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

4.1 Special terminology applies to solutions
4.2 Ionic compounds conduct electricity when dissolved in water
4.3 Acids and bases are classes of compounds with special properties
4.4 Naming acids and bases follows a system
4.5 Ionic reactions can often be predicted
4.6 The composition of a solution is described by its concentration
4.7 Molarity is used for problems in solution stoichiometry
4.8 Chemical analysis and titration are applications of solution stoichiometry
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. 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.

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

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 4.2a for a solution of copper sulfate, CuSO₄.

Solutes such as CuSO₄, 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

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.

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.)

FIG. 4.2 Electrical conductivity of solutions of electrolytes versus nonelectrolytes. (a) The copper sulfate solution is a strong conductor of electricity, and CuSO₄ is a strong electrolyte. (b) Neither sugar nor water is an electrolyte, and this sugar solution is a nonconductor. (Michael Watson.)
Keep in mind that a strong electrolyte is 100% dissociated in an aqueous solution.

Ethylene glycol, C\(_2\)H\(_4\)(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

\[
\text{CaCl}_2(\text{s}) \rightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{Cl}^- (\text{aq})
\]

We use the symbol \( \text{aq} \) 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 \( \text{CaCl}_2(\text{s}) \) releases three ions, one \( \text{Ca}^{2+}(\text{aq}) \) and two \( \text{Cl}^- (\text{aq}) \).

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

\[
\text{CaCl}_2 \rightarrow \text{Ca}^{2+} + 2\text{Cl}^-
\]

Polyatomic ions generally remain intact as dissociation occurs. When copper sulfate dissolves, for example, both \( \text{Cu}^{2+} \) and \( \text{SO}_4^{2-} \) ions are released.

\[
\text{CuSO}_4(\text{s}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})
\]
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 \( \text{NH}_4^+ \) (ammonium ion) and the anion is \( \text{SO}_4^{2-} \) (sulfate ion). The correct formula of the compound is therefore \((\text{NH}_4)_2\text{SO}_4\), which means there are two \( \text{NH}_4^+ \) ions for each \( \text{SO}_4^{2-} \) 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.

\[
(\text{NH}_4)_2\text{SO}_4(s) \rightarrow 2\text{NH}_4^+(aq) + \text{SO}_4^{2-}(aq)
\]

The subscript 2 becomes the coefficient for \( \text{NH}_4^+ \).

**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.

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**Example 4.1**

**Writing the Equation for the Dissociation of an Ionic Compound**

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**Practice Exercise 1:** Write equations that show the dissociation of the following compounds in water: (a) FeCl₃ 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) MgCl₂, (b) Al(NO₃)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, \( \text{Pb(NO}_3)_2 \), and potassium iodide, \( \text{KI} \), are mixed, a bright yellow precipitate of lead iodide, \( \text{PbI}_2 \), forms (Figure 4.4). The chemical equation for the reaction is

\[
\text{Pb(NO}_3)_2(aq) + 2\text{KI}(aq) \rightarrow \text{PbI}_2(s) + 2\text{KNO}_3(aq)
\]

where we have noted the insolubility of \( \text{PbI}_2 \) 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 \( \text{Pb(NO}_3)_2 \), \( \text{KI} \), and \( \text{KNO}_3 \) 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.

\[
\text{Pb(NO}_3)_2(aq) + 2\text{KI}(aq) \rightarrow \text{PbI}_2(s) + 2\text{KNO}_3(aq)
\]

\[
\text{Pb}^{2+}(aq) + 2\text{NO}_3^-(aq) + 2\text{K}^+(aq) + 2\text{I}^-(aq) \rightarrow \text{PbI}_2(s) + 2\text{K}^+(aq) + 2\text{NO}_3^-(aq)
\]
Notice that we have not separated PbI₂ into its ions in this equation. This is because PbI₂ has an extremely low solubility in water; it is essentially insoluble. When the Pb²⁺ and I⁻ ions meet in the solution, insoluble PbI₂ forms and separates as a precipitate. Therefore, after the reaction is over, the Pb²⁺ 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 Pb²⁺ and I⁻ ions come together to form the precipitate, while the other ions, K⁺ and NO₃⁻, 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 NO₃⁻.

\[
Pb^{2+}(aq) + 2NO_3^-(aq) + 2K^+(aq) + 2I^-(aq) \rightarrow PbI_2(s) + 2K^+(aq) + 2NO_3^-(aq)
\]

What remains is the net ionic equation,

\[
Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)
\]

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

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, Na\(C_{18}H_{35}O_2\). 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\(_2\)CO\(_3\)·10H\(_2\)O, often called washing soda, to the water. The carbonate ion forms insoluble precipitates with the hardness ions; an example is CaCO\(_3\).

\[
Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)
\]

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

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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 water pipes. When solutions containing HCO\(_3^-\) are heated, the ion decomposes as follows.

\[
2HCO_3^-(aq) \rightarrow H_2O + CO_2(g) + CO_3^{2-}(aq)
\]

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.)
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.

**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

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>lead acetate</td>
<td>Pb(C₂H₃O₂)₂</td>
</tr>
<tr>
<td>NaI</td>
<td>NaC₂H₃O₂</td>
</tr>
</tbody>
</table>

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.

\[ \text{Pb(C}_2\text{H}_3\text{O}_2)_2(aq) + 2\text{NaI(aq)} \rightarrow \text{PbI}_2(s) + 2\text{NaC}_2\text{H}_3\text{O}_2(aq) \]

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.

\[ \text{Pb}^{2+}(aq) + 2\text{C}_2\text{H}_3\text{O}_2^-(aq) + 2\text{Na}^+(aq) + 2\text{I}^- (aq) \rightarrow \text{PbI}_2(s) + 2\text{Na}^+(aq) + 2\text{C}_2\text{H}_3\text{O}_2^-(aq) \]

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 C₂H₃O₂⁻ (they're the same on both sides of the arrow). Let's cross them out.

\[ \text{Pb}^{2+}(aq) + 2\text{C}_2\text{H}_3\text{O}_2^-(aq) + 2\text{Na}^+(aq) + 2\text{I}^- (aq) \rightarrow \text{PbI}_2(s) + 2\text{Na}^+(aq) + 2\text{C}_2\text{H}_3\text{O}_2^-(aq) \]

What's left is the net ionic equation.

\[ \text{Pb}^{2+}(aq) + 2\text{I}^- (aq) \rightarrow \text{PbI}_2(s) \]

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.
4.3 Acids and Bases Are Classes of Compounds with Special Properties

Acids and bases are 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.

Practice Exercise 3: When solutions of \((\text{NH}_4)_2\text{SO}_4\) and \(\text{Ba(NO}_3)_2\) are mixed, a precipitate of \(\text{BaSO}_4\) forms, leaving soluble \(\text{NH}_4\text{NO}_3\) 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.

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 \((\text{Pb}^{2+}, 2\text{NO}_3^–, 2\text{K}^+, \text{and } 2\text{I}^–)\) is zero, which matches the sum of the charges on all of the formulas of the products \((\text{PbI}_2, 2\text{K}^+, \text{and } 2\text{NO}_3^–)\). In the net ionic equation the charges on both sides are also the same: on the left we have \(\text{Pb}^{2+} \text{ and } 2\text{I}^–\), with a net charge of zero, and on the right we have \(\text{PbI}_2\), 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).

4.3 Acids and Bases Are Classes of Compounds with Special Properties

Acids and bases are classes 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.

