

4

REACTIONS IN AQUEOUS SOLUTION

4.1 | General Properties of Aqueous Solutions



WHAT'S AHEAD

- 4.1 ► General Properties of Aqueous Solutions
- 4.2 ► Precipitation Reactions
- 4.3 ► Acids, Bases, and Neutralization Reactions
- 4.4 ► Oxidation–Reduction Reactions
- 4.5 ► Concentrations of Solutions
- 4.6 ► Solution Stoichiometry and Chemical Analysis

Water is the most abundant liquid on our planet. It covers nearly two-thirds of our planet, and this simple substance has been the key to much of Earth's evolutionary history. Life almost certainly originated in water, and the need for water by all forms of life has helped determine diverse biological structures. Indeed, most of the mass of our bodies is water, and it has a composition close to that of seawater. The chemical reactions responsible for life occur in water. By the end of this section, you should be able to

- Identify what occurs when a substance dissolves in water

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

Electrolytes and Nonelectrolytes

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

Not all substances that dissolve in water make the resulting solution conducting. **Figure 4.1** shows a simple experiment to test the electrical conductivity of three solutions: pure water, a solution of table sugar (sucrose) in water, and a solution of table salt (sodium chloride) in water. A light bulb is connected to a battery-powered electrical circuit that contains two electrodes submerged in a beaker of each solution. In order for the light bulb to turn on, there must be an electrical current (that is, a flow of electrically charged particles) between the two electrodes immersed in the solution. Because the light bulb does not turn on in pure water, we conclude that there are not enough charged particles in pure water to create a circuit; water must then mostly exist as H₂O molecules. The solution containing sucrose (C₁₂H₂₂O₁₁) also does not turn on the light bulb; therefore, we conclude that the sucrose molecules in solution are uncharged. But the solution containing NaCl does provide enough charged particles to create an electrical circuit and turn on the light bulb. This is experimental evidence that Na⁺ and Cl⁻ ions are formed in aqueous solution.

A substance (such as NaCl) whose aqueous solutions contain ions is called an **electrolyte**. A substance (such as C₁₂H₂₂O₁₁) that does not form ions in solution is called a **nonelectrolyte**. The different classifications of NaCl and C₁₂H₂₂O₁₁ arise largely because NaCl is an ionic compound, whereas C₁₂H₂₂O₁₁ is a molecular compound.

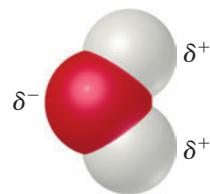


▲ **Figure 4.1** Completion of an electrical circuit with an electrolyte turns on the light.

How Compounds Dissolve in Water

Recall from Figure 2.17 that solid NaCl consists of an orderly arrangement of Na^+ and Cl^- ions. When NaCl dissolves in water, each ion separates from the solid structure and disperses throughout the solution [Figure 4.2(a)]. The ionic solid *dissociates* into its component ions as it dissolves.

Water is a very effective solvent for ionic compounds. Although H_2O has no overall charge, the O atom is rich in electrons and has a partial negative charge relative to the H atoms, while each H atom has a partial positive charge. The lowercase Greek letter delta (δ) is used to denote partial charge: A partial negative charge is denoted δ^- (“delta minus”), and a partial positive charge is denoted by δ^+ (“delta plus”). Cations are attracted by the negative end of H_2O , and anions are attracted by the positive end.

