forward ionization reaction to occur is very large, while the tendency of the reverse reaction to occur is extremely small. In aqueous HCl, for example, there is little tendency for Cl^- and H_3O^+ to react to form molecules of HCl and H_2O. As a result, all of the HCl molecules dissolved in water become converted to ions—the acid becomes 100% ionized. For this reason, *we do not use double arrows in describing what happens when HCl(g) or any other strong electrolyte undergoes ionization or dissociation.*

Practice Exercise 9: Earlier you learned that methylamine, CH_3NH_2 (a fishy smelling substance found in herring brine), is a base in water. Write the equation that shows that methylamine is a weak base. (Hint: How do we show an equilibrium exists in the solution?)

Practice Exercise 10: Nitrous acid, HNO_2, is a weak acid thought to be responsible for certain cancers of the intestinal system. Write the chemical equation that shows that HNO_2 is a weak acid in water.

4.4 NAMING ACIDS AND BASES FOLLOWS A SYSTEM

Although at first there seems to be little order in the naming of acids, there are patterns that help organize names of acids and the anions that come from them when the acids are neutralized.

Hydrogen compounds of nonmetals can be acids

The binary compounds of hydrogen with many of the nonmetals are acidic, and in their aqueous solutions they are referred to as **binary acids.** Some examples are HCl, HBr, and H_2S. In naming these substances as acids, we add the prefix *hydro-* and the suffix *-ic* to the stem of the nonmetal name, followed by the word *acid*. For example, aqueous solutions of hydrogen chloride and hydrogen sulfide are named as follows:

Name of the molecular compound		*Name of the binary acid in water*	
$HCl(g)$	hydrogen chloride	$HCl(aq)$	*hydro*chlor*ic acid*
$H_2S(g)$	hydrogen sulfide	$H_2S(aq)$	*hydro*sulfur*ic acid*

Notice that the gaseous molecular substances are named in the usual way as binary compounds. *It is their aqueous solutions that are named as acids.*

When an acid is neutralized, the salt that is produced contains the anion formed by removing a hydrogen ion, H^+, from the acid molecule. Thus HCl yields salts containing the chloride ion, Cl^-. Similarly, HBr gives salts containing the bromide ion, Br^-. In general, then, neutralization of a binary acid yields the simple anion of the nonmetal.

Oxoacids contain hydrogen, oxygen, and another element

Acids that contain hydrogen, oxygen, plus another element are called **oxoacids.** Examples are H_2SO_4 and HNO_3. These acids do not take the prefix *hydro-*. Many nonmetals form two or more oxoacids that differ in the number of oxygen atoms in their formulas. When there are two oxoacids, the one with the larger number of oxygens takes the suffix *-ic* and the one with the fewer number of oxygens takes the suffix *-ous*.

□ In the name of an acid, the prefix *hydro-* tells us it is a binary acid. If the prefix *hydro-* is absent, it tells us the substance is not a binary acid.

H_2SO_4	sulfur*ic acid*	HNO_3	nitr*ic acid*
H_2SO_3	sulfur*ous acid*	HNO_2	nitr*ous acid*

The halogens can occur in as many as four different oxoacids. The oxoacid with the most oxygens has the prefix *per-*, and the one with the least has the prefix *hypo-*.

$HClO_4$	*per*chlor*ic acid*	$HClO_2$	chlor*ous acid*
$HClO_3$	chlor*ic acid*	$HClO$	*hypo*chlor*ous acid* (usually written HOCl)

The neutralization of oxoacids produces negative polyatomic ions. The name of the polyatomic ion is related to that of its parent acid.

(l) *-ic* acids give *-ate* anions: HNO_3 (nitr*ic acid*) $\longrightarrow$ NO_3^- (nitr*ate* ion)

(2) *-ous* acids give *-ite* anions: H_2SO_3 (sulfur*ous acid*) $\longrightarrow$ SO_3^{2-} (sulf*ite* ion)

In naming polyatomic anions, the prefixes *per-* and *hypo-* carry over from the name of the parent acid. Thus perchloric acid, $HClO_4$, gives perchlorate ion, ClO_4^-, and hypochlorous acid, HClO, gives hypochlorite ion, ClO^-.

□ This relationship between name of the acid and name of the anion carries over to other acids that end in the suffix *-ic*. For example, acetic acid gives the anion acetate, and citric acid gives the anion citrate.

EXAMPLE 4.5
Naming Acids and Their Salts

Bromine forms four oxoacids, similar to those of chlorine. What is the name of the acid $HBrO_2$ and what is the name of the salt $NaBrO_3$?

ANALYSIS AND SOLUTION: Let's review the acids formed by chlorine and then reason by analogy. For chlorine we have

$HClO_4$	perchloric acid	$HClO_2$	chlorous acid
$HClO_3$	chloric acid	$HClO$	hypochlorous acid

The acid $HBrO_2$ is similar to chlorous acid, so to name it we will use the stem of the element name bromine (brom-) in place of chlor-. Therefore, the name of $HBrO_2$ is *bromous acid.*

To find the name of $NaBrO_3$, let's begin by asking "What acid would give this salt by neutralization?" Neutralization involves removing an H^+ from the acid molecule and replacing it with a cation, in this case Na^+. Therefore, the salt $NaBrO_3$ would be obtained by neutralizing the acid $HBrO_3$. This acid has one more oxygen than bromous acid, $HBrO_2$, so it would have the ending *-ic*. Thus, $HBrO_3$ is named bromic acid. Neutralizing an acid that has a name that ends in *-ic* gives an anion with a name that ends in *-ate*, so the anion BrO_3^- is the bromate ion. Therefore, the salt $NaBrO_3$ is *sodium bromate.*

ARE THE ANSWERS REASONABLE? There's really not much we can do to check the answers here. For the salt, if $HClO_3$ is chloric acid, then it seems reasonable that $HBrO_3$ would be bromic acid, which would mean that BrO_3^- is the bromate ion and $NaBrO_3$ is sodium bromate.

Practice Exercise 11: The formula for arsenic acid is H_3AsO_4. What is the name of the salt Na_3AsO_4? (Hint: Recall how the name of the anion is related to the name of the acid.)

Practice Exercise 12: Formic acid is $HCHO_2$. What is the name of the salt $Ca(CHO_2)_2$?

Practice Exercise 13: Name the water solutions of the following acids: HF, HBr. Name the sodium salts formed by neutralizing the acids with NaOH.

FIG. 4.13 **Many acid salts have useful applications.** As its active ingredient, this familiar product contains sodium hydrogen sulfate (sodium bisulfate), which the manufacturer calls "sodium acid sulfate." *(Robert Capece.)*

Acid salts can be formed by polyprotic acids

Monoprotic acids such as HCl and $HC_2H_3O_2$ have only one hydrogen that can be removed by neutralization and these acids form only one anion. However, polyprotic acids can be neutralized stepwise and the neutralization can be halted before all the hydrogens have been removed. For example, partial neutralization of H_2SO_4 gives the HSO_4^- ion, which forms salts such as $NaHSO_4$. This compound is called an **acid salt** because its anion, HSO_4^-, is capable of furnishing additional H^+.

In naming ions such as HSO_4^-, we specify the number of hydrogens that can still be neutralized if the anion were to be treated with additional base. Thus, HSO_4^- is called the hydrogen sulfate ion; it's the active ingredient in Sani-Flush (Figure 4.13). Similarly, $H_2PO_4^-$ is named as the dihydrogen phosphate ion. These anions give the following salts with Na^+:

$NaHSO_4$	sodium hydrogen sulfate
NaH_2PO_4	sodium dihydrogen phosphate

For acid salts of diprotic acids, the prefix ***bi-*** is still often used.

$NaHCO_3$	sodium bicarbonate or sodium hydrogen carbonate

Notice that the prefix bi- does *not* mean "two"; it means that there is an acidic hydrogen in the compound.

Practice Exercise 14: What is the formula for sodium bisulfite? What is the chemically correct name for this compound? (Hint: What information do we get from the prefix bi- and the suffix -ite?)

Practice Exercise 15: Write molecular equations for the stepwise neutralization of phosphoric acid by sodium hydroxide. What are the names of the salts that are formed?

Bases are named as hydroxides or molecules

Metal compounds that contain the ions OH^- or O^{2-}, such as NaOH and Na_2O, are ionic and are named just like any other ionic compound. Thus, NaOH is sodium hydroxide and Na_2O is sodium oxide.

Molecular bases such as NH_3 (ammonia) and CH_3NH_2(methylamine) are specified by just giving the name of the molecule.[6] There is nothing special in their names that tells us they are bases.

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[6] Solutions of ammonia are sometimes called *ammonium hydroxide*, although there is no evidence that the species NH_4OH actually exists.

4.5 IONIC REACTIONS CAN OFTEN BE PREDICTED

In our discussion of the reaction of KI with $Pb(NO_3)_2$ (page 132), you saw that the net ionic equation reveals a change in the number of ions in solution when the reaction takes place. Such changes characterize ionic reactions in general. In this section you will learn how we can use the existence or nonexistence of a net ionic equation as a criterion to determine whether or not an ionic reaction occurs in a solution of mixed solutes.

TOOLS
Predicting net ionic equations

In general, a net ionic equation will exist (and a reaction will occur) under the following conditions:

A precipitate is formed from a mixture of soluble reactants.
An acid reacts with a base.
A weak electrolyte is formed from a mixture of strong electrolytes.
A gas is formed from a mixture of reactants.

It is also important to note that *no net reaction will occur if all the substances in the ionic equation cancel*. There will be no net ionic equation, and therefore no net reaction!

Predicting precipitation reactions

The reaction between $Pb(NO_3)_2$ and KI,

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

is just one example of a large class of ionic reactions in which cations and anions change partners. The technical term we use to describe them is **metathesis,** but they are also sometimes called **double replacement reactions.** (In the formation of the products, PbI_2 and KNO_3, the I^- replaces NO_3^- in the lead compound and NO_3^- replaces I^- in the potassium compound.) Metathesis reactions in which a precipitate forms are sometimes called **precipitation reactions.**

FACETS OF CHEMISTRY 4.2

Painful Precipitates—Kidney Stones

Each year, more than a million people in the United States are hospitalized because of very painful kidney stone attacks. A kidney stone is a hard mass developed from crystals that separate from the urine and build up on the inner surfaces of the kidney. The formation of the stones is caused primarily by the buildup of Ca^{2+}, $C_2O_4^{2-}$, and PO_4^{3-} ions in the urine. When the concentrations of those ions become large enough, the urine becomes supersaturated with respect to calcium oxalate and/or calcium phosphate and precipitates begin to form (70% to 80% of all kidney stones are made up of calcium oxalate and phosphate). If the crystals remain tiny enough, they can travel through the urinary tract and pass out of the body in the urine without being noticed. Sometimes, however, they continue to grow without being passed and can cause intense pain if they become stuck in the urinary tract.

Kidney stones don't all look alike. Their color depends on what substances are mixed with the inorganic precipitates (e.g., proteins or blood). Most are yellow or brown, as seen in the accompanying photo, but they can be tan, gold, or even black. Stones can be round, jagged, or even have branches. They vary in size from mere specks to pebbles to stones as big as golf balls!

A calcium oxalate kidney stone. Kidney stones such as this can be extremely painful. *(Photo courtesy of L.C. Herring and Company, Orlando, FL.)*

TABLE 4.1 **Solubility Rules for Ionic Compounds in Water**

Soluble Compounds

1. All compounds of the alkali metals (Group IA) are soluble.
2. All salts containing NH_4^+, NO_3^-, ClO_4^-, ClO_3^-, and $C_2H_3O_2^-$ are soluble.
3. All chlorides, bromides, and iodides (salts containing Cl^-, Br^-, or I^-) are soluble *except* when combined with Ag^+, Pb^{2+}, and Hg_2^{2+} (note the subscript "2").
4. All sulfates (salts containing SO_4^{2-}) are soluble *except* those of Pb^{2+}, Ca^{2+}, Sr^{2+}, Hg_2^{2+}, and Ba^{2+}.

Insoluble Compounds

5. All metal hydroxides (ionic compounds containing OH^-) and all metal oxides (ionic compounds containing O^{2-}) are insoluble *except* those of Group IA and those of Ca^{2+}, Sr^{2+}, and Ba^{2+}.

   When metal oxides do dissolve, they react with water to form hydroxides. The oxide ion, O^{2-}, does not exist in water. For example,

   $$Na_2O(s) + H_2O \longrightarrow 2NaOH(aq)$$

6. All salts that contain PO_4^{3-}, CO_3^{2-}, SO_3^{2-}, and S^{2-} are insoluble *except* those of Group IA and NH_4^+.

TOOLS *Solubility rules*

Lead nitrate and potassium iodide react because one of the products is insoluble. This is what leads to a net ionic equation. Such reactions can be predicted if we know which substances are soluble and which are insoluble. To help us, we can use a set of **solubility rules** (Table 4.1) to tell us, in many cases, whether an ionic compound is soluble or insoluble. To make the rules easier to remember, they are divided into two categories. The first includes compounds that are soluble, with some exceptions. The second describes compounds that are generally insoluble, with some exceptions. Some examples will help clarify their use.

Rule 1 states that all compounds of the alkali metals are soluble in water. This means that you can expect *any* compound containing Na^+ or K^+, or any of the Group IA metal ions, *regardless of the anion*, to be soluble. If one of the reactants in a metathesis is Na_3PO_4, you now know from Rule 1 that it is soluble. Therefore, you would write it in *dissociated* form in the ionic equation. Similarly, Rule 6 states, in part, that all carbonate compounds are *insoluble* except those of the alkali metals and the ammonium ion. If one of the products in a metathesis reaction is $CaCO_3$, you'd expect it to be insoluble, because the cation is not an alkali metal or NH_4^+. Therefore, you would write its formula in undissociated form as $CaCO_3(s)$ in the ionic equation.

Let's look at an example that illustrates how we can use the rules to predict the outcome of a reaction.

EXAMPLE 4.6
Predicting Reactions and Writing Their Equations

Predict whether a reaction will occur when aqueous solutions of $Fe_2(SO_4)_3$ and $Pb(NO_3)_2$ are mixed. Write molecular, ionic, and net ionic equations for it.

ANALYSIS: We know the molecular equation will take the form

$$Fe_2(SO_4)_3 + Pb(NO_3)_2 \longrightarrow$$

To complete the equation we have to determine the makeup of the products. We begin, therefore, by predicting what a double replacement (metathesis) might produce. Then we proceed to expand the molecular equation into an ionic equation, and finally we drop spectator ions to obtain the net ionic equation. The existence of a net ionic equation tells us that a reaction does indeed take place. To accomplish all of this we need to know solubilities, and here our tool is the solubility rules.

□ The critical step in determining whether a reaction occurs is obtaining a net ionic equation.

SOLUTION: The reactants, $Pb(NO_3)_2$ and $Fe_2(SO_4)_3$, contain the ions Pb^{2+} and NO_3^-, and Fe^{3+} and SO_4^{2-}, respectively. To write the formulas of the products, we interchange anions. We combine Pb^{2+} with SO_4^{2-}, and for electrical neutrality, we must use one ion of each. Therefore, we write $PbSO_4$ as one possible product. For the other product, we combine Fe^{3+} with NO_3^-. Electrical neutrality now demands that we use *three* NO_3^- to *one* Fe^{3+} to make $Fe(NO_3)_3$. The correct formulas of the products, then, are $PbSO_4$ and $Fe(NO_3)_3$. The unbalanced molecular equation at this point is

$$Fe_2(SO_4)_3 + Pb(NO_3)_2 \longrightarrow Fe(NO_3)_3 + PbSO_4 \qquad \text{(unbalanced)}$$

Always write equations in two steps: First write correct formulas for the reactants and products, then adjust the coefficients to balance the equation.