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, \(\text{HCl}(aq)\), and the base sodium hydroxide, \(\text{NaOH}(aq)\), are mixed the following reaction occurs.

\[
\text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}
\]

*There is no charge written for the formula of a compound such as \(\text{PbI}_2\), so as we add up charges, we take the charge on \(\text{PbI}_2\) to be zero.

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.
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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, a Swedish chemist, was the first to suggest that an acid–base neutralization is simply the combination of a hydrogen ion with a hydronium 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, H₃O⁺. 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 H₃O⁺(aq). In fact, whenever you see the symbol H⁺(aq), you should realize that we are actually referring to H₃O⁺(aq).

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, H₃O⁺.
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, O²⁻. (Ionic compounds that contain OH⁻ or O²⁻ are bases, as described below.)

In aqueous solutions, acids give H₃O⁺

In general, acids are molecular substances that react with water to produce ions, one of which is the hydronium ion, H₃O⁺. 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

\[
\text{HCl}(g) + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+(aq) + \text{Cl}^-(aq)
\]

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 H₃O⁺. An example is acetic acid, HC₂H₃O₂, the acid that gives vinegar its sour taste. This acid reacts with water as follows.

\[
\text{HC}_2\text{H}_3\text{O}_2(aq) + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+(aq) + \text{C}_2\text{H}_3\text{O}_2^-(aq)
\]

**Fig. 4.7 Ionization of HCl in water.** Collisions between HCl molecules and water molecules lead to a transfer of H⁺ from HCl to H₂O, giving Cl⁻ and H₃O⁺ as products.

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*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.*
Phosphoric acid, $\text{H}_3\text{PO}_4$, 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 $\text{H}_3\text{PO}_4$ 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.

\[ \text{H}_3\text{PO}_4 \rightarrow \text{H}_2\text{PO}_4^- \rightarrow \text{HPO}_4^{2-} \rightarrow \text{PO}_4^{3-} \]

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\(_3\)PO\(_4\) with water to give H\(_2\)O\(^+\) and H\(_2\)PO\(_4^-\).

\[ \text{H}_3\text{PO}_4(aq) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+(aq) + \text{H}_2\text{PO}_4^-(aq) \]

The second and third steps are similar to the first.

\[ \text{H}_2\text{PO}_4^-(aq) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+(aq) + \text{HPO}_4^{2-}(aq) \]

\[ \text{HPO}_4^{2-}(aq) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+(aq) + \text{PO}_4^{3-}(aq) \]

**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\(_3\)C\(_6\)H\(_5\)O\(_7\), 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\(_2\)O\(_5\) whose aqueous solutions contain H\(_3\)O\(^+\) 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\(_3\)O\(^+\).

\[
\begin{align*}
\text{SO}_3(g) + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{SO}_4(aq) & \text{sulfuric acid} \\
\text{N}_2\text{O}_5(g) + \text{H}_2\text{O} & \rightarrow 2\text{HNO}_3(aq) & \text{nitric acid} \\
\text{CO}_2(g) + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{CO}_3(aq) & \text{carbonic acid}
\end{align*}
\]

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.
4.3 Acids and Bases Are Classes of Compounds with Special Properties

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.

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

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.

$$\text{CaO}(s) + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2(aq)$$

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$^-$.

$$\text{O}^{2-} + \text{H}_2\text{O} \rightarrow 2\text{OH}^-$$

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.

$$\text{NH}_3(aq) + \text{H}_2\text{O} \rightarrow \text{NH}_4^+(aq) + \text{OH}^-(aq)$$

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$_3$NH$_2$, in which a methyl group, CH$_3$, replaces a hydrogen in ammonia.

$$\text{CH}_3\text{NH}_2(aq) + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{NH}_3^+(aq) + \text{OH}^-(aq)$$

The hydrogen taken from the H$_2$O 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

$$\text{base} + \text{H}_2\text{O} \rightarrow \text{baseH}^+ + \text{OH}^-$$

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

$$B + \text{H}_2\text{O} \rightarrow B\text{H}^+ + \text{OH}^- \quad (4.3)$$

![FIG. 4.9 Ionization of ammonia in water](Image)

Collisions between NH$_3$ molecules and water molecules lead to a transfer of H$^+$ from H$_2$O to NH$_3$, giving NH$_4^+$ and OH$^-$ ions.
Dimethylamine, \((\text{CH}_3)_2\text{NH}\), 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 \((\text{CH}_3)_2\text{NH}\) and \(\text{H}_2\text{O}\). To write the equation, we need to know the formulas of the products. We’ve been told that \((\text{CH}_3)_2\text{NH}\) 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 \(\text{H}^+\) from \(\text{H}_2\text{O}\), leaving \(\text{OH}^-\) behind. Therefore, when an \(\text{H}^+\) is picked up by \((\text{CH}_3)_2\text{NH}\), the product will be \((\text{CH}_3)_2\text{NH}_2^+\). The equation for the reaction is

\[
(\text{CH}_3)_2\text{NH}(aq) + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_2\text{NH}_2^+(aq) + \text{OH}^- (aq)
\]

**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 \(\text{H}\) and a positive charge, and that the \(\text{H}^+\) has been added to the nitrogen. Also, notice that the water has become \(\text{OH}^-\) when it loses \(\text{H}^+\). The equation is therefore correct.

**Practice Exercise 7:** Triethylamine, \((\text{C}_2\text{H}_5)_3\text{N}\), 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, \(\text{HONH}_2\), 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 \(\text{NaCl}\) and \(\text{CaCl}_2\) break up essentially 100% into ions in water. No “molecules” of either \(\text{NaCl}\) or \(\text{CaCl}_2\) 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**.

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.

**Strong Acids**

- \(\text{HClO}_4(aq)\) perchloric acid
- \(\text{HCl}(aq)\) hydrochloric acid
- \(\text{HBr}(aq)\) hydrobromic acid
- \(\text{HI}(aq)\) hydroiodic acid\(^5\)
- \(\text{HNO}_3(aq)\) nitric acid
- \(\text{H}_2\text{SO}_4(aq)\) sulfuric acid

Metal hydroxides are ionic compounds, so they are also strong electrolytes. Those that are soluble are the hydroxides of Group I A 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.

\(^5\) Sometimes the first “o” in the name of \(\text{HI}(aq)\) is dropped for ease of pronunciation to give **hydriodic acid**.
4.3 Acids and Bases Are Classes of Compounds with Special Properties

Cl– Cl– Cl– Cl– Cl– Cl– Cl–

OH– OH–

H3O+ H3O+ H3O+ H3O+ H3O+ H3O+ H3O+

HC2H3O2

NH4+ NH4+ NH3

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 HC2H3O2.

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 NH3.