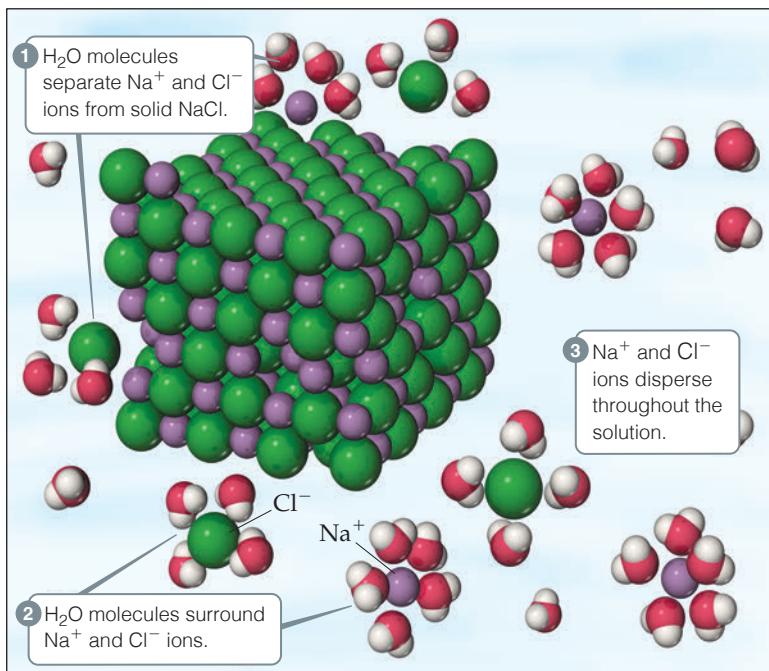


As an ionic compound dissolves, the ions become surrounded by H_2O molecules, as shown in Figure 4.2(a). The ions are said to be *solvated*. In chemical equations, we denote solvated ions by writing them as $\text{Na}^+(aq)$ and $\text{Cl}^-(aq)$, where *aq* is an abbreviation for “aqueous.” **Solvation** helps stabilize the ions in solution and prevents cations and anions from recombining. Furthermore, because the ions and their shells of surrounding water molecules are free to move about, the ions become dispersed uniformly throughout the solution.

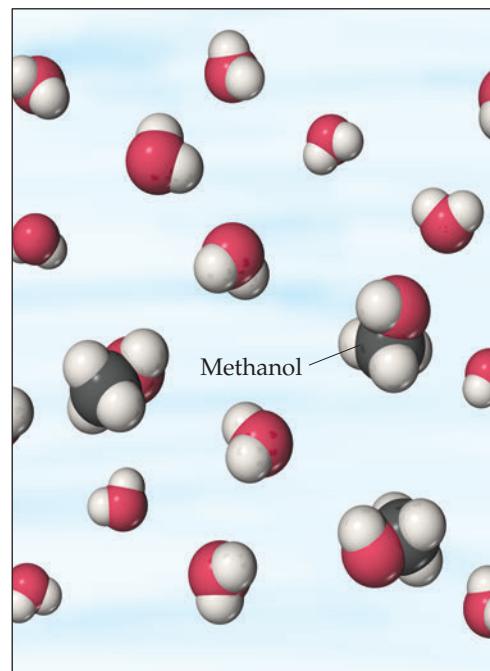
We can usually predict the nature of the ions in a solution of an ionic compound from the chemical name of the substance. Sodium sulfate (Na_2SO_4), for example,

Go Figure

Do both, just one, or neither of the following solutions conduct electricity? If just one, which one?



(a) Ionic compounds like sodium chloride, NaCl , form ions when they dissolve.



(b) Molecular substances like methanol, CH_3OH , dissolve without forming ions.

▲ Figure 4.2 Dissolution in water. (a) When an ionic compound, such as sodium chloride, NaCl , dissolves in water, H_2O molecules separate, surround, and uniformly disperse the ions into the liquid. (b) Molecular substances that dissolve in water, such as methanol, CH_3OH , usually do so without forming ions. We can think of methanol in water as a simple mixing of two molecular species. In both (a) and (b) the water molecules have been moved apart so that the solute particles can be seen clearly.

dissociates into sodium ions (Na^+) and sulfate ions (SO_4^{2-}). You must remember the formulas and charges of common ions (Tables 2.4 and 2.5) to understand the forms in which ionic compounds exist in aqueous solution.

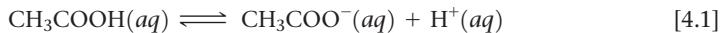
When a molecular compound such as sucrose or methanol [Figure 4.2(b)] dissolves in water, the solution usually consists of intact molecules dispersed throughout the solution. Consequently, most molecular compounds are nonelectrolytes. A few molecular substances do have aqueous solutions that contain ions. Acids are the most important of these solutions. For example, when $\text{HCl}(g)$ dissolves in water to form $\text{HCl}(aq)$, the molecule *ionizes*; that is, it dissociates into $\text{H}^+(aq)$ and $\text{Cl}^-(aq)$ ions.

Strong and Weak Electrolytes

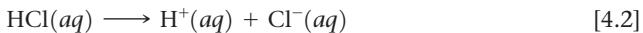
Electrolytes differ in the extent to which they conduct electricity. **Strong electrolytes** are those solutes that exist in solution completely or nearly completely as ions. Essentially all water-soluble ionic compounds (such as NaCl) and a few molecular compounds (such as HCl) are strong electrolytes.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

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

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



The half-arrows pointing in opposite directions mean that the reaction is significant in both directions. At any given moment some CH_3COOH molecules are ionizing to form H^+ and CH_3COO^- ions, and some of the H^+ and CH_3COO^- ions are recombining to form CH_3COOH . The balance between these opposing processes determines the relative numbers of ions and neutral molecules. This balance produces a state of **chemical equilibrium** in which the relative numbers of each type of ion or molecule in the reaction are constant over time. Chemists use half-arrows pointing in opposite directions to represent reactions that go both forward and backward to achieve equilibrium, such as the ionization of weak electrolytes. In contrast, a single reaction arrow is used for reactions that largely go forward, such as the ionization of strong electrolytes. Because HCl is a strong electrolyte, we write the equation for the ionization of HCl as



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

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

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



Sample Exercise 4.1

Relating Relative Numbers of Anions and Cations to Chemical Formulas



The accompanying diagram represents an aqueous solution of either $MgCl_2$, KCl , or K_2SO_4 with the water molecules left out for clarity. Which solution does the drawing best represent?