Next, let's determine solubilities. The reactants are ionic compounds and we are told that they are in solution, so we know they are water soluble. Solubility Rules 2 and 4 tell us this also. For the products, we find that Rule 2 says that all nitrates are soluble, so $Fe(NO_3)_3$ is soluble; Rule 4 tells us that the sulfate of Pb^{2+} is *insoluble*. This means that a precipitate of $PbSO_4$ will form. Writing (*aq*) and (*s*) following appropriate formulas, the unbalanced molecular equation is

$$Fe_2(SO_4)_3(aq) + Pb(NO_3)_2(aq) \longrightarrow Fe(NO_3)_3(aq) + PbSO_4(s) \qquad \text{(unbalanced)}$$

When balanced, we obtain the *molecular equation*.

$$Fe_2(SO_4)_3(aq) + 3Pb(NO_3)_2(aq) \longrightarrow 2Fe(NO_3)_3(aq) + 3PbSO_4(s)$$

Next, we expand this to give the *ionic equation* in which soluble compounds are written in dissociated (separated) form as ions, and insoluble compounds are written in "molecular" form. Once again, we are careful to apply the subscripts of the ions and the coefficients.

$$2Fe^{3+}(aq) + 3SO_4^{2-}(aq) + 3Pb^{2+}(aq) + 6NO_3^-(aq) \longrightarrow 2Fe^{3+}(aq) + 6NO_3^-(aq) + 3PbSO_4(s)$$

By removing spectator ions (Fe^{3+} and NO_3^-), we obtain

$$3Pb^{2+}(aq) + 3SO_4^{2-}(aq) \longrightarrow 3PbSO_4(s)$$

Finally, we reduce the coefficients to give us the correct *net ionic equation*.

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

The existence of the net ionic equation confirms that a reaction does take place between lead nitrate and iron(III) sulfate.

IS THE ANSWER REASONABLE? One of the main things we have to check in solving a problem such as this is that we've written the correct formulas of the products. For example, in this problem some students might be tempted (without thinking) to write $Pb(SO_4)_2$ and $Fe_2(NO_3)_3$, or even $Pb(SO_4)_3$ and $Fe_2(NO_3)_2$. *This is a common error*. Always be careful to figure out the charges on the ions that must be combined in the formula. Then take the ions in a ratio that gives an electrically neutral formula unit.

Once we're sure the formulas of the products are right, we check that we've applied the solubility rules correctly, which we have. Then we check that we've properly balanced the equation (We have.), that we've correctly divided the soluble compounds into their ions (We have.), and that we've eliminated the spectator ions to obtain the net ionic equation (We have.).

Practice Exercise 16: Show that in aqueous solutions there is no net reaction between $Zn(NO_3)_2$ and $Ca(C_2H_3O_2)_2$. (Hint: Write molecular, ionic, and net ionic equations.)

Practice Exercise 17: Predict the reaction that occurs on mixing the following solutions. Write molecular, ionic, and net ionic equations for the reactions that take place. (a) $AgNO_3$ and NH_4Cl, (b) sodium sulfide and lead acetate.

Predicting acid–base reactions

Earlier we discussed neutralization as one of the key properties of acids and bases. Many such reactions can be viewed as metathesis. An example is the reaction between HCl and NaOH.

$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \longrightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}$$

Writing this as an ionic equation gives

$$\mathrm{H^+}(aq) + \mathrm{Cl^-}(aq) + \mathrm{Na^+}(aq) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{Na^+}(aq) + \mathrm{Cl^-}(aq) + \mathrm{H_2O}$$

where we have used H^+ as shorthand for H_3O^+. The net ionic equation is obtained by removing spectator ions.

$$\mathrm{H^+}(aq) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{H_2O}$$

In this case, a net ionic equation exists because of the formation of a very weak electrolyte, H_2O, instead of a precipitate. In fact, we find this same net ionic equation for any reaction between a strong acid and a soluble strong base.

The formation of water in a neutralization reaction is such a strong driving force for reaction that it will form even if the acid is weak or if the base is insoluble, or both. Here are some examples.

Reaction of a weak acid with a strong base

Molecular equation:

$$\underset{\text{weak acid}}{\mathrm{HC_2H_3O_2}(aq)} + \underset{\text{strong base}}{\mathrm{NaOH}(aq)} \longrightarrow \mathrm{NaC_2H_3O_2}(aq) + \mathrm{H_2O}$$

Net ionic equation:

$$\mathrm{HC_2H_3O_2}(aq) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{C_2H_3O_2{}^-}(aq) + \mathrm{H_2O}$$

This reaction is illustrated in Figure 4.14.

Reaction of a strong acid with an insoluble base

Figure 4.15 shows the reaction of hydrochloric acid with milk of magnesia, which contains $Mg(OH)_2$.

Molecular equation:

$$\underset{\text{strong acid}}{2\mathrm{HCl}(aq)} + \underset{\text{insoluble base}}{\mathrm{Mg(OH)_2}(s)} \longrightarrow \mathrm{MgCl_2}(aq) + 2\mathrm{H_2O}$$

Net ionic equation:

$$2\mathrm{H^+}(aq) + \mathrm{Mg(OH)_2}(s) \longrightarrow \mathrm{Mg^{2+}}(aq) + 2\mathrm{H_2O}$$

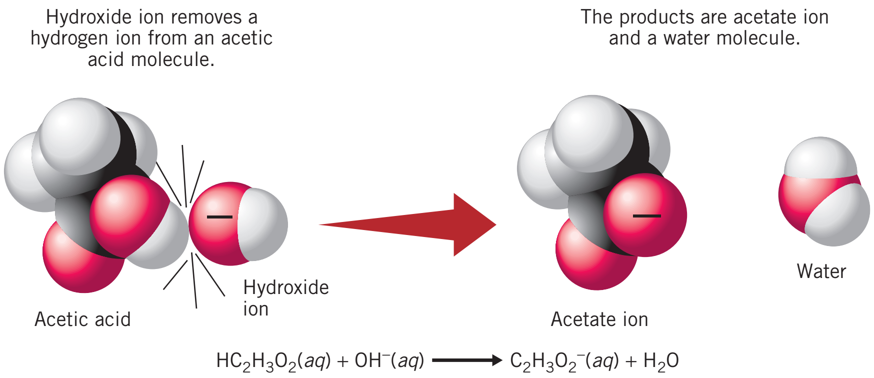


FIG. 4.14 **Net reaction of acetic acid with a strong base.** The neutralization of acetic acid by hydroxide ion occurs primarily by the removal of H^+ from acetic acid molecules by OH^- ions.

FIG. 4.15 **Hydrochloric acid is neutralized by milk of magnesia.** A solution of hydrochloric acid is added to a beaker containing milk of magnesia. The thick white solid in milk of magnesia is magnesium hydroxide, $Mg(OH)_2$, which is able to neutralize the acid. The mixture is clear where some of the solid $Mg(OH)_2$ has already reacted and dissolved. *(Andy Washnik.)*

Reaction of a weak acid with an insoluble base

Molecular equation:

$$2HC_2H_3O_2(aq) + Mg(OH)_2(s) \longrightarrow Mg(C_2H_3O_2)_2(aq) + 2H_2O$$

Net ionic equation:

$$2HC_2H_3O_2(aq) + Mg(OH)_2(s) \longrightarrow Mg^{2+}(aq) + 2C_2H_3O_2^{-}(aq) + 2H_2O$$

Notice that in the last two examples, the formation of water drives the reaction, even though one of the reactants is insoluble. To correctly write the ionic and net ionic equations, it is important to know both the solubility rules and which acids are strong and weak. If you've learned the list of strong acids, you can expect that any acid *not* on the list will be a weak acid. (Unless specifically told otherwise, you should assume weak acids to be water soluble.)

Reaction of an acid with a weak base

Acid–base neutralization doesn't always involve the formation of water. We see this in the reaction of an acid with a weak base such as NH_3. For a strong acid such as HCl, we have

Molecular equation:

$$HCl(aq) + NH_3(aq) \longrightarrow NH_4Cl(aq)$$

Net ionic equation (using H^+ as shorthand for H_3O^+):

$$H^+(aq) + NH_3(aq) \longrightarrow NH_4^{+}(aq)$$

Figure 4.16 depicts the transfer of H^+ from H_3O^+ to NH_3.

With a weak acid such as $HC_2H_3O_2$, we have

Molecular equation:

$$HC_2H_3O_2(aq) + NH_3(aq) \longrightarrow NH_4C_2H_3O_2(aq)$$

Ionic and net ionic equation:

$$HC_2H_3O_2(aq) + NH_3(aq) \longrightarrow NH_4^{+}(aq) + C_2H_3O_2^{-}(aq)$$

Even though solutions of $HC_2H_3O_2$ contain some H^+, and solutions of NH_3 contain some OH^-, when these solutions are mixed the predominant reaction is between molecules of acid and base. This is illustrated in Figure 4.17.

Practice Exercise 18: Write the molecular, ionic, and net ionic equations for the neutralization of $HNO_3(aq)$ by $Ca(OH)_2(aq)$. (Hint: First determine whether the acid and base are strong or weak.)

Practice Exercise 19: Write molecular, ionic, and net ionic equations for the reaction of (a) HCl with KOH, (b) $HCHO_2$ with LiOH, and (c) N_2H_4 with HCl.

Practice Exercise 20: Write molecular, ionic, and net ionic equations for the reaction of the weak base methylamine, CH_3NH_2, with formic acid, $HCHO_2$ (a weak acid).

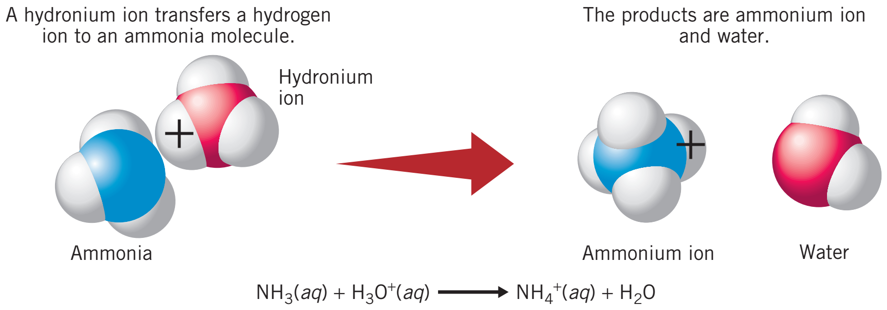


FIG. 4.16 Reaction of ammonia with a strong acid. The reaction occurs primarily by the direct attack of H_3O^+ on NH_3 molecules. Transfer of a proton to the ammonia molecule produces an ammonium ion and a water molecule.

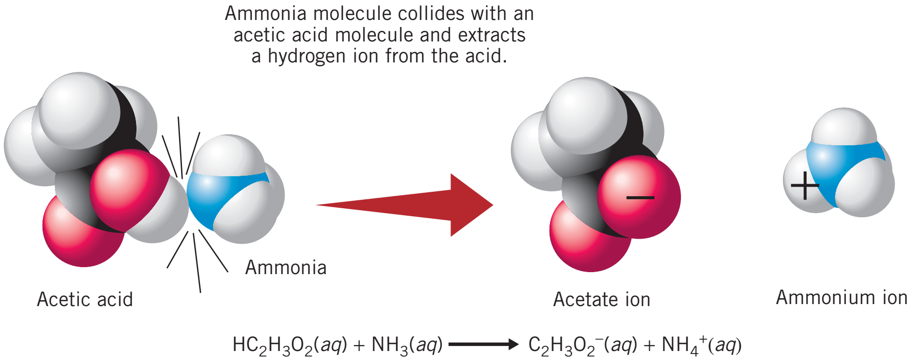


FIG. 4.17 Reaction of acetic acid with ammonia. The collision of an ammonia molecule with an acetic acid molecule leads to a transfer of H^+ from the acetic acid to ammonia and the formation of ions.

Predicting reactions in which a gas is formed

Sometimes a product of a metathesis reaction is a substance that normally is a gas at room temperature and is not very soluble in water. The most common example is carbon dioxide. This product forms when an acid reacts with either a bicarbonate or carbonate. For example, as a sodium bicarbonate solution is added to hydrochloric acid, bubbles of carbon dioxide are released (Figure 4.18). This is the same reaction that occurs if you take sodium bicarbonate to soothe an upset stomach. Stomach acid is HCl and its reaction with the $NaHCO_3$ both neutralizes the acid and produces CO_2 gas (burp!). The molecular equation for the metathesis reaction is

FIG. 4.18 The reaction of sodium bicarbonate with hydrochloric acid. The bubbles contain the gas carbon dioxide. *(Michael Watson.)*

$$HCl(aq) + NaHCO_3(aq) \longrightarrow NaCl(aq) + H_2CO_3(aq)$$

Carbonic acid, H_2CO_3, is too unstable to be isolated in pure form. When it forms in appreciable amounts as a product in a metathesis reaction, it decomposes into its anhydride (the gas CO_2) and water. Carbon dioxide is only slightly soluble in water, so most of the CO_2 bubbles out of the solution. The decomposition reaction is

$$H_2CO_3(aq) \longrightarrow H_2O + CO_2(g)$$

Therefore, the overall molecular equation for the reaction is

$$HCl(aq) + NaHCO_3(aq) \longrightarrow NaCl(aq) + H_2O + CO_2(g)$$

The ionic equation is

$$H^+(aq) + Cl^-(aq) + Na^+(aq) + HCO_3^-(aq) \longrightarrow Na^+(aq) + Cl^-(aq) + H_2O + CO_2(g)$$

and the net ionic equation is

$$H^+(aq) + HCO_3^-(aq) \longrightarrow H_2O + CO_2(g)$$

Similar results are obtained if we begin with a carbonate instead of a bicarbonate. In this case, hydrogen ions combine with carbonate ions to give H_2CO_3, which subsequently decomposes to water and CO_2.

$$2H^+(aq) + CO_3^{2-}(aq) \longrightarrow H_2CO_3(aq) \longrightarrow H_2O + CO_2(g)$$

The net reaction is

$$2H^+(aq) + CO_3^{2-}(aq) \longrightarrow H_2O + CO_2(g)$$

The release of CO_2 by the reaction of a carbonate with an acid is such a strong driving force for reaction that it enables insoluble carbonates to dissolve in acids (strong and weak). The reaction of limestone, $CaCO_3$, with hydrochloric acid is shown in Figure 4.19. The molecular and net ionic equations for the reaction are as follows:

FIG. 4.19 Limestone reacts with acid. Bubbles of CO_2 are formed in the reaction of limestone ($CaCO_3$) with hydrochloric acid. *(Andy Washnik.)*

$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O$$
$$CaCO_3(s) + 2H^+(aq) \longrightarrow Ca^{2+}(aq) + CO_2(g) + H_2O$$

Carbon dioxide is not the only gas formed in metathesis reactions. Table 4.2 lists others and the reactions that form them.

TOOLS

Gases formed in metathesis reactions

TABLE 4.2 Gases Formed in Metathesis Reactions

Gas	Formed by Reaction of Acids with:	Equation for Formation[a]
H_2S	Sulfides	$2H^+ + S^{2-} \longrightarrow H_2S$
HCN	Cyanides	$H^+ + CN^- \longrightarrow HCN$
CO_2	Carbonates	$2H^+ + CO_3^{2-} \longrightarrow (H_2CO_3) \longrightarrow H_2O + CO_2$
	Bicarbonates (hydrogen carbonates)	$H^+ + HCO_3^- \longrightarrow (H_2CO_3) \longrightarrow H_2O + CO_2$
SO_2	Sulfites	$2H^+ + SO_3^{2-} \longrightarrow (H_2SO_3) \longrightarrow H_2O + SO_2$
	Bisulfites (hydrogen sulfites)	$H^+ + HSO_3^- \longrightarrow (H_2SO_3) \longrightarrow H_2O + SO_2$
Gas	**Formed by Reaction of Bases with:**	**Equation for Formation**
NH_3	Ammonium salts[b]	$NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$

[a] Formulas in parentheses are of unstable compounds that break down according to the continuation of the sequence.

[b] In writing a metathesis reaction, you may be tempted sometimes to write NH_4OH as a formula for "ammonium hydroxide." That compound does not exist. In water, it is nothing more than a solution of NH_3.

EXAMPLE 4.7

Predicting Reactions and Writing Their Equations

What reaction (if any) occurs when solutions of ammonium carbonate, $(NH_4)_2CO_3$, and propionic acid, $HC_3H_5O_2$, are mixed?