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) HC2H3O2 is a weaker conductor than HCl because the extent of its ionization is far less, so the light is dimmer. (c) NH3 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, HC2H3O2, 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 H3O+ and C2H3O2− ions. The rest is present as molecules of HC2H3O2. This is because C2H3O2− ions have a strong tendency to react with H3O+ 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,

\[ \text{HC}_2\text{H}_3\text{O}_2(aq) + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+(aq) + \text{C}_2\text{H}_3\text{O}_2^-(aq) \]

and the other removes ions

\[ \text{H}_3\text{O}^+(aq) + \text{C}_2\text{H}_3\text{O}_2^-(aq) \rightarrow \text{HC}_2\text{H}_3\text{O}_2(aq) + \text{H}_2\text{O} \]

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 HC2H3O2 is ionized.
Chapter 4 Reactions of Ions and Molecules in Aqueous Solutions

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, \( \iff \). For acetic acid, we write

\[
\text{HC}_2\text{H}_3\text{O}_2(aq) + \text{H}_2\text{O} \iff \text{H}_3\text{O}^+(aq) + \text{C}_2\text{H}_3\text{O}_2^-(aq)
\]

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 4.10c.) In a solution of ammonia, only a small fraction of the solute is ionized to give \( \text{NH}_4^+ \) and \( \text{OH}^- \) because the ions have a strong tendency to react with each other. This leads to the dynamic equilibrium (Figure 4.12)

\[
\text{NH}_3(aq) + \text{H}_2\text{O} \iff \text{NH}_4^+(aq) + \text{OH}^-(aq)
\]

in which most of the base is present as \( \text{NH}_3 \) 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.
4.4 Naming Acids and Bases Follows a System

An ammonia molecule collides with a water molecule. The collision produces an ammonium ion and a hydroxide ion.

Ammonium ion collides with a hydroxide ion. The collision produces an ammonia molecule and a water molecule.

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 H₂O⁺ to react to form molecules of HCl and H₂O. 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, CH₃NH₂ (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, HNO₂, is a weak acid thought to be responsible for certain cancers of the intestinal system. Write the chemical equation that shows that HNO₂ 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 H₂S. 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:

<table>
<thead>
<tr>
<th>Name of the molecular compound</th>
<th>Name of the binary acid in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl(g) hydrogen chloride</td>
<td>HCl(aq) hydrochloric acid</td>
</tr>
<tr>
<td>H₂S(g) hydrogen sulfide</td>
<td>H₂S(aq) hydrosulfuric acid</td>
</tr>
</tbody>
</table>

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.
Bromine forms four oxoacids, similar to those of chlorine. What is the name of the acid HBrO₂ and what is the name of the salt NaBrO₃?

**ANALYSIS AND SOLUTION:**

Let’s review the acids formed by chlorine and then reason by analogy. For chlorine we have:

- HClO₄ perchloric acid
- HClO₂ chlorous acid
- HClO₃ chloric acid
- HClO hypochlorous acid

The acid HBrO₂ 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 HBrO₂ is bromous acid.

To find the name of NaBrO₃, 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 NaBrO₃ would be obtained by neutralizing the acid HBrO₃. This acid has one more oxygen than bromous acid, HBrO₂, so it would have the ending -ic. Thus, HBrO₃ 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 BrO₃⁻ is the bromate ion. Therefore, the salt NaBrO₃ is sodium bromate.

**ARE THE ANSWERS REASONABLE?**

There’s really not much we can do to check the answers here. For the salt, if HClO₃ is chloric acid, then it seems reasonable that HBrO₃ would be bromic acid, which would mean that BrO₃⁻ is the bromate ion and NaBrO₃ is sodium bromate.
4.4 Naming Acids and Bases Follows a System

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.)

Practice Exercise 11: The formula for arsenic acid is H₃AsO₄. What is the name of the salt Na₃AsO₄? (Hint: Recall how the name of the anion is related to the name of the acid.)

Practice Exercise 12: Formic acid is HCHO₂. What is the name of the salt Ca(CHO₂)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.

Acid salts can be formed by polyprotic acids
Monoprotic acids such as HCl and H₂C₂H₃O₂ 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 H₂SO₄ gives the HSO₄⁻ ion, which forms salts such as NaHSO₄. This compound is called an acid salt because its anion, HSO₄⁻, is capable of furnishing additional H⁺.

In naming ions such as HSO₄⁻, we specify the number of hydrogens that can still be neutralized if the anion were to be treated with additional base. Thus, HSO₄⁻ is called the hydrogen sulfate ion; it's the active ingredient in Sani-Flush (Figure 4.13). Similarly, H₂PO₄⁻ is named as the dihydrogen phosphate ion. These anions give the following salts with Na⁺:

- NaHSO₄ sodium hydrogen sulfate
- NaH₂PO₄ sodium dihydrogen phosphate

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

- NaHCO₃ 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 O₂⁻, such as NaOH and Na₂O, are ionic and are named just like any other ionic compound. Thus, NaOH is sodium hydroxide and Na₂O is sodium oxide.

Molecular bases such as NH₃ (ammonia) and CH₃NH₂ (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.

⁶Solutions of ammonia are sometimes called ammonium hydroxide, although there is no evidence that the species NH₄OH actually exists.
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!

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(NO₃)₂ and KI,

\[
Pb(NO₃)₂(aq) + 2KI(aq) \rightarrow PbI₂(s) + 2KNO₃(aq)
\]

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, PbI₂ and KNO₃, the I⁻ replaces NO₃⁻ in the lead compound and NO₃⁻ replaces I⁻ in the potassium compound.) Metathesis reactions in which a precipitate forms are sometimes called precipitation reactions.

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 Ca²⁺, C₂O₄²⁻, and PO₄³⁻ 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.)
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

$$\text{Fe}_2(\text{SO}_4)_3 + \text{Pb(NO}_3)_2 \rightarrow$$

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.

**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$_3$PO$_4$, 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.

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

<table>
<thead>
<tr>
<th>Soluble Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. All compounds of the alkali metals (Group IA) are soluble.</td>
</tr>
<tr>
<td>2. All salts containing NH$_4^+$, NO$_3^-$, ClO$_4^-$, ClO$_3^-$, and C$_2$H$_3$O$_2^-$ are soluble.</td>
</tr>
<tr>
<td>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”).</td>
</tr>
<tr>
<td>4. All sulfates (salts containing SO$_4^{2-}$) are soluble except those of Pb$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Hg$_2^{2+}$, and Ba$^{2+}$.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Insoluble Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>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$^{2+}$.</td>
</tr>
<tr>
<td>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$_4^+$.</td>
</tr>
</tbody>
</table>

Insoluble Compounds

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

$$\text{Na}_2\text{O}(s) + \text{H}_2\text{O} \rightarrow 2\text{NaOH}(aq)$$
Chapter 4 Reactions of Ions and Molecules in Aqueous Solutions

**SOLUTION:** The reactants, Pb(NO₃)₂ and Fe₂(SO₄)₃, contain the ions Pb²⁺ and NO₃⁻, and Fe³⁺ and SO₄²⁻, respectively. To write the formulas of the products, we interchange anions. We combine Pb²⁺ with SO₄²⁻, and for electrical neutrality, we must use one ion of each. Therefore, we write PbSO₄ as one possible product. For the other product, we combine Fe³⁺ with NO₃⁻. Electrical neutrality now demands that we use three NO₃⁻ to one Fe³⁺ to make Fe(NO₃)₃. The correct formulas of the products, then, are PbSO₄ and Fe(NO₃)₃. The unbalanced molecular equation at this point is

Fe₂(SO₄)₃ + Pb(NO₃)₂ → Fe(NO₃)₃ + PbSO₄ (unbalanced)

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(NO₃)₃ is soluble; Rule 4 tells us that the sulfate of Pb²⁺ is insoluble. This means that a precipitate of PbSO₄ will form. Writing (aq) and (s) following appropriate formulas, the unbalanced molecular equation is

Fe₂(SO₄)₃(aq) + Pb(NO₃)₂(aq) → Fe(NO₃)₃(aq) + PbSO₄(s) (unbalanced)

When balanced, we obtain the molecular equation.