ANALYSIS: Our tools for working a problem such as this are the list of strong acids (page 140), the solubility rules (Table 4.1, page 147), and the list of gases formed in metathesis reactions (Table 4.2). We begin by writing a potential metathesis equation in molecular form. Then we examine the reactants and products to see if any are weak electrolytes or substances that give gases. We also look for soluble or insoluble ionic compounds. Then we form the ionic equation and search for spectator ions which we eliminate to obtain the net ionic equation.

SOLUTION: We begin by constructing a molecular equation, treating the reaction as a metathesis. For the acid, we take the cation to be H^+ and the anion to be $C_3H_5O_2^-$. Therefore, after exchanging cations between the two anions we can obtain the following balanced molecular equation.

$$(NH_4)_2CO_3 + 2HC_3H_5O_2 \longrightarrow 2NH_4C_3H_5O_2 + H_2CO_3$$

In the statement of the problem we are told that we are working with a *solution* of $HC_3H_5O_2$, so we know it's soluble. Also, it is not on the list of strong acids, so we expect it to be a weak acid; we will write it in molecular form in the ionic equation.

Next, we recognize that H_2CO_3 decomposes into $CO_2(g)$ and H_2O. (This information is also found in Table 4.2.) Let's rewrite the molecular equation taking this into account.

$$(NH_4)_2CO_3 + 2HC_3H_5O_2 \longrightarrow 2NH_4C_3H_5O_2 + CO_2(g) + H_2O$$

Next, we need to determine which of the ionic substances are soluble. The solubility rules tell us that all ammonium salts are soluble, and we know that all salts are strong electrolytes. Therefore, we will write $(NH_4)_2CO_3$ and $NH_4C_3H_5O_2$ in dissociated form. Now we are ready to expand the molecular equation into the ionic equation.

$$2NH_4^+(aq) + CO_3^{2-}(aq) + 2HC_3H_5O_2(aq) \longrightarrow 2NH_4^+(aq) + 2C_3H_5O_2^-(aq) + CO_2(g) + H_2O$$

The only spectator ion is NH_4^+. Dropping this gives the net ionic equation.

$$CO_3^{2-}(aq) + 2HC_3H_5O_2(aq) \longrightarrow 2C_3H_5O_2^-(aq) + CO_2(g) + H_2O$$

IS THE ANSWER REASONABLE? There are some common errors that people make in working problems of this kind, so it is important to double-check. First, *proceed carefully*. Be sure you've written the formulas of the products correctly. (If you need review, you might look at Example 4.6 on page 147.) Look for weak acids. (You need to know the list of strong ones; if an acid isn't on the list, it's a weak acid.) Look for gases, or substances that decompose into gases. (Be sure you've studied Table 4.2.) Check for insoluble compounds. (You need to know the solubility rules in Table 4.1.) If you've learned what is expected of you, and checked each step, it is likely your result is correct.

EXAMPLE 4.8
Predicting Reactions and Writing Their Equations

What reaction (if any) occurs in water between potassium nitrate and ammonium chloride?

ANALYSIS: First, we have to convert the names of the compounds into chemical formulas. Here we use the principles of nomenclature rules from Chapter 2. The ions in potassium nitrate are K^+ and NO_3^-, so the salt has the formula KNO_3. In ammonium chloride, the ions are NH_4^+ and Cl^-, so the salt is NH_4Cl. Now we can proceed to writing molecular, ionic, and net ionic equations as in the preceding example.

SOLUTION: First we write the molecular equation, being sure to construct correct formulas for the products.

$$KNO_3 + NH_4Cl \longrightarrow KCl + NH_4NO_3$$

Looking over the substances in the equation, we don't find any that are weak acids or that decompose to give gases. Next, we check solubilities.

Solubility Rule 2 tells us that both KNO_3 and NH_4Cl are soluble. By solubility Rules 1 and 2, both products are also soluble in water. The anticipated molecular equation is therefore

$$\underset{\text{soluble}}{KNO_3(aq)} + \underset{\text{soluble}}{NH_4Cl(aq)} \longrightarrow \underset{\text{soluble}}{KCl(aq)} + \underset{\text{soluble}}{NH_4NO_3(aq)}$$

and the ionic equation is

$$K^+(aq) + NO_3^-(aq) + NH_4^+(aq) + Cl^-(aq) \longrightarrow K^+(aq) + Cl^-(aq) + NH_4^+(aq) + NO_3^-(aq)$$

Notice that the right side of the equation is the same as the left side except for the order in which the ions are written. When we eliminate spectator ions, everything goes. There is no net ionic equation, which means there is no net reaction.

IS THE ANSWER REASONABLE? Once again, we perform the same checks here as in Example 4.7, and they tell us our answer is right.

Practice Exercise 21: Knowing that salts of the formate ion, CHO_2^-, are water soluble, predict the reaction between $Co(OH)_2$ and formic acid, $HCHO_2$. Write molecular, ionic, and net ionic equations. (Hint: Apply the tools we used in Example 4.7.)

Practice Exercise 22: Predict whether a reaction will occur in aqueous solution between the following pairs of substances. Write molecular, ionic, and net ionic equations. (a) $KCHO_2$ and HCl, (b) $CuCO_3$ and $HC_2H_3O_2$, (c) calcium acetate and silver nitrate, and (d) sodium hydroxide and nickel(II) chloride.

4.6 THE COMPOSITION OF A SOLUTION IS DESCRIBED BY ITS CONCENTRATION

As you learned earlier, the composition of a solution is specified by giving its *concentration*. Percentage concentration (grams of solute per 100 g of solution) was used as an example. To deal with the stoichiometry of reactions in solution, however, percentage concentration is not a convenient way to express concentrations of solutes. Instead, we express the amount of solute in moles and the amount of solution in liters.

The **molar concentration,** or **molarity** (abbreviated M), of a solution is defined as *the number of moles of solute per liter of solution*. It is a ratio of moles of solute to the volume of the solution expressed in liters.

TOOLS
Molarity

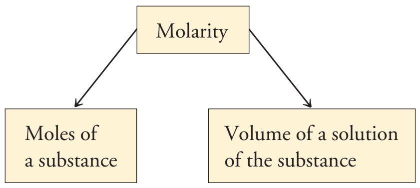
$$\text{Molarity } (M) = \frac{\text{moles of solute}}{\text{liters of solution}} \tag{4.4}$$

Thus, a solution that contains 0.100 mol of NaCl in 1.00 L has a molarity of 0.100 M, and we would refer to the solution as 0.100 *molar* NaCl or as 0.100 M NaCl. The same concentration would result if we dissolved 0.0100 mol of NaCl in 0.100 L (100 mL) of solution, because the *ratio* of moles of solute to volume of solution is the same.

$$\frac{0.100 \text{ mol NaCl}}{1.00 \text{ L NaCl soln}} = \frac{0.0100 \text{ mol NaCl}}{0.100 \text{ L NaCl soln}} = 0.100\ M \text{ NaCl}$$

Molarity is a conversion factor relating moles of solute and volume of a solution

Whenever we have to deal with a problem that involves an amount of a chemical and a volume of a solution of that substance, you can expect that solving the problem will involve molarity.



Molarity is a tool that provides the conversion factors we need to convert between moles and volume (either in liters or milliliters). Consider, for example, a solution labeled 0.100 M NaCl. The unit M always translates to mean "moles per liter," so we can write

$$0.100\ M \text{ NaCl} = \frac{0.100 \text{ mol NaCl}}{1.00 \text{ L soln}}$$

This gives us an equivalence relationship between "mol NaCl" and "L soln" that we can use to form two conversion factors.[7]

$$\begin{tikzcd} 0.100 \text{ mol NaCl} \arrow[r, phantom, "\Leftrightarrow"] \arrow[d] & 1.00 \text{ L soln} \arrow[d] \\ \dfrac{0.100 \text{ mol NaCl}}{1.00 \text{ L NaCl soln}} & \dfrac{1.00 \text{ L NaCl soln}}{0.100 \text{ mol NaCl}} \end{tikzcd}$$

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[7] Some students find it easier to translate the "1.00 L" part of these factors into the equivalent 1000 mL here rather than convert between liters and milliliters at some other stage of the calculation. Factors such as the two above, therefore, can be rewritten as follows whenever it is convenient. (Remember that "1000") in the following is regarded as having an infinite number of significant figures because, standing as it does for 1 L, it is part of the definition of molarity and is an exact number.)

$$\frac{0.100 \text{ mol NaCl}}{1000 \text{ mL NaCl soln}} \quad \text{and} \quad \frac{1000 \text{ mL NaCl soln}}{0.100 \text{ mol NaCl}}$$

EXAMPLE 4.9
Calculating the Molarity of a Solution

To study the effect of dissolved salt on the rusting of an iron sample, a student prepared a solution of NaCl by dissolving 1.461 g of NaCl in a total volume of 250.0 mL. What is the molarity of this solution?

ANALYSIS: The tool we'll use to solve this problem is Equation 4.4, which defines molarity as the ratio of *moles of solute* to *liters of solution*. If we can find these two pieces of information, we can arrange them as a ratio:

$$\text{Molarity} = \frac{?\ \text{mol NaCl}}{?\ \text{L soln}}$$

Therefore, we have to convert 1.461 g of NaCl to moles of NaCl and 250.0 mL to liters. Then we simply divide one by the other to find the molarity.

SOLUTION: The number of moles of NaCl is found using the formula mass of NaCl, 58.443 g mol^{-1}.

$$1.461\ \cancel{\text{g NaCl}} \times \frac{1\ \text{mol NaCl}}{58.443\ \cancel{\text{g NaCl}}} = 0.02500\ \text{mol NaCl}$$

To find the volume of the solution in liters, we move the decimal three places to the left, so 250.0 mL equals 0.2500 L.

▫ If necessary, practice converting between liters and milliliters. It's a task you will have to perform frequently.

The ratio of moles to liters, therefore, is

$$\frac{0.02500\ \text{mol NaCl}}{0.2500\ \text{L}} = 0.1000\ M\ \text{NaCl}$$

IS THE ANSWER REASONABLE? Let's use our answer to do a rough calculation of the amount of NaCl in the solution. If our answer is right, we should find a value not too far from the amount given in the problem (1.461 g). If we round the formula mass of NaCl to 60, and use 0.1 *M* as an approximate concentration, then one liter of the solution contains 0.1 mol of NaCl, or approximately 6 g of NaCl (one-tenth of 60 g). But 250 mL is only 1/4 of a liter, so the mass of NaCl will be approximately 1/4 of 6 g, or about 1.5 g. This is pretty close to the amount that was given in the problem, so our answer is probably correct.

Practice Exercise 23: A certain solution contains 16.9 g of HNO_3 dissolved in 125 mL of solution. Water is added until the volume is 175 mL. What is the molarity of HNO_3 in the final solution? (Hint: Does the amount of HNO_3 change when the water is added?)

Practice Exercise 24: Suppose 1.223 g of NaCl is added to the 250.0 mL of NaCl solution described in Example 4.9. If there is no change in the total volume of the solution, what is the molarity of the new NaCl solution?

EXAMPLE 4.10
Using Molar Concentrations

How many milliliters of 0.250 *M* NaCl solution must be measured to obtain 0.100 mol of NaCl?

ANALYSIS: We can restate the problem as follows:

$$0.100\ \text{mol NaCl} \Leftrightarrow ?\ \text{mL soln}$$

To relate moles and volume, the tool we use is the molarity.

$$0.250\ M\ \text{NaCl} = \frac{0.250\ \text{mol NaCl}}{1\ \text{L NaCl soln}}$$

The fraction on the right relates moles of NaCl to liters of the solution, which we can express as an equivalence.

$$0.250 \text{ mol NaCl} \Leftrightarrow 1 \text{ L NaCl soln}$$

The equivalence allows us to construct two conversion factors.

$$\frac{0.250 \text{ mol NaCl}}{1 \text{ L NaCl soln}} \quad \text{and} \quad \frac{1.00 \text{ L NaCl soln}}{0.250 \text{ mol NaCl}}$$

To obtain the answer, we select the one that will allow us to cancel the unit "mol NaCl."

SOLUTION: We operate with the second factor on 0.100 mol NaCl.

$$0.100 \cancel{\text{ mol NaCl}} \times \frac{1.00 \text{ L NaCl soln}}{0.250 \cancel{\text{ mol NaCl}}} = 0.400 \text{ L of } 0.250 \; M \text{ NaCl}$$

Because 0.400 L corresponds to 400 mL, 400 mL of 0.250 M NaCl provides 0.100 mol of NaCl.

IS THE ANSWER REASONABLE? The molarity tells us one liter contains 0.250 mol NaCl, so we need somewhat less than half of a liter (500 mL) to obtain just 0.100 mol. The answer, 400 mL, is reasonable.

Practice Exercise 25: A student measured 175 mL of 0.250 M HCl solution into a beaker. How many moles of HCl were in the beaker? (Hint: Molarity gives the equivalence between moles of solute and volume of solution in liters.)

Practice Exercise 26: How many milliliters of 0.250 M HCl solution contain 1.30 g of HCl?

Moles of solute can always be obtained from the volume and molarity of a solution

If you worked Practice Exercise 25 you learned that we can use the volume and molarity of a solution to calculate the number of moles of solute in it. This is such a useful relationship that it warrants special attention. Solving Equation 4.4 for *moles of solute* gives

TOOLS
Molarity times volume gives moles

$$\text{molarity} \times \text{volume (L)} = \text{moles of solute} \tag{4.5}$$

$$\frac{\text{mol solute}}{\cancel{\text{L soln}}} \times \cancel{\text{L soln}} = \text{mol solute}$$

Thus, *any time you know both the molarity and volume of a solution, you can easily calculate the number of moles of solute in it.* As you will see, this concept will be very useful in solving a variety of problems.

One situation in which Equation 4.5 is useful is when we must prepare some specific volume of a solution having a desired molarity (for example, 250 mL of 0.0800 M Na_2CrO_4). To proceed, we have to calculate the amount of solute that will be in the solution after it's made. Thus, in 250 mL of 0.0800 M Na_2CrO_4 there are

$$\frac{0.0800 \text{ mol } Na_2CrO_4}{1 \cancel{\text{ L soln}}} \times 0.250 \cancel{\text{ L soln}} = 0.0200 \text{ mol } Na_2CrO_4$$

Figure 4.20 shows how we would use a 250 mL volumetric flask to prepare such a solution. (A *volumetric flask* is a narrow-necked flask having an etched mark high on its neck. When filled to the mark, the flask contains precisely the volume given by the flask's label.)

■ In the laboratory, 250 mL is easily measured to a precision equal to or greater than ±1 mL, so we will take 250 mL to have three significant figures.

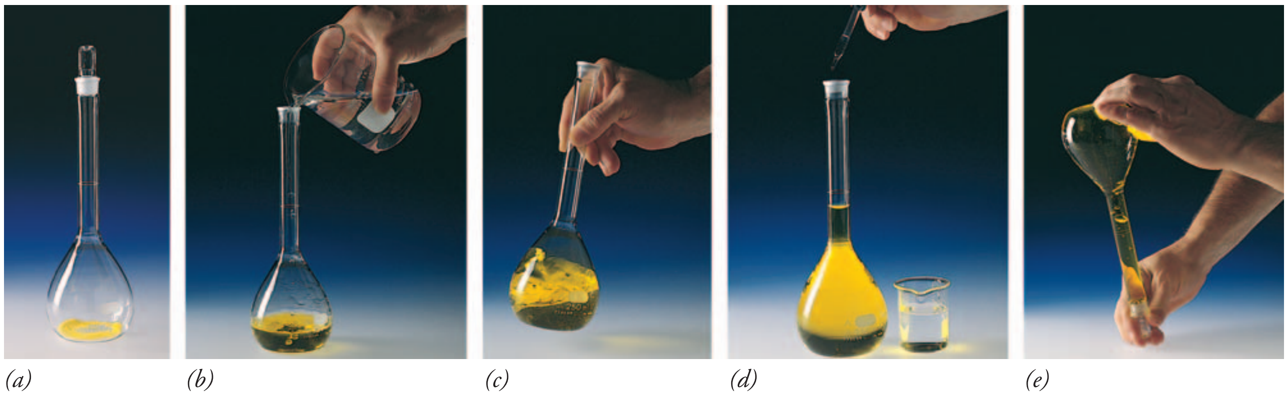


FIG. 4.20 **The preparation of a solution having a known molarity.** *(a)* A 250 mL volumetric flask, one of a number of sizes available for preparing solutions. When filled to the line etched around its neck, this flask contains exactly 250 mL of solution. The flask here already contains a weighed amount of solute. *(b)* Water is being added. *(c)* The solute is brought completely into solution before the level is brought up to the narrow neck of the flask. *(d)* More water is added to bring the level of the solution to the etched line. *(e)* The flask is stoppered and then inverted several times to mix its contents thoroughly. *(Michael Watson.)*

EXAMPLE 4.11
Preparing a Solution with a Known Molarity

Strontium nitrate, $Sr(NO_3)_2$, is used in fireworks to produce brilliant red colors. Suppose we need to prepare 250.0 mL of 0.100 *M* $Sr(NO_3)_2$ solution. How many grams of strontium nitrate are required?

ANALYSIS: The critical link in solving this problem is realizing that we know both the volume and molarity of the final solution, which permits us to calculate the number of moles of $Sr(NO_3)_2$ that will be in it. Once we know the number of moles of $Sr(NO_3)_2$, we can calculate its mass using the molar mass of the salt.

SOLUTION: You've learned that the product of molarity and volume equals moles of solute, so Equation 4.5 is the tool we need. The volume 250.0 mL converts to 0.2500 L. Therefore, multiplying the molarity by the volume in liters takes the following form.

$$\underset{\text{molarity}}{\underset{\uparrow}{\frac{0.100\ \text{mol Sr(NO}_3)_2}{1.00\ \cancel{\text{L Sr(NO}_3)_2\ \text{soln}}}}} \times \underset{\text{volume (L)}}{\underset{\uparrow}{0.2500\ \cancel{\text{L Sr(NO}_3)_2\ \text{soln}}}} = \underset{\text{moles of solute}}{\underset{\uparrow}{0.0250\ \text{mol Sr(NO}_3)_2}}$$

Finally, we convert from moles to grams using the molar mass of $Sr(NO_3)_2$, which is 211.63 g mol^{-1}.

$$0.0250\ \cancel{\text{mol Sr(NO}_3)_2} \times \frac{211.63\ \text{g Sr(NO}_3)_2}{1\ \cancel{\text{mol Sr(NO}_3)_2}} = 5.29\ \text{g Sr(NO}_3)_2$$

Thus, to prepare the solution we need to dissolve 5.29 g of $Sr(NO_3)_2$ in a total volume of 250.0 mL.

We could also have set this up as a chain calculation as follows, with the conversion factors strung together.

$$0.2500\ \cancel{\text{L Sr(NO}_3)_2\ \text{soln}} \times \frac{0.100\ \cancel{\text{mol Sr(NO}_3)_2}}{1.00\ \cancel{\text{L Sr(NO}_3)_2\ \text{soln}}} \times \frac{211.63\ \text{g Sr(NO}_3)_2}{1\ \cancel{\text{mol Sr(NO}_3)_2}} = 5.29\ \text{g Sr(NO}_3)_2$$

IS THE ANSWER REASONABLE? If we were working with a full liter of this solution, it would contain 0.1 mol of $Sr(NO_3)_2$. The molar mass of the salt is 211.63 g mol^{-1}, so 0.1 mol is slightly more than 20 g. However, we are working with just a quarter of a liter (250 mL), so the amount of $Sr(NO_3)_2$ needed is slightly more than a quarter of 20 g, or 5 g. The answer, 5.29 g, is close to this, so it makes sense.

Practice Exercise 27: Suppose you wished to prepare 50 mL of 0.2 *M* $Sr(NO_3)_2$ solution. Using the kind of approximate arithmetic we employed in the Is the Answer Reasonable step in the preceding example, estimate the number of grams of $Sr(NO_3)_2$ required. [Hint: How many moles of $Sr(NO_3)_2$ would be in one liter of the solution?]

Practice Exercise 28: How many grams of $AgNO_3$ are needed to prepare 250.0 mL of 0.0125 *M* $AgNO_3$ solution?

Diluting a solution reduces the concentration

Laboratory chemicals are usually purchased in concentrated form and must be *diluted* (made less concentrated) before being used. This is accomplished by adding more solvent to the solution, which spreads the solute through a larger volume and causes the concentration (the amount per unit volume) to decrease.

During dilution, the amount of solute remains constant. This means that the product of molarity and volume, which equals the moles of solute, must be the same for both the concentrated and diluted solution.

$$\underbrace{\begin{pmatrix}\text{Volume of}\\ \text{dilute solution}\\ \textit{to be prepared}\end{pmatrix} \times M_{\text{dilute}}}_{\substack{\text{moles of solute in}\\ \text{the dilute solution}}} = \underbrace{\begin{pmatrix}\text{Volume of}\\ \text{concentrated solution}\\ \textit{to be used}\end{pmatrix} \times M_{\text{conc}}}_{\substack{\text{moles of solute in the}\\ \text{concentrated solution}}}$$

TOOLS
Dilution of solutions

Or,

$$V_{\text{dil}} \cdot M_{\text{dil}} = V_{\text{conc}} \cdot M_{\text{conc}} \tag{4.6}$$

Any units can be used for volume in Equation 4.6 provided that the volume units are the same on both sides of the equation. We thus normally solve dilution problems using *milliliters* directly in Equation 4.6.

EXAMPLE 4.12

Preparing a Solution of Known Molarity by Dilution

How can we prepare 100.0 mL of 0.0400 *M* $K_2Cr_2O_7$ from 0.200 *M* $K_2Cr_2O_7$?

ANALYSIS: This is the way such a question comes up in the lab, but what it is really asking is, "How many milliliters of 0.200 *M* $K_2Cr_2O_7$ (the more concentrated solution) must be diluted to give a solution with a final volume of 100.0 mL and a final molarity of 0.0400 *M*?" Once we see the question this way, we realize that Equation 4.6 is the tool we need to solve the problem.

SOLUTION: It's a good idea to assemble the data first, noting what is missing (and therefore what has to be calculated).

$$\begin{aligned} V_{\text{dil}} &= 100.0 \text{ mL} & M_{\text{dil}} &= 0.0400\,M \\ V_{\text{conc}} &= ? & M_{\text{conc}} &= 0.200\,M \end{aligned}$$

Next, we use Equation 4.6 ($V_{\text{dil}} \times M_{\text{dil}} = V_{\text{conc}} \times M_{\text{conc}}$):

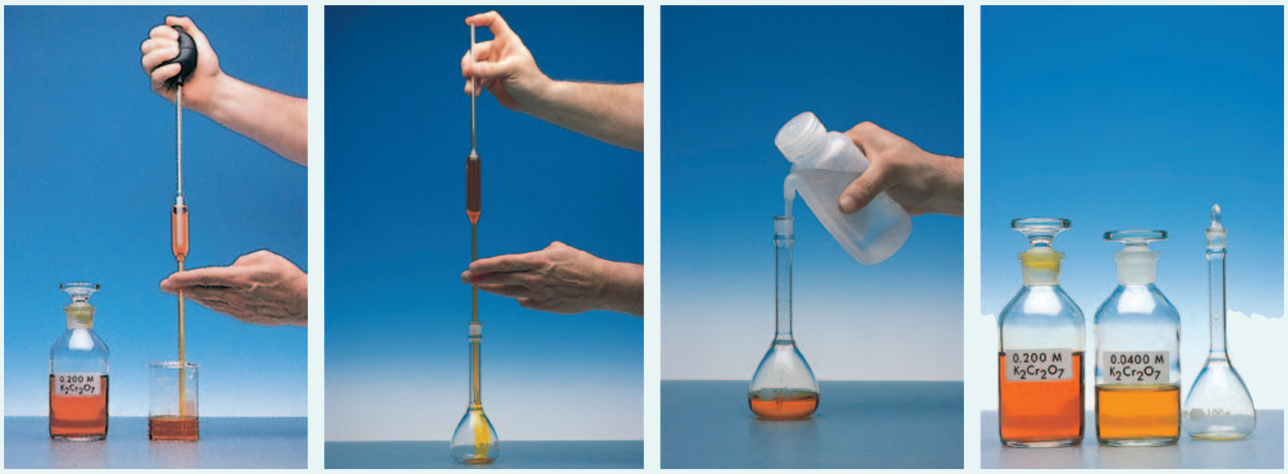
$$100.0 \text{ mL} \times 0.0400\ M = V_{\text{conc}} \times 0.200\ M$$

Solving for V_{conc} gives

$$V_{\text{conc}} = \frac{100.0 \text{ mL} \times 0.0400\ M}{0.200\ M}$$
$$= 20.0 \text{ mL}$$

Therefore, the answer to the question as asked is, We would withdraw 20.0 mL of 0.200 *M* $K_2Cr_2O_7$, place it in a 100 mL volumetric flask, and then add water until the final volume is exactly 100 mL. (See Figure 4.21.)

IS THE ANSWER REASONABLE? Notice that the concentrated solution is 5 times as concentrated as the dilute solution ($5 \times 0.04 = 0.2$). To reduce the concentration by a factor of 5 requires that we increase the volume by a factor of 5, and we see that 100 mL is 5 times 20 mL. The answer appears to be correct.



(*a*) (*b*) (*c*) (*d*)

FIG. 4.21 Preparing a solution by dilution. *(a)* The calculated volume of the more concentrated solution is withdrawn from the stock solution by means of a volumetric pipet. *(b)* The solution is allowed to drain entirely from the pipet into the volumetric flask. *(c)* Water is added to the flask, the contents are mixed, and the final volume is brought up to the etch mark on the narrow neck of the flask. *(d)* The new solution is put into a labeled container. *(OPC, Inc.)*

Practice Exercise 29: To what final volume must 100.0 mL of 0.125 *M* H_2SO_4 solution be diluted to give a 0.0500 *M* H_2SO_4 solution? (Hint: Write the equation we used for dilution problems.)

Practice Exercise 30: How many milliliters of water have to be *added* to 150 mL of 0.50 *M* HCl to reduce the concentration to 0.10 *M* HCl?

4.7 MOLARITY IS USED FOR PROBLEMS IN SOLUTION STOICHIOMETRY

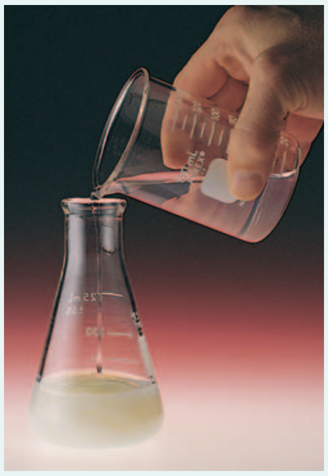
When we deal quantitatively with reactions in solution, we often work with volumes of solutions and molarity.

EXAMPLE 4.13
Stoichiometry Involving Reactions in Solution

One of the solids present in photographic film is silver bromide, AgBr. One way to prepare it is to mix solutions of silver nitrate and calcium bromide. Suppose we wished to prepare AgBr by the following precipitation reaction.

$$2AgNO_3(aq) + CaBr_2(aq) \longrightarrow 2AgBr(s) + Ca(NO_3)_2(aq)$$

How many milliliters of 0.125 *M* $CaBr_2$ solution must be used to react with the solute in 50.0 mL of 0.115 *M* $AgNO_3$?



Silver bromide (AgBr) precipitates when solutions of calcium bromide and silver nitrate are mixed. *(Michael Watson.)*

ANALYSIS: As you've learned, when we have a stoichiometry problem dealing with a chemical reaction, the tool that relates the amounts of the substances is their coefficients in the equation. For this problem, therefore, we can write

$$2 \text{ mol } AgNO_3 \Leftrightarrow 1 \text{ mol } CaBr_2$$

However, we're not given moles directly. Instead we have molarities and the volume of the $AgNO_3$ solution. The critical link in solving the problem is recognizing that the molarity and volume of the $AgNO_3$ solution provides a path to finding the number of moles of $AgNO_3$.

Knowing that we will use molarity as a tool in working the problem, let's outline the path to the answer. We can calculate the moles of $AgNO_3$ by multiplying the volume and molarity of the $AgNO_3$ solution. We then use the coefficients in the equation to translate to moles of $CaBr_2$. Finally, we use the molarity of the $CaBr_2$ solution as a conversion factor to find the volume of the solution needed. The calculation flow will look like the following.

$$\begin{tikzcd}
\text{mol } AgNO_3 \arrow[r, "\text{coefficients of}", "\text{balanced equation}"'] & \text{mol } CaBr_2 \arrow[d, "\text{moles of } CaBr_2 \text{ and molarity of } CaBr_2 \text{ solution}"] \\
\textbf{AgNO}_\mathbf{3}\textbf{ soln} \arrow[u, "\text{volume and molarity of } AgNO_3 \text{ solution}"] & \textbf{CaBr}_\mathbf{2}\textbf{ soln}
\end{tikzcd}$$

Given: 50.0 mL of 0.115 M $AgNO_3$

To find: ? mL of 0.125 M $CaBr_2$

SOLUTION: First, we find the moles of $AgNO_3$ taken. Changing 50.0 mL to 0.0500 L,

$$\underset{\text{volume (L)}}{0.0500 \text{ L}} \ \cancel{AgNO_3 \text{ soln}} \times \overset{\text{molarity}}{\frac{0.115 \text{ mol } AgNO_3}{1.00 \text{ L } \cancel{AgNO_3 \text{ soln}}}} = 5.75 \times 10^{-3} \text{ mol } AgNO_3$$

Next, we use the coefficients of the equation to calculate the amount of $CaBr_2$ required.

$$5.75 \times 10^{-3} \ \cancel{\text{mol } AgNO_3} \times \frac{1 \text{ mol } CaBr_2}{2 \ \cancel{\text{mol } AgNO_3}} = 2.88 \times 10^{-3} \text{ mol } CaBr_2$$

Finally we calculate the volume (mL) of 0.125 M $CaBr_2$ that contains this many moles of $CaBr_2$. Here we use the fact that the molarity of the $CaBr_2$ solution, 0.125 M, gives two possible conversion factors:

$$\frac{0.125 \text{ mol } CaBr_2}{1.00 \text{ L } CaBr_2 \text{ soln}} \quad \text{and} \quad \frac{1.00 \text{ L } CaBr_2 \text{ soln}}{0.125 \text{ mol } CaBr_2}$$

We use the one that cancels the unit "mol $CaBr_2$."

$$2.88 \times 10^{-3} \ \cancel{\text{mol } CaBr_2} \times \frac{1.00 \text{ L } CaBr_2 \text{ soln}}{0.125 \ \cancel{\text{mol } CaBr_2}} = 0.0230 \text{ L } CaBr_2 \text{ soln}$$

Thus 0.0230 L, or 23.0 mL, of 0.125 M $CaBr_2$ has enough solute to combine with the $AgNO_3$ in 50.0 mL of 0.115 M $AgNO_3$.

IS THE ANSWER REASONABLE? The molarities of the two solutions are about the same, but only 1 mol of $CaBr_2$ is needed for each 2 mol $AgNO_3$. Therefore, the volume of $CaBr_2$ solution needed (23.0 mL) should be about half the volume of $AgNO_3$ solution taken (50.0 mL), which it is.

Practice Exercise 31: How many milliliters of 0.0475 M H_3PO_4 could be completely neutralized by 45.0 mL of 0.100 M KOH? The balanced equation for the reaction is

$$H_3PO_4(aq) + 3KOH(aq) \longrightarrow K_3PO_4(aq) + 3H_2O$$

(Hint: Outline the path of the calculations as in the preceding example.)