Fe₂(SO₄)₃(aq) + 3Pb(NO₃)₂(aq) → 2Fe(NO₃)₃(aq) + 3PbSO₄(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.

2Fe³⁺(aq) + 3SO₄²⁻(aq) + 3Pb²⁺(aq) + 6NO₃⁻(aq) → 2Fe³⁺(aq) + 6NO₃⁻(aq) + 3PbSO₄(s)

By removing spectator ions (Fe³⁺ and NO₃⁻), we obtain

3Pb²⁺(aq) + 3SO₄²⁻(aq) → 3PbSO₄(s)

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

Pb²⁺(aq) + SO₄²⁻(aq) → PbSO₄(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(SO₄)₂ and Fe₂(NO₃)₃, or even Pb(SO₄)₂ and Fe₂(NO₃)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(NO₃)₂ and Ca(C₂H₃O₂)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) AgNO₃ and NH₄Cl, (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.

\[ \text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O} \]

Writing this as an ionic equation gives

\[ \text{H}^+(aq) + \text{Cl}^-(aq) + \text{Na}^+(aq) + \text{OH}^-(aq) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq) + \text{H}_2\text{O} \]

where we have used H\(^+\) as shorthand for H\(_3\)O\(^+\). The net ionic equation is obtained by removing spectator ions.

\[ \text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O} \]

In this case, a net ionic equation exists because of the formation of a very weak electrolyte, H\(_2\)O, 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:*

\[ \text{HC}_2\text{H}_3\text{O}_2(aq) + \text{NaOH}(aq) \rightarrow \text{NaC}_2\text{H}_3\text{O}_2(aq) + \text{H}_2\text{O} \]

*Net ionic equation:*

\[ \text{HC}_2\text{H}_3\text{O}_2(aq) + \text{OH}^-(aq) \rightarrow \text{C}_2\text{H}_3\text{O}_2^- (aq) + \text{H}_2\text{O} \]

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:*

\[ 2\text{HCl}(aq) + \text{Mg(OH)}_2(s) \rightarrow \text{MgCl}_2(aq) + 2\text{H}_2\text{O} \]

*Net ionic equation:*

\[ 2\text{H}^+(aq) + \text{Mg(OH)}_2(s) \rightarrow \text{Mg}^{2+}(aq) + 2\text{H}_2\text{O} \]

**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.)
Chapter 4 Reactions of Ions and Molecules in Aqueous Solutions

Reaction of a weak acid with an insoluble base

Molecular equation:

$$2\text{HC}_2\text{H}_3\text{O}_2(aq) + \text{Mg(OH)}_2(s) \rightarrow \text{Mg(C}_2\text{H}_3\text{O}_2)_2(aq) + 2\text{H}_2\text{O}$$

Net ionic equation:

$$2\text{HC}_2\text{H}_3\text{O}_2(aq) + \text{Mg(OH)}_2(s) \rightarrow \text{Mg}^{2+}(aq) + 2\text{C}_2\text{H}_3\text{O}_2^- (aq) + 2\text{H}_2\text{O}$$

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:

$$\text{HCl(aq)} + \text{NH}_3(aq) \rightarrow \text{NH}_4\text{Cl(aq)}$$

Net ionic equation (using $\text{H}^+$ as shorthand for $\text{H}_3\text{O}^+$):

$$\text{H}^+(aq) + \text{NH}_3(aq) \rightarrow \text{NH}_4^+(aq)$$

Figure 4.16 depicts the transfer of $\text{H}^+$ from $\text{H}_3\text{O}^+$ to $\text{NH}_3$.

With a weak acid such as $\text{HC}_2\text{H}_3\text{O}_2$, we have

Molecular equation:

$$\text{HC}_2\text{H}_3\text{O}_2(aq) + \text{NH}_3(aq) \rightarrow \text{NH}_4\text{C}_2\text{H}_3\text{O}_2(aq)$$

Ionic and net ionic equation:

$$\text{HC}_2\text{H}_3\text{O}_2(aq) + \text{NH}_3(aq) \rightarrow \text{NH}_4^+(aq) + \text{C}_2\text{H}_3\text{O}_2^-(aq)$$

Even though solutions of $\text{HC}_2\text{H}_3\text{O}_2$ contain some $\text{H}^+$, and solutions of $\text{NH}_3$ contain some $\text{OH}^-$, 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 $\text{HNO}_3(aq)$ by $\text{Ca(OH)}_2(aq)$. (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$_2$H$_4$ with HCl.

Practice Exercise 20: Write molecular, ionic, and net ionic equations for the reaction of the weak base methylamine, CH$_3$NH$_2$, with formic acid, HCHO$_2$ (a weak acid).
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 NaHCO₃ both neutralizes the acid and produces CO₂ gas (burp!). The molecular equation for the metathesis reaction is

\[ \text{HCl(aq)} + \text{NaHCO}_3(aq) \rightarrow \text{NaCl(aq)} + \text{H}_2\text{CO}_3(aq) \]

Carbonic acid, H₂CO₃, 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 CO₂) and water. Carbon dioxide is only slightly soluble in water, so most of the CO₂ bubbles out of the solution. The decomposition reaction is

\[ \text{H}_2\text{CO}_3(aq) \rightarrow \text{H}_2\text{O} + \text{CO}_2(g) \]

Therefore, the overall molecular equation for the reaction is

\[ \text{HCl(aq)} + \text{NaHCO}_3(aq) \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O} + \text{CO}_2(g) \]

The ionic equation is

\[ \text{H}^+(aq) + \text{Cl}^-(aq) + \text{Na}^+(aq) + \text{HCO}_3^-(aq) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq) + \text{H}_2\text{O} + \text{CO}_2(g) \]

and the net ionic equation is

\[ \text{H}^+(aq) + \text{HCO}_3^-(aq) \rightarrow \text{H}_2\text{O} + \text{CO}_2(g) \]

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 H₂CO₃, which subsequently decomposes to water and CO₂:

\[ 2\text{H}^+(aq) + \text{CO}_3^{2-}(aq) \rightarrow \text{H}_2\text{CO}_3(aq) \rightarrow \text{H}_2\text{O} + \text{CO}_2(g) \]

The net reaction is

\[ 2\text{H}^+(aq) + \text{CO}_3^{2-}(aq) \rightarrow \text{H}_2\text{O} + \text{CO}_2(g) \]

The release of CO₂ 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, CaCO₃, with hydrochloric acid is shown in Figure 4.19.