Practice Exercise 32: How many milliliters of 0.124 M NaOH contain enough NaOH to react with the H_2SO_4 in 15.4 mL of 0.108 M H_2SO_4 according to the following equation?

$$2NaOH(aq) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O$$

Net ionic equations can be used in stoichiometric calculations

In the preceding problem, we worked with a molecular equation in solving a stoichiometry problem. Ionic and net ionic equations can also be used, but this requires that we work with the concentrations of the ions in solution.

Calculating concentrations of ions in solutions of electrolytes

The concentrations of the ions in a solution of an electrolyte are obtained from the formula and molar concentration of the solute. For example, suppose we are working with a solution labeled "0.10 M $CaCl_2$." In 1.0 L of this solution there is 0.10 mol of $CaCl_2$, which is fully dissociated into Ca^{2+} and Cl^- ions.

$$CaCl_2 \longrightarrow Ca^{2+} + 2Cl^-$$

From the stoichiometry of the dissociation, we see that 1 mol Ca^{2+} and 2 mol Cl^- are formed from each 1 mol of $CaCl_2$. Therefore, 0.10 mol $CaCl_2$ will yield 0.10 mol Ca^{2+} and 0.20 mol Cl^-. In 0.10 M $CaCl_2$, then, the concentration of Ca^{2+} is 0.10 M and the concentration of Cl^- is 0.20 M. Thus,

> *The concentration of a particular ion equals the concentration of the salt multiplied by the number of ions of that kind in one formula unit of the salt.*

□ The solution doesn't actually contain any $CaCl_2$, even though this is the solute used to prepare the solution. Instead, the solution contains Ca^{2+} and Cl^- ions.

TOOLS *Molarity of ions in a salt solution*

EXAMPLE 4.14
Calculating the Concentrations of Ions in a Solution

What are the molar concentrations of the ions in 0.20 M aluminum sulfate?

ANALYSIS: First, we need the formula for the solute. Aluminum forms the Al^{3+} ion and sulfate ion is SO_4^{2-}. For electrical neutrality, the formula of the salt must be $Al_2(SO_4)_3$. In the solution, the concentrations of the ions are determined by the stoichiometry of the salt. Therefore, we determine the number of ions of each kind formed from one formula unit of $Al_2(SO_4)_3$. These values are then used along with the given concentration of the salt to calculate the ion concentrations.

SOLUTION: When $Al_2(SO_4)_3$ dissolves, it dissociates as follows:

$$Al_2(SO_4)_3(s) \longrightarrow 2Al^{3+}(aq) + 3SO_4^{2-}(aq)$$

Each formula unit of $Al_2(SO_4)_3$ yields two Al^{3+} ions and three SO_4^{2-} ions. Therefore, 0.20 mol $Al_2(SO_4)_3$ yields 0.40 mol Al^{3+} and 0.60 mol SO_4^{2-}, and we conclude that the solution contains 0.40 M Al^{3+} and 0.60 M SO_4^{2-}.

IS THE ANSWER REASONABLE? The answers here have been obtained by simple mole reasoning. We could have found the answers in a more formal manner using the factor-label method. For example, for Al^{3+}, we have

$$\frac{0.20\ \cancel{\text{mol Al}_2(\text{SO}_4)_3}}{1.0\ \text{L soln}} \times \frac{2\ \text{mol Al}^{3+}}{1\ \cancel{\text{mol Al}_2(\text{SO}_4)_3}} = \frac{0.40\ \text{mol Al}^{3+}}{1.0\ \text{L soln}} = 0.40\ M\ \text{Al}^{3+}$$

A similar calculation would give the concentration of $SO_4^{\ 2-}$ as 0.60 *M*. Study both methods. With just a little practice, you will have little difficulty with the reasoning approach we used first.

EXAMPLE 4.15

Calculating the Concentration of a Salt from the Concentration of One of Its Ions

A student found that the sulfate ion concentration in a solution of $Al_2(SO_4)_3$ was 0.90 *M*. What was the concentration of $Al_2(SO_4)_3$ in the solution?

ANALYSIS: Once again, we use the formula of the salt to determine the number of ions released when it dissociates. This time we use the information to work backward to find the salt concentration.

SOLUTION: Let's set up the problem using the factor label method to be sure of our procedure. We will use the fact that 1 mol $Al_2(SO_4)_3$ yields 3 mol $SO_4^{\ 2-}$ in solution.

$$1\ \text{mol Al}_2(\text{SO}_4)_3 \Leftrightarrow 3\ \text{mol SO}_4^{\ 2-}$$

Therefore,

$$\frac{0.90\ \cancel{\text{mol SO}_4^{\ 2-}}}{1.0\ \text{L soln}} \times \frac{1\ \text{mol Al}_2(\text{SO}_4)_3}{3\ \cancel{\text{mol SO}_4^{\ 2-}}} = \frac{0.30\ \text{mol Al}_2(\text{SO}_4)_3}{1.0\ \text{L soln}} = 0.30\ M\ \text{Al}_2(\text{SO}_4)_3$$

The concentration of $Al_2(SO_4)_3$ is 0.30 *M*.

IS THE ANSWER REASONABLE? We'll use the reasoning approach to check our answer. We know that 1 mol $Al_2(SO_4)_3$ yields 3 mol $SO_4^{\ 2-}$ in solution. Therefore, the number of moles of $Al_2(SO_4)_3$ is only one-third the number of moles of $SO_4^{\ 2-}$. So the concentration of $Al_2(SO_4)_3$ must be one-third of 0.90 *M*, or 0.30 *M*.

Practice Exercise 33: What are the molar concentrations of the ions in 0.40 *M* $FeCl_3$? (Hint: How many ions of each kind are formed when $FeCl_3$ dissociates?)

Practice Exercise 34: In a solution of Na_3PO_4, the $PO_4^{\ 3-}$ concentration was determined to be 0.250 *M*. What was the sodium ion concentration in the solution?

Net ionic equations can be used in stoichiometry calculations

You have seen that a net ionic equation is convenient for describing the net chemical change in an ionic reaction. Let's study an example that illustrates how such equations can be used in stoichiometric calculations.

EXAMPLE 4.16

Stoichiometric Calculations Using a Net Ionic Equation

How many milliliters of 0.100 *M* $AgNO_3$ solution are needed to react completely with 25.0 mL of 0.400 *M* $CaCl_2$ solution? The net ionic equation for the reaction is

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

ANALYSIS: In many ways, this problem is similar to Example 4.13. However, to use the net ionic equation, we will need to work with the concentrations of the ions. Therefore, the tools we will use to solve this problem are the formulas of the salts (to find the molar concentrations of the ions) and the coefficients of the equation (to relate moles of Ag^+ and Cl^-).

To solve the problem, the first step will be to calculate the molarities of the ions in the solutions being mixed. Next, using the volume and molarity of the Cl^- solution, we will calculate the moles of Cl^- available. Then we'll use the coefficients of the equation to find the moles of Ag^+ that react. Finally, we'll use the molarity of the Ag^+ solution to determine the volume of the 0.100 *M* $AgNO_3$ solution needed.

SOLUTION: We begin by finding the concentrations of the ions in the reacting solutions:

0.100 *M* $AgNO_3$ contains 0.100 *M* Ag^+ and 0.100 *M* NO_3^-
0.400 *M* $CaCl_2$ contains 0.400 *M* Ca^{2+} and 0.800 *M* Cl^-

We're only interested in the Ag^+ and Cl^-; the Ca^{2+} and NO_3^- are spectator ions. For our purposes, then, the solution concentrations are 0.100 *M* Ag^+ and 0.800 *M* Cl^-. Having these values, we can now restate the problem: How many milliliters of 0.100 *M* Ag^+ solution are needed to react completely with 25.0 mL of 0.800 *M* Cl^- solution?

$$25.0 \text{ mL } Cl^- \text{ soln} \Leftrightarrow ?\text{ mL } Ag^+ \text{ soln}$$

The moles of Cl^- available for reaction are obtained from the molarity and volume (0.0250 L) of the Cl^- solution.

$$0.0250 \cancel{\text{L } Cl^- \text{ soln}} \times \frac{0.800 \text{ mol } Cl^-}{1.00 \cancel{\text{L } Cl^- \text{ soln}}} = 0.0200 \text{ mol } Cl^-$$

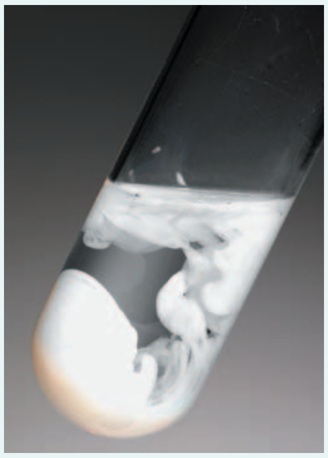
The coefficients of the equation tell us the Ag^+ and Cl^- combine in a 1-to-1 mole ratio, so 0.0200 mol Cl^- ⇔ 0.0200 mol Ag^+. Finally, we calculate the volume of the Ag^+ solution using its molarity as a conversion factor. As we've done earlier, we use the factor that makes the units cancel correctly.

$$0.0200 \cancel{\text{mol } Ag^+} \times \frac{1.00 \text{ L } Ag^+ \text{ soln}}{0.100 \cancel{\text{mol } Ag^+}} = 0.200 \text{ L } Ag^+ \text{ soln}$$

Our calculations tell us that we must use 0.200 L or 200 mL of the $AgNO_3$ solution. We could also have used the following chain calculation, of course.

$$0.0250 \cancel{\text{L } Cl^- \text{ soln}} \times \frac{0.800 \cancel{\text{mol } Cl^-}}{1.00 \cancel{\text{L } Cl^- \text{ soln}}} \times \frac{1 \cancel{\text{mol } Ag^+}}{1 \cancel{\text{mol } Cl^-}} \times \frac{1.00 \text{ L } Ag^+ \text{ soln}}{0.100 \cancel{\text{mol } Ag^+}} = 0.200 \text{ L } Ag^+ \text{ soln}$$

IS THE ANSWER REASONABLE? The silver ion concentration is one-eighth as large as the chloride ion concentration. Since the ions react one-for-one, we will need eight times as much silver ion solution as chloride solution. Eight times the amount of chloride solution, 25 mL, is 200 mL, which is the answer we obtained. Therefore, the answer appears to be correct.



A solution of $AgNO_3$ is added to a solution of $CaCl_2$, producing a precipitate of AgCl. *(Andy Washnik.)*

Simple reasoning works well here. Since the coefficients of Ag^+ and Cl^- are the same, the numbers of moles that react must be equal.

Practice Exercise 35: Suppose 18.4 mL of 0.100 *M* $AgNO_3$ solution was needed to react completely with 20.5 mL of $CaCl_2$ solution. What is the molarity of the $CaCl_2$ solution? Use the net ionic equation in the preceding example to work the problem. (Hint: How can you calculate molarity from moles and volume, and how can you calculate the molarity of the $CaCl_2$ solution from the molarity of Cl^-?)

Practice Exercise 36: How many milliliters of 0.500 *M* KOH are needed to react completely with 60.0 mL of 0.250 *M* $FeCl_2$ solution to precipitate $Fe(OH)_2$? The net ionic equation is $Fe^{2+}(aq) + 2OH^-(aq) \longrightarrow Fe(OH)_2(s)$.

4.8

CHEMICAL ANALYSIS AND TITRATION ARE APPLICATIONS OF SOLUTION STOICHIOMETRY

Chemical analyses fall into two categories. In a **qualitative analysis** we simply determine which substances are present in a sample without measuring their amounts. In a **quantitative analysis,** our goal is to measure the amounts of the various substances in a sample.

When chemical reactions are used in a quantitative analysis, a useful strategy is to capture *all* of a desired chemical species in a compound with a known formula. From the amount of this compound obtained, we can determine how much of the desired chemical species was present in the original sample. The calculations required for these kinds of problems are not new; they are simply applications of the stoichiometric calculations you've already learned.

EXAMPLE 4.17

Calculation Involving a Quantitative Analysis

A certain insecticide is a compound known to contain carbon, hydrogen, and chlorine. Reactions were carried out on a 0.134 g sample of the compound that converted all of its chlorine to chloride ion dissolved in water. This aqueous solution required 37.80 mL of 0.0500 *M* $AgNO_3$ to precipitate all the chloride ion as AgCl. What was the percentage by mass of Cl in the original insecticide sample? The precipitation reaction was

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

ANALYSIS: The percentage Cl in the sample will be calculated as follows:

$$\%\ \text{Cl by mass} = \frac{\text{mass of Cl in sample}}{\text{mass of sample}} \times 100\%$$

So, we need to determine the mass of Cl. We can use Equation 4.5 (page 156) and the volume and molarity of the $AgNO_3$ solution to find the number of moles of Ag^+ that reacts with the Cl^- in the solution. The ionic equation tells us Ag^+ and Cl^- react in a 1-to-1 mole ratio, so the moles of Ag^+ equals the moles of Cl^- that react. This is the same as the number of moles of Cl in the sample. Then we'll use the molar mass of Cl as a tool to change moles of Cl to grams of Cl.

□ The molar mass of a chlorine atom and a chloride ion differ by such a small amount that we can use them interchangeably.

SOLUTION: In 0.0500 *M* $AgNO_3$, the molarity of Ag^+ is 0.0500 *M*. Applying Equation 4.5,

$$0.03780\ \cancel{\text{L Ag}^+\ \text{soln}} \times \frac{0.0500\ \text{mol Ag}^+}{1.00\ \cancel{\text{L Ag}^+\ \text{soln}}} = 1.89 \times 10^{-3}\ \text{mol Ag}^+$$

From the stoichiometry of the equation, when 1.89×10^{-3} mol Ag^+ reacts, 1.89×10^{-3} mol Cl^- reacts. This is the amount of Cl^- that came from the sample, so the sample must have contained 1.89×10^{-3} mol Cl. The atomic mass of Cl is 35.45, so 1 mol Cl = 35.45 g Cl. Therefore, the mass of Cl in the sample was

$$1.89 \times 10^{-3}\ \cancel{\text{mol Cl}} \times \frac{35.45\ \text{g Cl}}{1\ \cancel{\text{mol Cl}}} = 6.70 \times 10^{-2}\ \text{g Cl}$$

The percentage by mass of Cl in the sample is

$$\begin{aligned}\%\ \text{Cl} &= \frac{6.70 \times 10^{-2}\ \text{g Cl}}{0.134\ \text{g sample}} \times 100\% \\ &= 50.0\%\end{aligned}$$

The insecticide was 50.0% Cl by mass.

IS THE ANSWER REASONABLE? Although we could do some approximate arithmetic to check our calculation, that's more easily done with the calculator. Therefore, let's look over the reasoning and calculations to see if they make sense. We've used the molarity and volume of the $AgNO_3$ solution to calculate the number of moles of Ag^+ that reacted (1.89×10^{-3} mol Ag^+). This has to be the same as the moles of Cl^- that reacted, and because the Cl^- came from the sample, the sample must have contained 1.89×10^{-3} mol of Cl. The mass of this Cl was calculated in the usual way using the molar mass of Cl. The value we obtained, 0.067 g, is half the sample weight of 0.134 g, so half (50%) of the sample weight was Cl. The answer, therefore, seems to be correct.

Practice Exercise 37: A solution containing Na_2SO_4 was treated with 0.150 *M* $BaCl_2$ solution until all the sulfate ion had reacted to form $BaSO_4$. The net reaction

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

required 28.40 mL of the $BaCl_2$ solution. How many grams of Na_2SO_4 were in the solution? (Hint: How do moles of SO_4^{2-} relate to moles of Na_2SO_4?)

Practice Exercise 38: A sample of a mixture containing $CaCl_2$ and $MgCl_2$ weighed 2.000 g. The sample was dissolved in water and H_2SO_4 was added until the precipitation of $CaSO_4$ was complete.

$$CaCl_2(aq) + H_2SO_4(aq) \longrightarrow CaSO_4(s) + 2HCl(aq)$$

The $CaSO_4$ was filtered, dried completely, and weighed. A total of 0.736 g of $CaSO_4$ was obtained.