The molecular and net ionic equations for the reaction are as follows:

\[ \text{CaCO}_3(s) + 2\text{HCl(aq)} \rightarrow \text{CaCl}_2(aq) + \text{CO}_2(g) + \text{H}_2\text{O} \]
\[ \text{CaCO}_3(s) + 2\text{H}^+(aq) \rightarrow \text{Ca}^{2+}(aq) + \text{CO}_2(g) + \text{H}_2\text{O} \]

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

<table>
<thead>
<tr>
<th>Gas Formed by Reaction of Acids with:</th>
<th>Equation for Formation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>H₂S</strong> Sulfides</td>
<td>2H⁺ + S²⁻ → H₂S</td>
</tr>
<tr>
<td><strong>HCN</strong> Cyanides</td>
<td>H⁺ + CN⁻ → HCN</td>
</tr>
<tr>
<td><strong>CO₂</strong> Carbonates</td>
<td>2H⁺ + CO₃²⁻ → (H₂CO₃) → H₂O + CO₂</td>
</tr>
<tr>
<td><strong>Bicarbonates</strong></td>
<td>H⁺ + HCO₃⁻ → (H₂CO₃) → H₂O + CO₂</td>
</tr>
<tr>
<td><strong>SO₂</strong> Sulfites</td>
<td>2H⁺ + SO₃²⁻ → (H₂SO₃) → H₂O + SO₂</td>
</tr>
<tr>
<td><strong>Bisulfites</strong></td>
<td>H⁺ + HSO₃⁻ → (H₂SO₃) → H₂O + SO₂</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Gas Formed by Reaction of Bases with:</th>
<th>Equation for Formation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NH₃</strong> Ammonium salts</td>
<td>NH₄⁺ + OH⁻ → NH₃ + H₂O</td>
</tr>
</tbody>
</table>

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

In writing a metathesis reaction, you may be tempted sometimes to write NH₄OH as a formula for "ammonium hydroxide." That compound does not exist. In water, it is nothing more than a solution of NH₃.

**EXAMPLE 4.7**  Predicting Reactions and Writing Their Equations

What reaction (if any) occurs when solutions of ammonium carbonate, \((NH₄)₂CO₃\), and propionic acid, \(HC₃H₅O₂\), 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 \(C₃H₅O₂⁻\). Therefore, after exchanging cations between the two anions we can obtain the following balanced molecular equation.

\[
(NH₄)₂CO₃ + 2HC₃H₅O₂ → 2NH₄C₃H₅O₂ + H₂CO₃
\]

In the statement of the problem we are told that we are working with a solution of \(HC₃H₅O₂\), 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 \(H₂CO₃\) decomposes into \(CO₂(g)\) and \(H₂O\). (This information is also found in Table 4.2.) Let’s rewrite the molecular equation taking this into account.

\[
(NH₄)₂CO₃ + 2HC₃H₅O₂ → 2NH₄C₃H₅O₂ + CO₂(g) + H₂O
\]

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 \((NH₄)₂CO₃\) and \(NH₄C₃H₅O₂\) in dissociated form. Now we are ready to expand the molecular equation into the ionic equation.

\[
2NH₄⁺(aq) + CO₃²⁻(aq) + 2HC₃H₅O₂⁻(aq) → 2NH₄⁺(aq) + 2C₃H₅O₂⁻(aq) + CO₂(g) + H₂O
\]

The only spectator ion is \(NH₄⁺\). Dropping this gives the net ionic equation.

\[
CO₃²⁻(aq) + 2HC₃H₅O₂⁻(aq) → 2C₃H₅O₂⁻(aq) + CO₂(g) + H₂O
\]
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

$$KNO_3(aq) + NH_4Cl(aq) \longrightarrow KCl(aq) + NH_4NO_3(aq)$$

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.
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.

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

(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 \(M\) 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.

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

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

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

This gives us an equivalence relationship between “mol NaCl” and “L soln” that we can use to form two conversion factors.\(^7\)

\[
\frac{0.100 \text{ mol NaCl}}{1.00 \text{ L NaCl soln}} \leftrightarrow \frac{1.00 \text{ L soln}}{0.100 \text{ mol NaCl}}
\]

\(^7\) 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.)

\[
\frac{0.100 \text{ mol NaCl}}{1000 \text{ mL NaCl soln}} \quad \text{and} \quad \frac{1000 \text{ mL NaCl soln}}{0.100 \text{ mol NaCl}}
\]
4.6 The Composition of a Solution Is Described by Its Concentration

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.

\[
1.461 \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.443 \text{ g NaCl}} = 0.02500 \text{ mol NaCl}
\]

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.

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 HNO₃ dissolved in 125 mL of solution. Water is added until the volume is 175 mL. What is the molarity of HNO₃ in the final solution? (Hint: Does the amount of HNO₃ 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:

\[
0.100 \text{ mol NaCl} \iff ? \text{ mL soln}
\]

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

\[
0.250 \text{ M NaCl} = \frac{0.250 \text{ mol NaCl}}{1 \text{ L NaCl soln}}
\]
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.

\[
0.100 \frac{\text{mol NaCl}}{0.250 \text{ mol NaCl}} \times \frac{1.00 \text{ L NaCl soln}}{\text{0.250 L NaCl}} = 0.400 \text{ L of } 0.250 \text{ M NaCl}
\]

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

\[
\text{molarity} \times \text{volume (L)} = \text{moles of solute}
\]

\[
\frac{\text{mol solute}}{1 \text{ L soln}} \times \frac{\text{L soln}}{} = \text{mol solute}
\]

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<sub>2</sub>CrO<sub>4</sub>). 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<sub>2</sub>CrO<sub>4</sub> there are

\[
0.0800 \text{ mol Na}_2\text{CrO}_4 \times \frac{1 \text{ mol Na}_2\text{CrO}_4}{1 \text{ L soln}} = 0.0200 \text{ mol Na}_2\text{CrO}_4
\]

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.)
Strontium nitrate, \(\text{Sr(NO}_3\text{)}_2\), is used in fireworks to produce brilliant red colors. Suppose we need to prepare 250.0 mL of 0.100 \(M\) \(\text{Sr(NO}_3\text{)}_2\) 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 \(\text{Sr(NO}_3\text{)}_2\) that will be in it. Once we know the number of moles of \(\text{Sr(NO}_3\text{)}_2\), 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.

\[
\frac{0.100 \text{ mol } \text{Sr(NO}_3\text{)}_2}{1.00 \text{ L } \text{Sr(NO}_3\text{)}_2 \text{ soln}} \times \frac{0.2500 \text{ L } \text{Sr(NO}_3\text{)}_2 \text{ soln}}{1 \text{ mol } \text{Sr(NO}_3\text{)}_2} = 0.0250 \text{ mol } \text{Sr(NO}_3\text{)}_2
\]

Finally, we convert from moles to grams using the molar mass of \(\text{Sr(NO}_3\text{)}_2\), which is 211.63 g mol\(^{-1}\).

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

Thus, to prepare the solution we need to dissolve 5.29 g of \(\text{Sr(NO}_3\text{)}_2\) 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.

\[
0.2500 \text{ L } \text{Sr(NO}_3\text{)}_2 \text{ soln} \times \frac{0.100 \text{ mol } \text{Sr(NO}_3\text{)}_2}{1.00 \text{ L } \text{Sr(NO}_3\text{)}_2 \text{ soln}} \times \frac{211.63 \text{ g } \text{Sr(NO}_3\text{)}_2}{1 \text{ mol } \text{Sr(NO}_3\text{)}_2} = 5.29 \text{ g } \text{Sr(NO}_3\text{)}_2
\]
How can we prepare 100.0 mL of 0.0400 M K₂Cr₂O₇ from 0.200 M K₂Cr₂O₇?

**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 K₂Cr₂O₇ (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).

\[
\begin{align*}
\text{Volume of dilute solution to be prepared} & = V_{\text{dil}} \\
\text{Volume of concentrated solution to be used} & = V_{\text{conc}} \\
\text{Moles of solute in the dilute solution} & = M_{\text{dil}} \\
\text{Moles of solute in the concentrated solution} & = M_{\text{conc}}
\end{align*}
\]

\[
\frac{V_{\text{dil}} \times M_{\text{dil}}}{M_{\text{conc}} \times V_{\text{dil}}} = \frac{V_{\text{conc}} \times M_{\text{conc}}}{V_{\text{conc}}}
\]

Or,

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

(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 K₂Cr₂O₇ from 0.200 M K₂Cr₂O₇?