(a) How many moles of Ca^{2+} were in the $CaSO_4$?
(b) How many moles of Ca^{2+} were in the original 2.000 g sample?
(c) How many moles of $CaCl_2$ were in the 2.000 g sample?
(d) How many grams of $CaCl_2$ were in the 2.000 g sample?
(e) What was the percentage by mass of $CaCl_2$ in the original mixture?

Acid–base titrations are useful in chemical analyses

Titration is an important laboratory procedure used in performing chemical analyses. The apparatus is shown in Figure 4.22. The long tube is called a **buret**, which is marked for volumes, usually in increments of 0.10 mL. The valve at the bottom of the buret is called a **stopcock,** and it permits the analyst to control the amount of **titrant** (the solution in the buret) that is delivered to the receiving vessel (the beaker shown in the drawing).

In a typical titration, a solution containing one reactant is placed in the receiving vessel. Carefully measured volumes of a solution of the other reactant are then added from the buret. (One of the two solutions is of a precisely known concentration and is called a **standard solution.**) This addition is continued until something (usually a visual effect, like a color change) signals that the two reactants have been combined in just the right proportions to give a complete reaction.

In acid–base titrations, an **acid–base indicator** is used to detect the completion of the reaction by a change in color. Indicators are dyes that have one color in an acidic solution and a different color in a basic solution. Litmus was mentioned earlier. Phenolphthalein is

◻ The theory of acid–base indicators is discussed in Chapter 16.

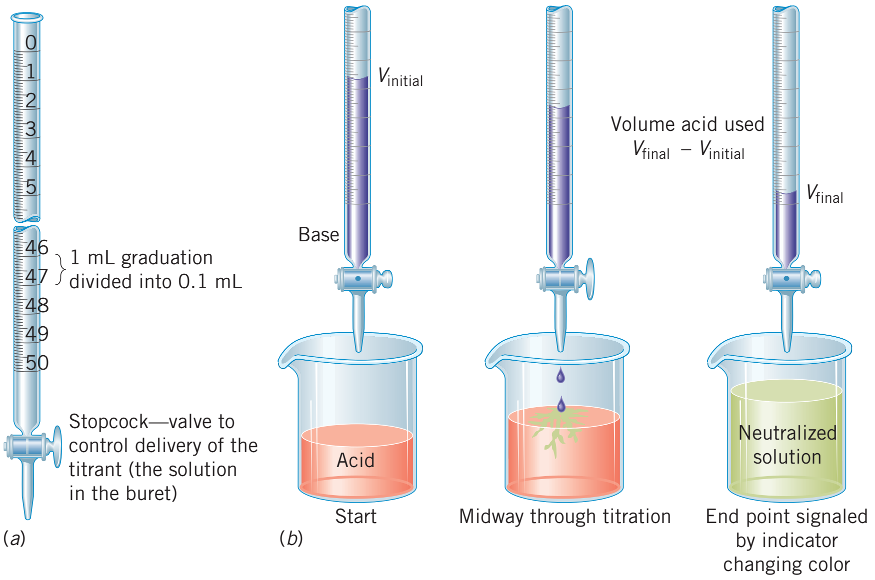


FIG. 4.22 Titration. *(a)* A buret. *(b)* The titration of an acid by a base in which an acid–base indicator is used to signal the end point, which is the point at which all of the acid has been neutralized and addition of the base is halted.

a common indicator for titrations; it changes from colorless to pink when a solution changes from acidic to basic. This color change is very abrupt, and occurs with the addition of only one final drop of the titrant just as the end of the reaction is reached. When we observe the color change, the **end point** has been reached and the addition of titrant is stopped. We then record the total volume of the titrant that's been added to the receiving flask.

EXAMPLE 4.18

Calculation Involving Acid–Base Titration

A student prepares a solution of hydrochloric acid that is approximately 0.1 *M* and wishes to determine its precise concentration. A 25.00 mL portion of the HCl solution is transferred to a flask, and after a few drops of indicator are added, the HCl solution is titrated with 0.0775 *M* NaOH solution. The titration requires exactly 37.46 mL of the standard NaOH solution to reach the end point. What is the molarity of the HCl solution?

A solution of HCl is titrated with a solution of NaOH using phenolphthalein as the acid–base indicator. The pink color that phenolphthalein has in a basic solution can be seen where a drop of the NaOH solution has entered the HCl solution, to which a few drops of the indicator had been added. *(Michael Watson.)*

ANALYSIS: This is really a straightforward stoichiometry calculation involving a chemical reaction. The first step in solving it is to write the balanced equation, which will give us the stoichiometric equivalency between HCl and NaOH. The reaction is an acid–base neutralization, so the product is a salt plus water. Following the procedures developed earlier, the reaction is

$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \longrightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}$$

Solving the problem will follow the same route as in Example 4.13. Our tools will be the molarity and volume of the NaOH solution (to calculate moles of NaOH that react), the coefficients of the equation (to obtain moles of HCl), and the definition of molarity (to calculate the molarity of the HCl solution from moles HCl and the volume of the HCl sample taken).

SOLUTION: From the molarity and volume of the NaOH solution, we calculate the number of moles of NaOH consumed in the titration.

$$0.03746\ \cancel{\text{L NaOH soln}} \times \frac{0.0775\ \text{mol NaOH}}{1.00\ \cancel{\text{L NaOH soln}}} = 2.90 \times 10^{-3}\ \text{mol NaOH}$$

The coefficients in the equation tell us that NaOH and HCl react in a 1-to-1 mole ratio,

$$2.90 \times 10^{-3}\ \cancel{\text{mol NaOH}} \times \frac{1\ \text{mol HCl}}{1\ \cancel{\text{mol NaOH}}} = 2.90 \times 10^{-3}\ \text{mol HCl}$$

so in this titration, 2.90×10^{-3} mol HCl was in the flask. To calculate the molarity of the HCl, we simply apply the definition of molarity. We take the ratio of the number of moles of HCl that reacted (2.90×10^{-3} mol HCl) to the volume (in liters) of the HCl solution used (25.00 mL, or 0.02500 L).

$$\begin{aligned}\text{Molarity of HCl soln} &= \frac{2.90 \times 10^{-3}\ \text{mol HCl}}{0.02500\ \text{L HCl soln}} \\ &= 0.116\ M\ \text{HCl}\end{aligned}$$

The molarity of the hydrochloric acid is 0.116 *M*.

IS THE ANSWER REASONABLE? If the concentrations of the NaOH and HCl were the same, the volumes used would have been equal. However, the volume of the NaOH solution used is larger than the volume of HCl solution. This must mean that the HCl solution is more concentrated than the NaOH solution. The value we obtained, 0.116 *M*, is larger than 0.0775 *M*, so our answer makes sense.

Practice Exercise 39: In a titration, a sample of H_2SO_4 solution having a volume of 15.00 mL required 36.42 mL of 0.147 M NaOH solution for *complete* neutralization. What is the molarity of the H_2SO_4 solution? (Hint: Check to be sure your chemical equation is written correctly and balanced.)

Practice Exercise 40: "Stomach acid" is hydrochloric acid. A sample of gastric juice having a volume of 5.00 mL required 11.00 mL of 0.0100 M KOH solution for neutralization in a titration. What was the molar concentration of HCl in this fluid? If we assume a density of 1.00 g mL^{-1} for the fluid, what was the percentage by weight of HCl?

SUMMARY

Solution Vocabulary. A **solution** is a homogeneous mixture in which one or more **solutes** are dissolved in a **solvent.** A solution may be **dilute** or **concentrated,** depending on the amount of solute dissolved in a given amount of solvent. **Concentration** (e.g., **percentage concentration**) is a ratio of the amount of solute to either the amount of solvent or the amount of solution. The amount of solute required to give a **saturated** solution at a given temperature is called the solute's **solubility. Unsaturated** solutions will dissolve more solute, but **supersaturated** solutions are unstable and tend to give a **precipitate.**

Electrolytes. Substances that **dissociate** or **ionize** in water to produce cations and anions are **electrolytes;** those that do not are called **nonelectrolytes.** Electrolytes include salts and metal hydroxides as well as molecular acids and bases that ionize by reaction with water. In water, ionic compounds are completely dissociated into ions and are **strong electrolytes.**

Ionic and Net Ionic Equations. Reactions that occur in solution between ions and are called **ionic reactions.** Solutions of soluble strong electrolytes often yield an insoluble product which appears as a **precipitate.** Equations for these reactions can be written in three different ways. In **molecular equations,** complete formulas for all reactants and products are used. In an **ionic equation,** soluble strong electrolytes are written in dissociated (ionized) form; "molecular" formulas are used for solids and weak electrolytes. A **net ionic equation** is obtained by eliminating **spectator ions** from the ionic equation, and such an equation allows us to identify other combinations of reactants that give the same net reaction. An ionic or net ionic equation is balanced only if both atoms *and* net charge are balanced.

Acids and Bases as Electrolytes. An **acid** is a substance that produces hydronium ions, H_3O^+, when dissolved in water, and a **base** produces hydroxide ions, OH^-, when dissolved in water. The oxides of nonmetals are generally **acidic anhydrides** and react with water to give acids. Metal oxides are usually **basic anhydrides** because they tend to react with water to give metal hydroxides or bases.

Strong acids and bases are also strong electrolytes. **Weak acids and bases** are **weak electrolytes,** which are incompletely ionized in water. In a solution of a weak electrolyte there is a **chemical equilibrium (dynamic equilibrium)** between the nonionized molecules of the solute and the ions formed by the reaction of the solute with water.

Predicting Metathesis Reactions. **Metathesis** or **double replacement** reactions take place when anions and cations of two salts change partners. A metathesis reaction will occur if there is a net ionic equation. This happens if (1) a precipitate forms from soluble reactants, (2) an acid–base neutralization occurs, (3) a gas is formed, or (4) a weak electrolyte forms from soluble strong electrolytes. You should learn the **solubility rules** (Table 4.1), and remember that all salts are strong electrolytes. Remember that all strong acids and bases are strong electrolytes, too. Strong acids react with strong bases in neutralization reactions to produce a salt and water. Acids react with insoluble oxides and hydroxides to form water and the corresponding salt. Many **acid–base neutralization** reactions can be viewed as a type of metathesis reaction in which one product is water. Be sure to learn the reactions that produce gases in metathesis reactions, which are found in Table 4.2.

Molar Concentration, Dilution, and Solution Stoichiometry. **Molarity** is the ratio of moles of solute to liters of solution. Molarity provides two conversion factors relating moles of solute and the volume of a solution.

$$\frac{\text{mol solute}}{\text{1 L soln}} \quad \text{and} \quad \frac{\text{1 L soln}}{\text{mol solute}}$$

Concentrated solutions of known molarity can be diluted quantitatively using volumetric glassware such as pipets and volumetric flasks. When a solution is diluted by adding solvent, the amount of solute doesn't change but the concentration decreases.

In ionic reactions, the concentrations of the ions in a solution of a salt can be derived from the molar concentration of the salt, taking into account the number of ions formed per formula unit of the salt.

Titration is a technique used to make quantitative measurements of the amounts of solutions needed to obtain a complete reaction. The apparatus is a long tube called a **buret** that has a **stopcock** at one end, which is used to control the flow of **titrant.** In an acid–base titration, the **end point** is normally detected visually using an **acid–base indicator.** A color change indicates complete reaction, at which time addition of titrant is stopped and the volume added is recorded.

TOOLS FOR PROBLEM SOLVING

In this chapter you learned to apply the following concepts as tools in solving problems dealing with reactions in aqueous solutions. Study each one carefully so that you know what each is used for. When faced with solving a problem, recall what each tool does and consider whether it will be helpful in finding a solution. This will aid you in selecting the tools you need.

Criteria for a balanced ionic or net ionic equation *(page 135)* For an equation that includes the formulas of ions to be balanced, it must satisfy two criteria. The number of atoms of each kind must be the same on both sides, and the total net electrical charge shown on both sides must be the same.

Equation for the ionization of an acid in water *(page 137)* Equation 4.2 describes how acids react with water to form hydronium ion plus an anion.

$$\mathrm{H}A + \mathrm{H_2O} \longrightarrow \mathrm{H_3O^+} + A^-$$

Use this tool to write equations for ionizations of acids and to determine the formula of the anion formed when the acid molecule loses an H^+. The equation also applies to acid anions such as HSO_4^- which gives SO_4^{2-} when it loses an H^+. Often H_2O is omitted from the equation and the hydronium ion is abbreviated as H^+.

Equation for the ionization of a molecular base in water *(page 139)* Equation 4.3 describes how molecules of molecular bases acquire H^+ from H_2O to form a cation plus a hydroxide ion.

$$B + \mathrm{H_2O} \longrightarrow B\mathrm{H^+} + \mathrm{OH^-}$$

Use this tool to write equations for ionizations of bases and to determine the formula of the cation formed when the base molecule gains an H^+. *Molecular bases are weak and are not completely ionized.*

Table of strong acids *(page 140)* Formulas of the most common strong acids are given here. If you learn this list and encounter an acid that's *not* on the list, you can assume it to be a weak acid. The most common strong acids are HCl, HNO_3, and H_2SO_4. *Remember that strong acids are completely ionized in water.*

Predicting the existence of a net ionic equation *(page 146)* A net ionic equation will exist and a reaction will occur when:

- A precipitate is formed from a mixture of soluble reactants.
- An acid reacts with a base. *This includes strong or weak acids reacting with strong or weak bases or insoluble metal hydroxides or oxides.*
- A weak electrolyte is formed from a mixture of strong electrolytes.
- A gas is formed from a mixture of reactants.

These criteria are tools to determine whether or not a net reaction will occur in a solution.

Solubility rules *(page 147)* The rules in Table 4.1 are the tool we use to determine whether a particular salt is soluble in water. (If a salt is soluble, it's completely dissociated into ions.) They also serve as a tool to help predict the course of metathesis reactions.

Substances that form gases in metathesis reactions *(page 152)* Use Table 4.2 as a tool to help predict the outcome of metathesis reactions. The most common gas formed in such reactions is CO_2, which comes from the reaction of an acid with a carbonate or bicarbonate.

Molarity *(page 154)* Molarity provides the connection between moles of a solute and the volume of its solution. The definition provided by Equation 4.4 serves as a tool for calculating molarity from values of moles of solute and volume of solution (in liters).

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

Molarity is the tool we use to write an equivalence between moles of solute and volume of solution, from which appropriate conversion factors can be formed.

Product of molarity and volume gives moles *(page 156)* For any problem in which you're given both molarity and volume of a solution of a substance, you can always calculate the number of moles of the substance using Equation 4.5.

$$\text{Molarity} \times \text{volume (L)} = \text{moles of solute}$$

Recognizing this relationship is very important when working stoichiometry problems involving solutions.

Dilution problems *(page 158)* Equation 4.6 is the tool we use for working dilution problems.

$$V_{\text{dil}} \cdot M_{\text{dil}} = V_{\text{conc}} \cdot M_{\text{conc}}$$

The volume units must be the same on both sides of the equation.

Concentrations of ions in a solution of a salt *(page 161)* When using a net ionic equation to work stoichiometry problems, we need the concentrations of the ions in the solutions. *The concentration of a particular ion equals the concentration of the salt multiplied by the number of ions of that kind in one formula unit of the salt.*

Overview of stoichiometry problems In this chapter you encountered another way that the data in stoichiometry problems are presented. Figure 4.23 gives an overview of the various paths through problems that involve chemical reactions. All funnel through the coefficients of the equation as the means to convert from moles of one substance to moles of another. The starting and finishing quantities can be moles, grams, or volumes of solutions of known molarity.

TOOLS Paths through stoichiometry problems

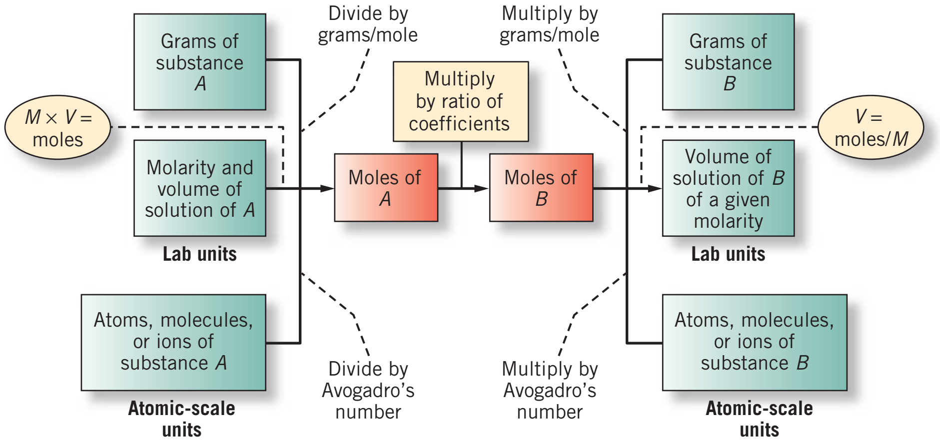


FIG. 4.23 **Paths for working stoichiometry problems involving chemical reactions.** The critical link is the conversion between moles of one substance and moles of another using the coefficients of the balanced equation. We can calculate moles in several ways: from numbers of atomic-sized formula units, and from laboratory units of grams or the volumes of solutions of known molarities. Similarly, we can present the answer either in moles, grams, number of formula units, or a volume of solution of known molarity.

QUESTIONS, PROBLEMS, AND EXERCISES

Answers to problems whose numbers are printed in color are given in Appendix B. More challenging problems are marked with asterisks. ILW = Interactive Learningware solution is available at *www.wiley.com/college/brady*. OH = an Office Hours video is available for this problem.

REVIEW QUESTIONS

Solution Terminology

4.1 Define the following: (a) solvent, (b) solute, (c) concentration.

4.2 Define the following: (a) concentrated, (b) dilute, (c) saturated, (d) unsaturated, (e) supersaturated, (f) solubility.

4.3 Why are chemical reactions often carried out using solutions?

4.4 Describe what will happen if a crystal of sugar is added to (a) a saturated sugar solution, (b) a supersaturated solution of sugar, and (c) an unsaturated solution of sugar.

4.5 What is the meaning of the term *precipitate*? What condition must exist for a precipitate to form spontaneously in a solution?

Electrolytes

4.6 What is an *electrolyte*? What is a *nonelectrolyte*?

4.7 Why is an electrolyte able to conduct electricity while a nonelectrolyte cannot? What does it mean when we say that an ion is "hydrated?"

4.8 Define *dissociation* as it applies to ionic compounds that dissolve in water.

4.9 Write equations for the dissociation of the following in water: (a) $CaCl_2$, (b) $(NH_4)_2SO_4$, (c) $NaC_2H_3O_2$.

Ionic Reactions

4.10 How do molecular, ionic, and net ionic equations differ? What are spectator ions?

4.11 The following equation shows the formation of cobalt(II) hydroxide, a compound used to improve the drying properties of lithographic inks.

$$Co^{2+}(aq) + 2Cl^-(aq) + 2Na^+(aq) + 2OH^-(aq) \longrightarrow Co(OH)_2(s) + 2Na^+(aq) + 2Cl^-(aq)$$

Which are the spectator ions? Write the net ionic equation.

4.12 What two conditions must be fulfilled by a balanced ionic equation? The following equation is not balanced. How do we know? Find the errors and fix them.

$$3Co^{3+}(aq) + 2HPO_4^{2-}(aq) \longrightarrow Co_3(PO_4)_2(s) + 2H^+(aq)$$

Acids, Bases, and Their Reactions

4.13 Give two general properties of an acid. Give two general properties of a base.

4.14 If you believed a solution was basic, which color litmus paper (blue or pink) would you use to test the solution to see if you were correct? What would you observe if you've selected correctly? Why would the other color litmus paper not lead to a conclusive result?

4.15 How did Arrhenius define an acid and a base?

4.16 Which of the following undergo dissociation in water? Which undergo ionization? (a) NaOH, (b) HNO_3, (c) NH_3, (d) H_2SO_4.

4.17 Which of the following would yield an acidic solution when they react with water? Which would give a basic solution? (a) P_4O_{10}, (b) K_2O, (c) SeO_3, (d) Cl_2O_7.

4.18 What is a *dynamic equilibrium*? Using acetic acid as an example, describe why all the $HC_2H_3O_2$ molecules are not ionized in water.

4.19 Why don't we use double arrows in the equation for the reaction of a strong acid with water?

4.20 Which of the following are strong acids? (a) HCN, (b) HNO_3, (c) H_2SO_3, (d) HCl, (e) $HCHO_2$, (f) HNO_2.

4.21 Which of the following produce a strongly basic solution when dissolved in water? (a) C_5H_5N, (b) $Ba(OH)_2$, (c) KOH, (d) $C_6H_5NH_2$, (e) Cs_2O, (f) N_2O_5.

4.22 Methylamine, CH_3NH_2, reacts with hydronium ion in very much the same manner as ammonia.

$$CH_3NH_2(aq) + H_3O^+(aq) \longrightarrow CH_3NH_3^+(aq) + H_2O$$

On the basis of what you have learned so far in this course, sketch the molecular structures of CH_3NH_2 and $CH_3NH_3^+$ (the methylammonium ion).

Nomenclature of Acids and Bases

4.23 Name the following: (a) $H_2Se(g)$, (b) $H_2Se(aq)$

4.24 Iodine, like chlorine, forms several acids. What are the names of the following? (a) HIO_4, (b) HIO_3, (c) HIO_2, (d) HIO, (e) HI.

4.25 For the acids in the preceding question, (a) write the formulas and (b) name the ions formed by removing a hydrogen ion (H^+) from each acid.

4.26 Write the formula for (a) chromic acid, (b) carbonic acid, and (c) oxalic acid. (Hint: Check the table of polyatomic ions.)

4.27 Name the following acid salts: (a) $NaHCO_3$, (b) KH_2PO_4, (c) $(NH_4)_2HPO_4$.

4.28 Write the formulas for all the acid salts that could be formed from the reaction of NaOH with the acid H_3PO_4.

4.29 Name the following oxoacids and give the names and formulas of the salts formed from them by neutralization with NaOH: (a) HOCl, (b) HIO_2, (c) $HBrO_3$, (d) $HClO_4$.

4.30 The formula for the arsenate ion is AsO_4^{3-}. What is the formula for arsenous acid?

4.31 Butyric acid, $HC_4H_7O_2$, gives rancid butter is bad odor. What is the name of the salt $NaC_4H_7O_2$?

4.32 Calcium propionate, $Ca(C_3H_5O_2)_2$ is used in baked foods as a preservative and to prevent the growth of mold. What is the name of the acid $HC_3H_5O_2$?

Predicting Ionic Reactions

4.33 What factors lead to the existence of a net ionic equation in a reaction between ions?

4.34 What is another name for *metathesis reaction*?

4.35 Silver bromide is "insoluble." What does this mean about the concentrations of Ag^+ and Br^- in a saturated solution of AgBr? Explain why a precipitate of AgBr forms when solutions of the soluble salts $AgNO_3$ and NaBr are mixed.

4.36 If a solution of trisodium phosphate, Na_3PO_4, is poured into seawater, precipitates of calcium phosphate and magnesium phosphate are formed. (Magnesium and calcium ions are among the principal ions found in seawater.) Write net ionic equations for the reactions.

4.37 Washing soda is $Na_2CO_3 \cdot 10H_2O$. Explain, using chemical equations, how this substance is able to remove Ca^{2+} ions from "hard water."

4.38 With which of the following will the weak acid $HCHO_2$ react? Where there is a reaction, write the formulas of the products. (a) KOH, (b) MgO, (c) NH_3

4.39 Suppose you suspected that a certain solution contained ammonium ions. What simple chemical test could you perform that would tell you whether your suspicion was correct?

4.40 What gas is formed if HCl is added to (a) $NaHCO_3$, (b) Na_2S, and (c) K_2SO_3?

Molarity and Dilution

4.41 What is the definition of molarity? Show that the ratio of millimoles (mmol) to milliliters (mL) is equivalent to the ratio of moles to liters.

4.42 A solution is labeled 0.25 *M* HCl. Construct two conversion factors that relate moles of HCl to the volume of solution expressed in liters.

4.43 When the units *molarity* and *liter* are multiplied, what are the resulting units?

4.44 When a solution labeled 0.50 *M* HNO_3 is diluted with water to give 0.25 *M* HNO_3, what happens to the number of moles of HNO_3 in the solution?

4.45 Two solutions, A and B, are labeled "0.10 *M* $CaCl_2$" and "0.20 *M* $CaCl_2$," respectively. Both solutions contain the same number of moles of $CaCl_2$. If solution A has a volume of 50 mL, what is the volume of solution B?

Chemical Analyses and Titrations

4.46 What is the difference between a qualitative analysis and a quantitative analysis?

4.47 Describe each of the following: (a) buret, (b) titration, (c) titrant, and (d) end point.

4.48 What is the function of an indicator in a titration? What color is phenolphthalein in (a) an acidic solution and (b) a basic solution?

REVIEW PROBLEMS

Ionic Reactions

4.49 Write ionic and net ionic equations for these reactions.
(a) $(NH_4)_2CO_3(aq) + MgCl_2(aq) \longrightarrow 2NH_4Cl(aq) + MgCO_3(s)$
(b) $CuCl_2(aq) + 2NaOH(aq) \longrightarrow Cu(OH)_2(s) + 2NaCl(aq)$
(c) $3FeSO_4(aq) + 2Na_3PO_4(aq) \longrightarrow Fe_3(PO_4)_2(s) + 3Na_2SO_4(aq)$
(d) $2AgC_2H_3O_2(aq) + NiCl_2(aq) \longrightarrow 2AgCl(s) + Ni(C_2H_3O_2)_2(aq)$

OH **4.50** Write balanced ionic and net ionic equations for these reactions.
(a) $CuSO_4(aq) + BaCl_2(aq) \longrightarrow CuCl_2(aq) + BaSO_4(s)$
(b) $Fe(NO_3)_3(aq) + LiOH(aq) \longrightarrow LiNO_3(aq) + Fe(OH)_3(s)$
(c) $Na_3PO_4(aq) + CaCl_2(aq) \longrightarrow Ca_3(PO_4)_2(s) + NaCl(aq)$
(d) $Na_2S(aq) + AgC_2H_3O_2(aq) \longrightarrow NaC_2H_3O_2(aq) + Ag_2S(s)$

Acids and Bases as Electrolytes

4.51 Pure $HClO_4$ is molecular. In water it is a strong acid. Write an equation for its ionization in water.

4.52 HBr is a molecular substance that is a strong acid in water. Write an equation for its ionization in water.

OH **4.53** Hydrazine is a toxic substance that can form when household ammonia is mixed with a bleach such as Clorox. Its formula is N_2H_4, and it is a weak base. Write a chemical equation showing the reaction of hydrazine with water.

4.54 Pyridine, C_5H_5N, is a fishy smelling compound used as an intermediate in making insecticides. It is a weak base. Write a chemical equation showing its reaction with water.

4.55 Nitrous acid, HNO_2, is a weak acid that can form when sodium nitrite, a meat preservative, reacts with stomach acid (HCl). Write an equation showing the ionization of HNO_2 in water.

4.56 Pentanoic acid, $HC_5H_9O_2$, is found in a plant called valerian, which cats seem to like almost as much as catnip. Also called valeric acid, it is a weak acid. Write an equation showing its reaction with water.

4.57 Carbonic acid, H_2CO_3, is a weak diprotic acid formed in rainwater as it passes through the atmosphere and dissolves carbon dioxide. Write chemical equations for the equilibria involved in the stepwise ionization of H_2CO_3 in water.

4.58 Phosphoric acid, H_3PO_4, is a weak acid found in some soft drinks. It undergoes ionization in three steps. Write chemical equations for the equilibria involved in each of these reactions.

Metathesis Reactions

4.59 Write *balanced* ionic and net ionic equations for these reactions.
(a) $FeSO_4(aq) + K_3PO_4(aq) \longrightarrow Fe_3(PO_4)_2(s) + K_2SO_4(aq)$
(b) $AgC_2H_3O_2(aq) + AlCl_3(aq) \longrightarrow AgCl(s) + Al(C_2H_3O_2)_3(aq)$

4.60 Write *balanced* ionic and net ionic equations for these reactions.
(a) $Fe(NO_3)_3(aq) + KOH(aq) \longrightarrow KNO_3(aq) + Fe(OH)_3(s)$
(b) $Na_3PO_4(aq) + SrCl_2(aq) \longrightarrow Sr_3(PO_4)_2(s) + NaCl(aq)$

4.61 Aqueous solutions of sodium sulfide and copper(II) nitrate are mixed. A precipitate of copper(II) sulfide forms at once. The solution that remains contains sodium nitrate. Write the molecular, ionic, and net ionic equations for this reaction.

4.62 If an aqueous solution of iron(III) sulfate (a compound used in dyeing textiles and also for etching aluminum) is mixed with a solution of barium chloride, a precipitate of barium sulfate forms and the solution that remains contains iron(III) chloride. Write the molecular, ionic, and net ionic equations for this reaction.

4.63 Use the solubility rules to decide which of the following compounds are *soluble* in water.

(a) $Ca(NO_3)_2$	(d) silver nitrate
(b) $FeCl_2$	(e) barium sulfate
(c) $Ni(OH)_2$	(f) copper(II) carbonate

4.64 Predict which of the following compounds are *soluble* in water.

(a) $HgBr_2$	(d) ammonium phosphate
(b) $Sr(NO_3)_2$	(e) lead(II) iodide
(c) Hg_2Br_2	(f) lead(II) acetate

Acid–Base Neutralization Reactions

4.65 Complete and balance the following equations. For each, write the molecular, ionic, and net ionic equations. (All the products are soluble in water.)
(a) $Ca(OH)_2(aq) + HNO_3(aq) \longrightarrow$
(b) $Al_2O_3(s) + HCl(aq) \longrightarrow$
(c) $Zn(OH)_2(s) + H_2SO_4(aq) \longrightarrow$

4.66 Complete and balance the following equations. For each, write the molecular, ionic, and net ionic equations. (All the products are soluble in water.)
(a) $HC_2H_3O_2(aq) + Mg(OH)_2(s) \longrightarrow$
(b) $HClO_4(aq) + NH_3(aq) \longrightarrow$
(c) $H_2CO_3(aq) + NH_3(aq) \longrightarrow$

4.67 How would the electrical conductivity of a solution of $Ba(OH)_2$ change as a solution of H_2SO_4 is added slowly to it? Use a net ionic equation to justify your answer.

4.68 How would the electrical conductivity of a solution of $HC_2H_3O_2$ change as a solution of NH_3 is added slowly to it? Use a net ionic equation to justify your answer.