**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 K₂Cr₂O₇ (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).

\[
\begin{align*}
V_{\text{dil}} & = 100.0 \text{ mL} \\
M_{\text{dil}} & = 0.0400 \text{ M} \\
V_{\text{conc}} & = ? \\
M_{\text{conc}} & = 0.200 \text{ M}
\end{align*}
\]
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.

\[
2\text{AgNO}_3(\text{aq}) + \text{CaBr}_2(\text{aq}) \rightarrow 2\text{AgBr(s)} + \text{Ca(NO}_3)_2(\text{aq})
\]

How many milliliters of 0.125 M CaBr₂ solution must be used to react with the solute in 50.0 mL of 0.115 M AgNO₃?
Chapter 4 Reactions of Ions and Molecules in Aqueous Solutions

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

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**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.

**SOLUTION:** First, we find the moles of AgNO\(_3\) taken. Changing 50.0 mL to 0.0500 L,

\[
0.0500 \text{ L AgNO}_3 \text{ soln} \times \frac{0.115 \text{ mol AgNO}_3}{1.00 \text{ L AgNO}_3 \text{ soln}} = 5.75 \times 10^{-3} \text{ mol AgNO}_3
\]

Next, we use the coefficients of the equation to calculate the amount of CaBr\(_2\) required.

\[
5.75 \times 10^{-3} \text{ mol AgNO}_3 \times \frac{1 \text{ mol CaBr}_2}{2 \text{ mol AgNO}_3} = 2.88 \times 10^{-3} \text{ mol CaBr}_2
\]

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\(_2\).”

\[
2.88 \times 10^{-3} \text{ mol CaBr}_2 \times \frac{1.00 \text{ L CaBr}_2 \text{ soln}}{0.125 \text{ mol CaBr}_2} = 0.0230 \text{ L CaBr}_2 \text{ soln}
\]

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.
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:

\[
Al_2(SO_4)_3(s) \rightarrow 2Al^{3+}(aq) + 3SO_4^{2-}(aq)
\]

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\(_4^{2-}\).
How many milliliters of 0.100 M AgNO₃ solution are needed to react completely with 25.0 mL of 0.400 M CaCl₂ solution? The net ionic equation for the reaction is:

\[ \text{Ag}^+ (aq) + \text{Cl}^- (aq) \rightarrow \text{AgCl} (s) \]

**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:

\[
0.100 \text{ M AgNO}_3 \text{ contains } 0.100 \text{ M Ag}^{+} \text{ and } 0.100 \text{ M NO}_3^{-} \\
0.400 \text{ M CaCl}_2 \text{ contains } 0.400 \text{ M Ca}^{2+} \text{ and } 0.800 \text{ M Cl}^{-}
\]

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.

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

The coefficients of the equation tell us the Ag\(^+\) and Cl\(^-\) combine in a 1-to-1 mole ratio, so 0.0200 mol Cl\(^-\) \(\leftrightarrow\) 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.

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

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.

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

**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.

**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) \(\rightarrow\) 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.
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 AgNO₃ 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

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

**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 AgNO₃ 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.

**SOLUTION:** In 0.0500 M AgNO₃, the molarity of Ag⁺ is 0.0500 M. Applying Equation 4.5,

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

From the stoichiometry of the equation, when $$1.89 \times 10^{-3} \text{ mol Ag}^+$$ reacts, $$1.89 \times 10^{-3} \text{ mol Cl}^-$$ reacts. This is the amount of Cl⁻ that came from the sample, so the sample must have contained $$1.89 \times 10^{-3} \text{ mol Cl}^-$$ that react. This is the same as the number of moles of Cl in the sample. Therefore, the mass of Cl in the sample was

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

The percentage by mass of Cl in the sample is

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

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 AgNO₃ 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 Na₂SO₄ was treated with 0.150 M BaCl₂ solution until all the sulfate ion had reacted to form BaSO₄. The net reaction

\[ \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq) \rightarrow \text{BaSO}_4(s) \]

required 28.40 mL of the BaCl₂ solution. How many grams of Na₂SO₄ were in the solution? (Hint: How do moles of SO₄²⁻ relate to moles of Na₂SO₄?)

### Practice Exercise 38:
A sample of a mixture containing CaCl₂ and MgCl₂ weighed 2.000 g. The sample was dissolved in water and H₂SO₄ was added until the precipitation of CaSO₄ was complete.

\[ \text{CaCl}_2(aq) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{CaSO}_4(s) + 2\text{HCl}(aq) \]

The CaSO₄ was filtered, dried completely, and weighed. A total of 0.736 g of CaSO₄ was obtained.

(a) How many moles of Ca²⁺ were in the CaSO₄?
(b) How many moles of Ca²⁺ were in the original 2.000 g sample?
(c) How many moles of CaCl₂ were in the 2.000 g sample?
(d) How many grams of CaCl₂ were in the 2.000 g sample?
(e) What was the percentage by mass of CaCl₂ 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...
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?

**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

\[
\text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}
\]

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.

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

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

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

so in this titration, 2.90 \times 10^{-3} \text{ 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 \times 10^{-3} \text{ mol HCl}) to the volume (in liters) of the HCl solution used (25.00 mL, or 0.02500 L).

\[
\text{Molarity of HCl soln} = \frac{2.90 \times 10^{-3} \text{ mol HCl}}{0.02500 \text{ L HCl soln}} = 0.116 \text{ M HCl}
\]

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.
In a titration, a sample of $\text{H}_2\text{SO}_4$ 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 $\text{H}_2\text{SO}_4$ 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, $\text{H}_3\text{O}^+$, when dissolved in water, and a base produces hydroxide ions, $\text{OH}^-$, 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 non-ionized 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.

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

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.
Chapter 4  Reactions of Ions and Molecules in Aqueous Solutions

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.

\[ \text{HA} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{A}^- \]

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 \( \text{H}^+ \). The equation also applies to acid anions such as \( \text{HSO}_4^- \) which gives \( \text{SO}_4^{2-} \) when it loses an \( \text{H}^+ \). Often \( \text{H}_2\text{O} \) is omitted from the equation and the hydronium ion is abbreviated as \( \text{H}^+ \).

Equation for the ionization of a molecular base in water (page 139) Equation 4.3 describes how molecules of molecular bases acquire \( \text{H}^+ \) from \( \text{H}_2\text{O} \) to form a cation plus a hydroxide ion.

\[ \text{B} + \text{H}_2\text{O} \rightarrow \text{BH}^+ + \text{OH}^- \]

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 \( \text{H}^+ \). 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 \( \text{HCl}, \text{HNO}_3 \), and \( \text{H}_2\text{SO}_4 \). 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 \( \text{CO}_2 \), 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.

\[ \text{grams of substance } A \times V = \text{moles} \]

\[ M \times V = \text{moles} \]

\[ \text{Moles of } A \rightarrow \text{Moles of } B \]

\[ \text{Atoms, molecules, or ions of substance } A \]

\[ \text{Multiply by ratio of coefficients} \]

\[ \text{Divide by Avogadro’s number} \]

\[ \text{Multiply by Avogadro’s number} \]

\[ \text{Atoms, molecules, or ions of substance } B \]

\[ \text{Grams of substance } B \]

\[ \text{Grams of substance } B \]

\[ \text{Volume of solution of } B \]

\[ \text{Lab units} \]

\[ \text{Lab units} \]

\[ \text{Atomic-scale units} \]

\[ \text{Atomic-scale units} \]

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) CaCl₂, (b) (NH₄)₂SO₄, (c) NaC₂H₃O₂.

**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.

\[ \text{Co}^{2+}(aq) + 2\text{Cl}^-(aq) + 2\text{Na}^+(aq) + 2\text{OH}^- (aq) \rightarrow \text{Co(OH)}_2(s) + 2\text{Na}^+(aq) + 2\text{Cl}^- (aq) \]

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.

\[ 3\text{Co}^{3+}(aq) + 2\text{HPO}_4^{2-}(aq) \rightarrow \text{Co}_3(\text{PO}_4)_2(s) + 2\text{H}^+(aq) \]

**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 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) HNO₃, (c) NH₃, (d) H₂SO₄.

4.17 Which of the following would yield an acidic solution when they react with water? Which would give a basic solution? (a) P₄O₁₀, (b) K₂O, (c) SeO₃, (d) Cl₂O₇.

4.18 What is a dynamic equilibrium? Using acetic acid as an example, describe why all the HC₃H₅O₂ 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) HNO₃, (c) H₂SO₄, (d) HCl, (e) HCHO₂, (f) HNO₂.

4.21 Which of the following produce a strongly basic solution when dissolved in water? (a) C₅H₅N, (b) Ba(OH)₂, (c) KOH, (d) C₅H₅NH₂, (e) Cs₂O, (f) N₂O₅.

4.22 Methylamine, CH₃NH₂, reacts with hydronium ion in very much the same manner as ammonia.

\[ \text{CH}_3\text{NH}_2(aq) + \text{H}_3\text{O}^+(aq) \rightarrow \text{CH}_3\text{NH}_3^+(aq) + \text{H}_2\text{O} \]

On the basis of what you have learned so far in this course, sketch the molecular structures of CH₃NH₂ and CH₃NH₃⁺ (the methylammonium ion).

**Nomenclature of Acids and Bases**

4.23 Name the following: (a) H₂Se(g), (b) H₂Se(aq)

4.24 Iodine, like chlorine, forms several acids. What are the names of the following? (a) HI₆, (b) HIO₃, (c) HIO₂, (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) NaHCO₃, (b) KH₂PO₄, (c) (NH₄)₂HPO₄.

4.28 Write the formulas for all the acid salts that could be formed from the reaction of NaOH with the acid H₃PO₄.

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) HIO₂, (c) HBrO₃, (d) HClO₄.

4.30 The formula for the arsenate ion is AsO₄³⁻. What is the formula for arsenic acid?

4.31 Butyric acid, HC₃H₇O₂, gives rancid butter is bad odor. What is the name of the salt NaC₃H₇O₂?

4.32 Calcium propionate, Ca(C₃H₅O₂)₂, is used in baked foods as a preservative and to prevent the growth of mold. What is the name of the acid HC₃H₅O₂?

**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 AgNO₃ and NaBr are mixed.

4.36 If a solution of trisodium phosphate, Na₃PO₄, 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 Na₂CO₃·10H₂O. Explain, using chemical equations, how this substance is able to remove Ca²⁺ ions from “hard water.”

4.38 With which of the following will the weak acid HCHO₂ react? Where there is a reaction, write the formulas of the products. (a) KOH, (b) MgO, (c) NH₃

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) NaHCO₃, (b) Na₂S, and (c) K₂SO₃?

**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 HNO₃ is diluted with water to give 0.25 M HNO₃, what happens to the number of moles of HNO₃ in the solution?

4.45 Two solutions, A and B, are labeled “0.10 M CaCl₂” and “0.20 M CaCl₂,” respectively. Both solutions contain the same number of moles of CaCl₂. 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?
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Questions, Problems, and Exercises

Ionic Reactions

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

4.50 Write balanced ionic and net ionic equations for these reactions.
(a) \( CuSO_4(aq) + BaCl_2(aq) \rightarrow CuCl_2(aq) + BaSO_4(s) \)
(b) \( Fe(NO_3)_3(aq) + LiOH(aq) \rightarrow LiNO_3(aq) + Fe(OH)_3(s) \)
(c) \( Na_3PO_4(aq) + CaCl_2(aq) \rightarrow Ca_3(PO_4)_2(s) + NaCl(aq) \)
(d) \( Na_3S(aq) + AgC_2H_3O_2(aq) \rightarrow NaC_2H_3O_2(aq) + Ag_2S(s) \)

Acids and Bases as Electrolytes

4.51 Pure HClO4 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.

Metathesis Reactions

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 Nitric 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, H(C_3H_7COOH), 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) \( FeSO_4(aq) + K_3PO_4(aq) \rightarrow Fe_3(PO_4)_2(s) + K_2SO_4(aq) \)
(b) \( AgC_2H_3O_2(aq) + AlCl_3(aq) \rightarrow AgCl(s) + Al(C_2H_3O_2)_2(aq) \)

4.60 Write balanced ionic and net ionic equations for these reactions.
(a) Fe(NO_3)_3(aq) + KOH(aq) \rightarrow KNO_3(aq) + Fe(OH)_3(s) \)
(b) Na_3PO_4(aq) + SrCl_2(aq) \rightarrow Sr_3(PO_4)_3(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) HgBr_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) \( Ca(OH)_2(aq) + HNO_3(aq) \rightarrow \)
(b) \( Al_2O_3(s) + HCl(aq) \rightarrow \)
(c) \( Zn(OH)_2(s) + H_2SO_4(aq) \rightarrow \)

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) \( HC_2H_3O_2(aq) + Mg(OH)_2(s) \rightarrow \)
(b) \( HClO_4(aq) + NH_3(aq) \rightarrow \)
(c) \( H_2CO_3(aq) + NH_3(aq) \rightarrow \)

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) \( HNO_3(aq) + K_2CO_3(aq) \rightarrow \)
(b) \( Ca(OH)_2(aq) + NH_4NO_3(aq) \rightarrow \)

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

Predicting Ionic Reactions

4.71 Explain why the following reactions take place.
(a) \( CrCl_3 + 3NaOH \rightarrow Cr(OH)_3 + 3NaCl \)
(b) \( ZnO + 2HBr \rightarrow ZnBr_2 + H_2O \)
4.72 Explain why the following reactions take place.
(a) MnCO₃ + H₂SO₄ → MnSO₄ + H₂O + CO₂
(b) Na₂C₃O₄ + 2HNO₃ → 2NaNO₃ + H₂C₂O₄

4.73 Complete and balance the molecular, ionic, and net ionic equations for the following reactions.
(a) HNO₃ + Cr(OH)₃ →
(b) HClO₄ + NaOH →
(c) Cu(OH)₂ + H₂C₂O₄ →
(d) ZnO + H₂SO₄ →

4.74 Complete and balance molecular, ionic, and net ionic equations for the following reactions.
(a) NaHSO₄ + HBr →
(b) (NH₄)₂CO₃ + NaOH →
(c) (NH₄)₂CO₃ + Ba(OH)₂ →
(d) FeS + HCl →