Ionic Reactions That Produce Gases

4.69 Write balanced net ionic equations for these reactions:
(a) $HNO_3(aq) + K_2CO_3(aq)$
(b) $Ca(OH)_2(aq) + NH_4NO_3(aq)$

4.70 Write balanced net ionic equations for these reactions:
(a) $H_2SO_4(aq) + NaHSO_3(aq)$
(b) $HNO_3(aq) + (NH_4)_2CO_3(aq)$

Predicting Ionic Reactions

4.71 Explain why the following reactions take place.
(a) $CrCl_3 + 3NaOH \longrightarrow Cr(OH)_3 + 3NaCl$
(b) $ZnO + 2HBr \longrightarrow ZnBr_2 + H_2O$

OH **4.72** Explain why the following reactions take place.
(a) $MnCO_3 + H_2SO_4 \longrightarrow MnSO_4 + H_2O + CO_2$
(b) $Na_2C_2O_4 + 2HNO_3 \longrightarrow 2NaNO_3 + H_2C_2O_4$

4.73 Complete and balance the molecular, ionic, and net ionic equations for the following reactions.
(a) $HNO_3 + Cr(OH)_3 \longrightarrow$
(b) $HClO_4 + NaOH \longrightarrow$
(c) $Cu(OH)_2 + HC_2H_3O_2 \longrightarrow$
(d) $ZnO + H_2SO_4 \longrightarrow$

4.74 Complete and balance molecular, ionic, and net ionic equations for the following reactions.
(a) $NaHSO_3 + HBr \longrightarrow$
(b) $(NH_4)_2CO_3 + NaOH \longrightarrow$
(c) $(NH_4)_2CO_3 + Ba(OH)_2 \longrightarrow$
(d) $FeS + HCl \longrightarrow$

ILW **4.75** Write balanced molecular, ionic, and net ionic equations for the following pairs of reactants. If all ions cancel, indicate that no reaction (N.R.) takes place.
(a) sodium sulfite and barium nitrate
(b) formic acid ($HCHO_2$) and potassium carbonate
(c) ammonium bromide and lead(II) acetate
(d) ammonium perchlorate and copper(II) nitrate

4.76 Write balanced molecular, ionic, and net ionic equations for the following pairs of reactants. If all ions cancel, indicate that no reaction (N.R.) takes place.
(a) ammonium sulfide and sodium hydroxide
(b) chromium(III) sulfate and potassium carbonate
(c) silver nitrate and chromium(III) acetate
(d) strontium hydroxide and magnesium chloride

***4.77** Choose reactants that would yield the following net ionic equations. Write molecular equations for each.
(a) $HCO_3^-(aq) + H^+(aq) \longrightarrow H_2O + CO_2(g)$
(b) $Fe^{2+}(aq) + 2OH^-(aq) \longrightarrow Fe(OH)_2(s)$
(c) $Ba^{2+}(aq) + SO_3^{2-}(aq) \longrightarrow BaSO_3(s)$
(d) $2Ag^+(aq) + S^{2-}(aq) \longrightarrow Ag_2S(s)$
(e) $ZnO(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2O$

***4.78** Suppose that you wished to prepare copper(II) carbonate by a precipitation reaction involving Cu^{2+} and CO_3^{2-}. Which of the following pairs of reactants could you use as solutes?
(a) $Cu(OH)_2 + Na_2CO_3$
(b) $CuSO_4 + (NH_4)_2CO_3$
(c) $Cu(NO_3)_2 + CaCO_3$
(d) $CuCl_2 + K_2CO_3$
(e) $CuS + NiCO_3$

Molar Concentration

OH **4.79** Calculate the molarity of a solution prepared by dissolving
(a) 4.00 g of sodium hydroxide in 100.0 mL of solution
(b) 16.0 g of calcium chloride in 250.0 mL of solution

4.80 Calculate the molarity of a solution that contains
(a) 3.60 g of sulfuric acid in 450.0 mL of solution
(b) 2.0×10^{-3} mol iron(II) nitrate in 12.0 mL of solution

4.81 How many milliliters of 0.265 *M* $NaC_2H_3O_2$ are needed to supply 14.3 g $NaC_2H_3O_2$?

4.82 How many milliliters of 0.615 *M* HNO_3 contain 1.67 g HNO_3?

ILW **4.83** Calculate the number of grams of each solute that has to be taken to make each of the following solutions.
(a) 125 mL of 0.200 *M* NaCl
(b) 250.0 mL of 0.360 *M* $C_6H_{12}O_6$ (glucose)
(c) 250.0 mL of 0.250 *M* H_2SO_4

4.84 How many grams of solute are needed to make each of the following solutions?
(a) 250.0 mL of 0.100 *M* potassium sulfate
(b) 100.0 mL of 0.250 *M* iron(III) chloride
(c) 500.0 mL of 0.400 *M* barium acetate

Dilution of Solutions

4.85 If 25.0 mL of 0.56 *M* H_2SO_4 is diluted to a volume of 125 mL, what is the molarity of the resulting solution?

4.86 A 150 mL sample of 0.45 *M* HNO_3 is diluted to 450 mL. What is the molarity of the resulting solution?

ILW **4.87** To what volume must 25.0 mL of 18.0 *M* H_2SO_4 be diluted to produce 1.50 *M* H_2SO_4?

4.88 To what volume must 50.0 mL of 1.50 *M* HCl be diluted to produce 0.200 *M* HCl?

4.89 How many milliliters of water must be added to 150.0 mL of 2.50 *M* KOH to give a 1.00 *M* solution? (Assume volumes are additive.)

4.90 How many milliliters of water must be added to 120.0 mL of 1.50 *M* HCl to give 1.00 *M* HCl?

Concentrations of Ions in Solutions of Electrolytes

4.91 Calculate the number of moles of each of the ions in the following solutions.
(a) 32.3 mL of 0.45 *M* $CaCl_2$
(b) 50.0 mL of 0.40 *M* $AlCl_3$

4.92 Calculate the number of moles of each of the ions in the following solutions.
(a) 18.5 mL of 0.40 *M* $(NH_4)_2CO_3$
(b) 30.0 mL of 0.35 *M* $Al_2(SO_4)_3$

4.93 Calculate the concentrations of each of the ions in (a) 0.25 *M* $Cr(NO_3)_2$, (b) 0.10 *M* $CuSO_4$, (c) 0.16 *M* Na_3PO_4, and (d) 0.075 *M* $Al_2(SO_4)_3$.

4.94 Calculate the concentrations of each of the ions in (a) 0.060 *M* $Ca(OH)_2$, (b) 0.15 *M* $FeCl_3$, (c) 0.22 *M* $Cr_2(SO_4)_3$, and (d) 0.60 *M* $(NH_4)_2SO_4$.

4.95 In a solution of $Al_2(SO_4)_3$ the Al^{3+} concentration is 0.12 *M*. How many grams of $Al_2(SO_4)_3$ are in 50.0 mL of this solution?

4.96 In a solution of $NiCl_2$, the Cl^- concentration is 0.055 *M*. How many grams of $NiCl_2$ are in 250 mL of this solution?

Solution Stoichiometry

OH **4.97** How many milliliters of 0.25 *M* $NiCl_2$ solution are needed to react completely with 20.0 mL of 0.15 *M* Na_2CO_3 solution? How many grams of $NiCO_3$ will be formed? The reaction is

$$Na_2CO_3(aq) + NiCl_2(aq) \longrightarrow NiCO_3(s) + 2NaCl(aq)$$

4.98 How many milliliters of 0.100 *M* NaOH are needed to completely neutralize 25.0 mL of 0.250 *M* $H_2C_4H_4O_6$? The reaction is

$$2NaOH(aq) + H_2C_4H_4O_6(aq) \longrightarrow Na_2C_4H_4O_6(aq) + 2H_2O$$

4.99 What is the molarity of an aqueous solution of potassium hydroxide if 21.34 mL is exactly neutralized by 20.78 mL of 0.116 *M* HCl? Write and balance the molecular equation for the reaction.

4.100 What is the molarity of an aqueous phosphoric acid solution if 12.88 mL is completely neutralized by 26.04 mL of 0.1024 *M* NaOH? Write and balance the molecular equation for the reaction.

4.101 Aluminum sulfate, $Al_2(SO_4)_3$, is used in water treatment to remove fine particles suspended in the water. When made basic, a gel-like precipitate forms that removes the fine particles as it settles. In an experiment, a student planned to react $Al_2(SO_4)_3$ with $Ba(OH)_2$. How many grams of $Al_2(SO_4)_3$ are needed to react with 85.0 mL of 0.0500 *M* $Ba(OH)_2$?

4.102 How many grams of baking soda, $NaHCO_3$, are needed to react with 162 mL of stomach acid having an HCl concentration of 0.052 *M*?

4.103 How many milliliters of 0.150 *M* $FeCl_3$ solution are needed to react completely with 20.0 mL of 0.0450 *M* $AgNO_3$ solution? How many grams of AgCl will be formed? The net ionic equation for the reaction is

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

4.104 How many grams of cobalt(II) chloride are needed to react completely with 60.0 mL of 0.200 *M* KOH solution? The net ionic equation for the reaction is

$$Co^{2+}(aq) + 2OH^-(aq) \longrightarrow Co(OH)_2(s)$$

ILW **4.105** Consider the reaction of aluminum chloride with silver acetate. How many milliliters of 0.250 *M* aluminum chloride would be needed to react completely with 20.0 mL of 0.500 *M* silver acetate solution? The net ionic equation for the reaction is

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

4.106 How many milliliters of ammonium sulfate solution having a concentration of 0.250 *M* are needed to react completely with 50.0 mL of 1.00 *M* sodium hydroxide solution? The net ionic equation for the reaction is

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

***4.107** Suppose that 4.00 g of solid Fe_2O_3 is added to 25.0 mL of 0.500 *M* HCl solution. What will the concentration of the Fe^{3+} be when all the HCl has reacted? What mass of Fe_2O_3 will not have reacted?

***4.108** Suppose 3.50 g of solid $Mg(OH)_2$ is added to 30.0 mL of 0.500 *M* H_2SO_4 solution. What will the concentration of Mg^{2+} be when all of the acid has been neutralized? How many grams of $Mg(OH)_2$ will not have dissolved?

***4.109** Suppose that 25.0 mL of 0.440 *M* NaCl is added to 25.0 mL of 0.320 *M* $AgNO_3$.
(a) How many moles of AgCl would precipitate?
(b) What would be the concentrations of each of the ions in the reaction mixture after the reaction?

***4.110** A mixture is prepared by adding 25.0 mL of 0.185 *M* Na_3PO_4 to 34.0 mL of 0.140 *M* $Ca(NO_3)_2$.
(a) What mass of $Ca_3(PO_4)_2$ will be formed?
(b) What will be the concentrations of each of the ions in the mixture after the reaction?

Titrations and Chemical Analyses

4.111 In a titration, 23.25 mL of 0.105 *M* NaOH was needed to react with 21.45 mL of HCl solution. What is the molarity of the acid?

4.112 A 12.5 mL sample of vinegar, containing acetic acid, was titrated using 0.504 *M* NaOH solution. The titration required 20.65 mL of the base.
(a) What was the molar concentration of acetic acid in the vinegar?
(b) Assuming the density of the vinegar to be 1.0 g mL^{-1}, what was the percentage (by mass) of acetic acid in the vinegar?

ILW **OH** **4.113** Lactic acid, $HC_3H_5O_3$, is a monoprotic acid that forms when milk sours. An 18.5 mL sample of a solution of lactic acid required 17.25 mL of 0.155 *M* NaOH to reach an end point in a titration. How many moles of lactic acid were in the sample?

4.114 Ascorbic acid (vitamin C) is a diprotic acid having the formula $H_2C_6H_6O_6$. A sample of a vitamin supplement was analyzed by titrating a 0.1000 g sample dissolved in water with 0.0200 *M* NaOH. A volume of 15.20 mL of the base was required to completely neutralize the ascorbic acid. What was the percentage by mass of ascorbic acid in the sample?

4.115 Magnesium sulfate forms a hydrate known as *Epsom salts*. A student dissolved 1.24 g of this hydrate in water and added a barium chloride solution until the precipitation reaction was complete. The precipitate was filtered, dried, and found to weigh 1.174 g. Determine the formula for Epsom salts.

4.116 A sample of iron chloride weighing 0.300 g was dissolved in water and the solution was treated with $AgNO_3$ solution to precipitate the chloride as AgCl. After precipitation was complete, the AgCl was filtered, dried, and found to weigh 0.678 g. Determine the empirical formula of the iron chloride.

4.117 A certain lead ore contains the compound $PbCO_3$. A sample of the ore weighing 1.526 g was treated with nitric acid, which dissolved the $PbCO_3$. The resulting solution was filtered from undissolved rock and required 29.22 mL of 0.122 *M* Na_2SO_4 to completely precipitate all the lead as $PbSO_4$. What is the percentage by mass of lead in the ore?

4.118 An ore of barium contains $BaCO_3$. A 1.542 g sample of the ore was treated with HCl to dissolve the $BaCO_3$. The resulting solution was filtered to remove insoluble material and then treated with H_2SO_4 to precipitate $BaSO_4$. The precipitate was filtered, dried, and found to weigh 1.159 g. What is the percentage by mass of barium in the ore? (Assume all the barium is precipitated as $BaSO_4$.)

4.119 To a mixture of NaCl and Na_2CO_3 with a mass of 1.243 g was added 50.00 mL of 0.240 *M* HCl (an excess of HCl). The mixture was warmed to expel all of the CO_2 and then the unreacted HCl was titrated with 0.100 *M* NaOH. The titration required 22.90 mL of the NaOH solution. What was the percentage by mass of NaCl in the original mixture of NaCl and Na_2CO_3?

4.120 A mixture was known to contain both KNO_3 and K_2SO_3. To 0.486 g of the mixture, dissolved in enough water to give 50.00 mL of solution, was added 50.00 mL of 0.150 *M* HCl (an excess of HCl). The reaction mixture was heated to drive off all of the SO_2, and then 25.00 mL of the reaction mixture was titrated with 0.100 *M* KOH. The titration required 13.11 mL of the KOH solution to reach an end point. What was the percentage by mass of K_2SO_3 in the original mixture of KNO_3 and K_2SO_3?

ADDITIONAL EXERCISES

4.121 Classify each of the following as a strong electrolyte, weak electrolyte, or nonelectrolyte.

(a) KCl
(b) $C_3H_5(OH)_3$ (glycerin)
(c) NaOH
(d) $C_{12}H_{22}O_{11}$ (sucrose, or table sugar)
(e) $HC_2H_3O_2$ (acetic acid)
(f) CH_3OH (methyl alcohol)
(g) H_2SO_4
(h) NH_3

OH **4.122** Complete the following and write molecular, ionic, and net ionic equations. State whether a net reaction occurs in each case.

(a) $CaCO_3 + HNO_3 \longrightarrow$
(b) $CaCO_3 + H_2SO_4 \longrightarrow$
(c) $FeS + HBr \longrightarrow$
(d) $KOH + SnCl_2 \longrightarrow$

OH ***4.123** Aspirin is a monoprotic acid called acetylsalicylic acid. Its formula is $HC_9H_7O_4$. A certain pain reliever was analyzed for aspirin by dissolving 0.250 g of it in water and titrating it with 0.0300 *M* KOH solution. The titration required 29.40 mL of base. What is the percentage by weight of aspirin in the drug?

***4.124** In an experiment, 40.0 mL of 0.270 *M* barium hydroxide was mixed with 25.0 mL of 0.330 *M* aluminum sulfate.

(a) Write the net ionic equation for the reaction that takes place.
(b) What is the total mass of precipitate that forms?
(c) What are the molar concentrations of the ions that remain in the solution after the reaction is complete?

***4.125** Qualitative analysis of an unknown acid found only carbon, hydrogen, and oxygen. In a quantitative analysis, a 10.46 mg sample was burned in oxygen and gave 22.17 mg CO_2 and 3.40 mg H_2O. The molecular mass was determined to be 166 g mol^{-1}. When a 0.1680 g sample of the acid was titrated with 0.1250 *M* NaOH, the end point was reached after 16.18 mL of the base had been added.

(a) Calculate the percentage composition of the acid.
(b) What is its empirical formula?
(c) What is its molecular formula?
(d) Is the acid mono-, di-, or triprotic?

***4.126** How many milliliters of 0.10 *M* HCl must be added to 50.0 mL of 0.40 *M* HCl to give a final solution that has a molarity of 0.25 *M*?

EXERCISES IN CRITICAL THINKING

4.127 Compare the advantages and disadvantages of performing a titration using the mass of the sample and titrant rather than the volume.

4.128 What kinds of experiments could you perform to measure the solubility of a substance in water? Describe the procedure you would use and the measurements you would make. What factors would limit the precision of your measurements?

4.129 Describe experiments, both qualitative and quantitative, that you could perform to show that lead chloride is more soluble in water than lead iodide.

4.130 How could you check the accuracy of a 100 mL volumetric flask?

4.131 Suppose a classmate doubted that an equilibrium really exists between acetic acid and its ions in an aqueous solution. What argument would you use to convince that person that such an equilibrium does exist?

4.132 When Arrhenius originally proposed that ions exist in solution, his idea was not well received. Propose another explanation for the conduction of electricity in molten salts and aqueous salt solutions.

4.133 Carbon dioxide is one obvious contributor to excessive global warming. What is your plan for controlling CO_2 emissions? What are the advantages and disadvantages of your plan?