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 sulfate and barium nitrate
(b) formic acid (HCHO₂) 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) HCO₃⁻(aq) + H⁺(aq) → H₂O + CO₂(g)
(b) Fe²⁺(aq) + 2OH⁻(aq) → Fe(OH)₂(s)
(c) Ba²⁺(aq) + SO₄²⁻(aq) → BaSO₄(s)
(d) 2Ag⁺(aq) + S²⁻(aq) → Ag₂S(s)
(e) ZnO(s) + 2H⁺(aq) → Zn²⁺(aq) + H₂O

4.78 Suppose that you wished to prepare copper(II) carbonate by a precipitation reaction involving Cu²⁺ and CO₃²⁻. Which of the following pairs of reactants could you use as solutes?
(a) Cu(OH)₂ + Na₂CO₃
(b) CuSO₄ + (NH₄)₂CO₃
(c) Cu(NO₃)₂ + CaCO₃

Molar Concentration
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 of iron(II) nitrate in 12.0 mL of solution

4.81 How many milliliters of 0.265 M Na₂C₃O₄ are needed to supply 14.3 g Na₂C₃O₄? 4.82 How many milliliters of 0.615 M HNO₃ contain 1.67 g HNO₃?

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 C₆H₁₁O₆ (glucose)
(c) 250.0 mL of 0.250 M H₂SO₄

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 H₂SO₄ 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 HNO₃ is diluted to 450 mL. What is the molarity of the resulting solution?

4.87 To what volume must 25.0 mL of 18.0 M H₂SO₄ be diluted to produce 1.50 M H₂SO₄?
4.88 To what volume must 50.0 mL of 1.50 M HCl be diluted to produce 0.200 M HCl?

How many milliliters of water must be added to 150.0 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 CaCl₂
(b) 50.0 mL of 0.40 M Al₂(SO₄)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 (NH₄)₂CO₃
(b) 30.0 mL of 0.35 M Al₂(SO₄)₃

4.93 Calculate the concentrations of each of the ions in (a) 0.25 M Cr(NO₃)₃, (b) 0.10 M CuSO₄, (c) 0.16 M Na₃PO₄, and (d) 0.075 M Al₂(SO₄)₃.

4.94 Calculate the concentrations of each of the ions in (a) 0.060 M Ca(OH)₂, (b) 0.15 M FeCl₃, (c) 0.22 M Cr₂(SO₄)₃, and (d) 0.60 M (NH₄)₂SO₄.

4.95 In a solution of Al₂(SO₄)₃, the Al³⁺ concentration is 0.12 M. How many grams of Al₂(SO₄)₃ are in 50.0 mL of this solution?
4.96 In a solution of NiCl₂, the Cl⁻ concentration is 0.055 M. How many grams of NiCl₂ are in 250 mL of this solution?

Solution Stoichiometry
4.97 How many milliliters of 0.25 M NiCl₂ solution are needed to react completely with 20.0 mL of 0.15 M Na₂CO₃ solution? How many grams of NiCO₃ will be formed? The reaction is

Na₂CO₃(aq) + NiCl₂(aq) → NiCO₃(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 H₂C₃O₄? The reaction is

2NaOH(aq) + H₂C₂H₃O₂(aq) → Na₂C₂H₃O₂(aq) + 2H₂O
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, Al₂(SO₄)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 Al₂(SO₄)₃ with Ba(OH)₂. How many grams of Al₂(SO₄)₃ are needed to react with 85.0 mL of 0.0500 M Ba(OH)₂?

4.102 How many grams of baking soda, NaHCO₃, 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 FeCl₃ solution are needed to react completely with 20.0 mL of 0.0450 M AgNO₃ solution? How many grams of AgCl will be formed? The net ionic equation for the reaction is

\[ \text{Ag}^+ \text{(aq)} + \text{Cl}^- \text{(aq)} \rightarrow \text{AgCl} \text{(s)} \]

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

\[ \text{Co}^{2+} \text{(aq)} + 2\text{OH}^- \text{(aq)} \rightarrow \text{Co(OH)}_2 \text{(s)} \]

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

\[ \text{Ag}^+ \text{(aq)} + \text{Cl}^- \text{(aq)} \rightarrow \text{AgCl} \text{(s)} \]

4.106 How many milliliters of ammonium sulfate 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

\[ \text{NH}_4^+ \text{(aq)} + \text{OH}^- \text{(aq)} \rightarrow \text{NH}_3 \text{(g)} + \text{H}_2\text{O} \]

4.107 Suppose that 4.00 g of solid Fe₂O₃ is added to 25.0 mL of 0.500 M HCl solution. What will the concentration of the Fe³⁺ be when all the HCl has reacted? What mass of FeCl₃ 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 H₂SO₄ solution. What will the concentration of Mg²⁺ 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 AgNO₃.

(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 Na₂PO₄ to 34.0 mL of 0.140 M Ca(NO₃)₂.

(a) What mass of Ca₃(PO₄)₂ will be formed?

(b) What will be the concentrations of each of the ions in the mixture after the reaction?

**Questions, Problems, and Exercises**

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?

4.113 Lactic acid, HC₃H₅O₃, 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 H₂C₆H₅O₆. 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 AgNO₃ 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 PbCO₃. A sample of the ore weighing 1.526 g was treated with nitratic acid, which dissolved the PbCO₃. The resulting solution was filtered from undissolved rock and required 29.22 mL of 0.122 M Na₂SO₄ to completely precipitate all the lead as PbSO₄. What is the percentage by mass of lead in the ore?

4.118 An ore of barium contains BaCO₃. A 1.542 g sample of the ore was treated with HCl to dissolve the BaCO₃. The resulting solution was filtered to remove insoluble material and then treated with H₂SO₄ to precipitate BaSO₄. 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 BaSO₄.)

4.119 To a mixture of NaCl and Na₂CO₃, 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 CO₂, 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 Na₂CO₃?

4.120 A mixture was known to contain both KNO₃ and K₂SO₄. 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 SO₂, 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 K₂SO₄ in the original mixture of KNO₃ and K₂SO₄?
ADDITIONAL EXERCISES

4.121 Classify each of the following as a strong electrolyte, weak electrolyte, or nonelectrolyte.
(a) KCl
(b) C\textsubscript{3}H\textsubscript{5}(OH)\textsubscript{3} (glycerin)
(c) NaOH
(d) C\textsubscript{12}H\textsubscript{22}O\textsubscript{11} (sucrose, or table sugar)
(e) HC\textsubscript{2}H\textsubscript{3}O\textsubscript{2} (acetic acid)
(f) CH\textsubscript{3}OH (methyl alcohol)
(g) H\textsubscript{2}SO\textsubscript{4}
(h) NH\textsubscript{3}

4.122 Complete the following and write molecular, ionic, and net ionic equations. State whether a net reaction occurs in each case.
(a) CaCO\textsubscript{3} + HNO\textsubscript{3} →
(b) CaCO\textsubscript{3} + H\textsubscript{2}SO\textsubscript{4} →
(c) FeS + HBr →
(d) KOH + SnCl\textsubscript{2} →

4.123 Aspirin is a monoprotic acid called acetylsalicylic acid. Its formula is H\textsubscript{\textit{C}}\textsubscript{\textit{9}}H\textsubscript{\textit{7}}O\textsubscript{\textit{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\textsubscript{2} and 3.40 mg H\textsubscript{2}O. The molecular mass was determined to be 166 g mol\textsuperscript{-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?