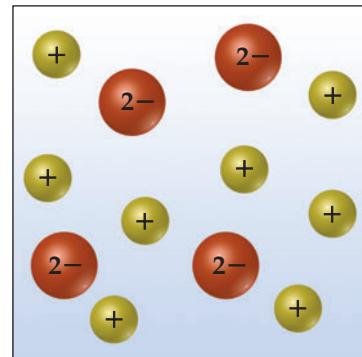
SOLUTION

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

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

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

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



► Practice Exercise

If you were to draw diagrams representing aqueous solutions of (a) $NiSO_4$, (b) $Ca(NO_3)_2$, (c) Na_3PO_4 , (d) $Al_2(SO_4)_3$, how many anions would you show if each diagram contained six cations?

Self-Assessment Exercise

- 4.1** Which of the following groups of substances contain only strong electrolytes?
 (a) KBr , SO_2 , $CaCl_2$
 (b) HCl , NH_3 , $NaOH$
 (c) $NaNO_3$, HCl , Rb_2SO_4

Exercises

- 4.2** State whether each of the following statements is true or false. Justify your answer in each case.
 (a) Electrolyte solutions conduct electricity because electrons are moving through the solution.
 (b) If you add a nonelectrolyte to an aqueous solution that already contains an electrolyte, the electrical conductivity will not change.
4.3 We have learned in this chapter that many ionic solids dissolve in water as strong electrolytes; that is, as separated ions in solution. Which statement is most correct about this process? (a) Water is a strong acid and therefore is good at dissolving ionic solids. (b) Water is good at solvating

ions because the hydrogen and oxygen atoms in water molecules bear partial charges. (c) The hydrogen and oxygen bonds of water are easily broken by ionic solids.

- 4.4** Ignoring protolysis reactions (i.e. proton transfer reaction), specify what ions are present in a solution upon dissolving each of the following substances in water: (a) Li_2CO_3 , (b) $(NH_4)_3PO_4$, (c) $Na_2Cr_2O_7$, (d) $NaPF_6$.
4.5 When carbon dioxide dissolves in water, it is in equilibrium with carbonic acid H_2CO_3 , which is a weak electrolyte. What solutes are present in an aqueous solution of this compound? Write the chemical equation for the ionization of H_2CO_3 .

4.1 (c)

Answers to Self-Assessment Exercises



4.2 | Precipitation Reactions

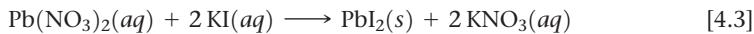


“Hard” water contains calcium and magnesium ions. These ions can react with soap to form a white solid that forms around baths, showers and basins. This is an example of a chemical reaction between two soluble materials to form an insoluble product. Scum, as it is called, is harmless, though unsightly, and there are many cleaning products designed to remove it.

By the end of this section, you should be able to

- Predict if a precipitate forms when two aqueous solutions are mixed

Figure 4.3 shows two clear solutions being mixed. One solution contains potassium iodide, KI, dissolved in water, and the other contains lead nitrate, $\text{Pb}(\text{NO}_3)_2$, dissolved in water. The reaction between these two solutes produces a water-insoluble yellow solid. Reactions that result in the formation of an insoluble product are called **precipitation reactions**. A **precipitate** is an insoluble solid formed by a reaction in solution. In Figure 4.3 the precipitate is lead iodide (PbI_2), a compound that has a very low solubility in water:



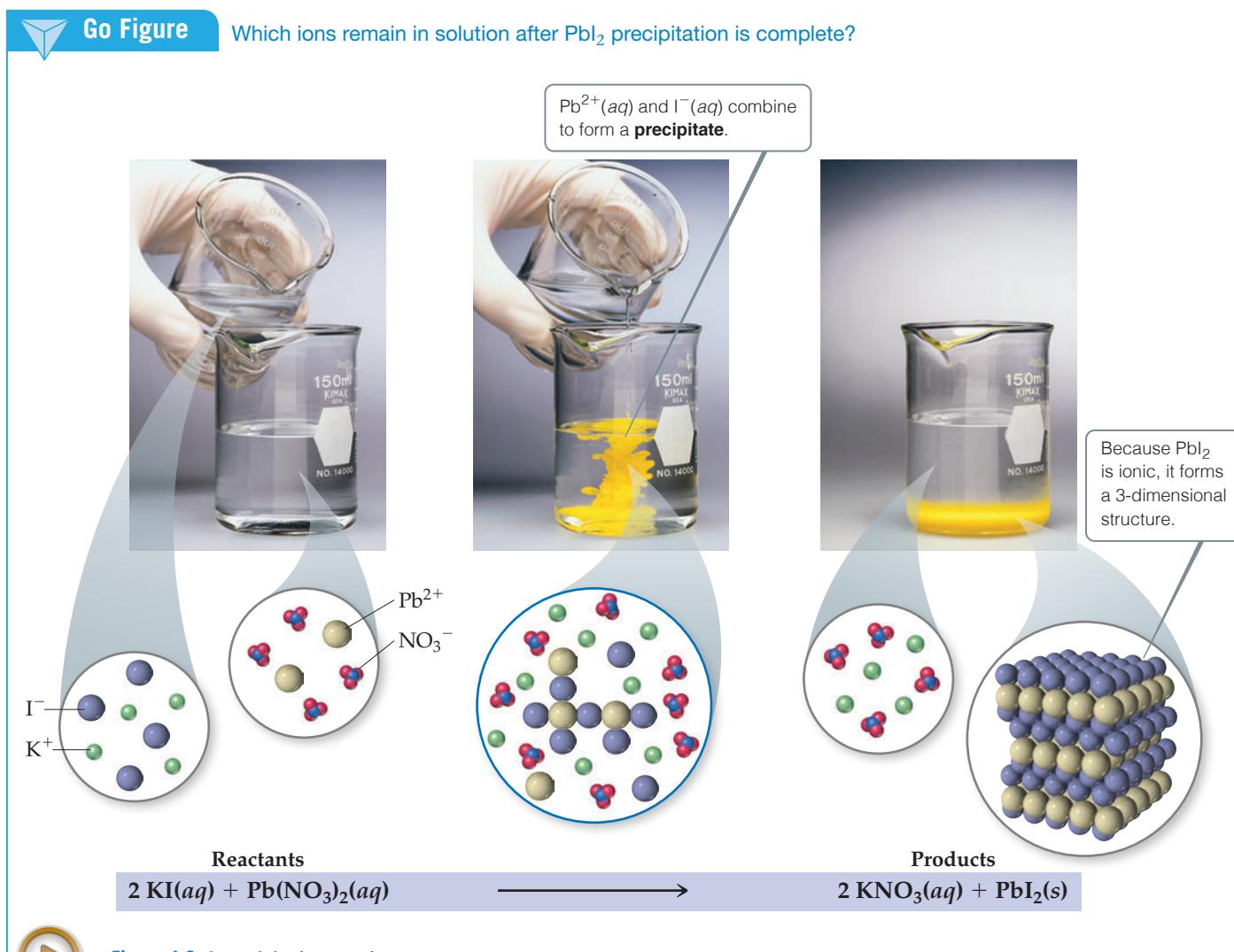
The other product of this reaction, potassium nitrate (KNO_3), remains in solution.

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

Solubility Guidelines for Ionic Compounds

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

Unfortunately, there are no rules based on simple physical properties such as ionic charge to guide us in predicting whether a particular ionic compound will be soluble. Experimental observations, however, have led to guidelines for predicting solubility for ionic compounds. For example, experiments show that all common ionic compounds that contain the nitrate anion, NO_3^- , are soluble in water. **Table 4.1** summarizes the



▲ Figure 4.3 A precipitation reaction.

TABLE 4.1 Solubility Guidelines for Common Ionic Compounds in Water

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

solubility guidelines for common ionic compounds. The table is organized according to the anion in the compound, but it also reveals many important facts about cations. Note that *all common ionic compounds of the alkali metal ions (group 1 of the periodic table) and of the ammonium ion (NH_4^+) are soluble in water.*

How to Predict Whether a Precipitate Forms When Strong Electrolytes Mix

1. Note the ions present in the reactants.
2. Consider the possible cation–anion combinations.
3. Use Table 4.1 to determine if any of the combinations is insoluble.

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



Exchange (Metathesis) Reactions

Notice in Equation 4.4 that the reactant cations exchange anions— Mg^{2+} ends up with OH^- , and Na^+ ends up with NO_3^- . The chemical formulas of the products are based on the charges of the ions—two OH^- ions are needed to give a neutral compound with Mg^{2+} , and one NO_3^- ion is needed to give a neutral compound with Na^+ . *The equation can be balanced only after the chemical formulas of the products have been determined.*

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



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

How To Balance a Metathesis Reaction

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



Sample Exercise 4.2

Using Solubility Rules

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

SOLUTION

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

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

Solve

(a) According to Table 4.1, most carbonates are insoluble. But carbonates of the alkali metal cations (such as sodium ion) are an

exception to this rule and are soluble. Thus, Na_2CO_3 is soluble in water.

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

► Practice Exercise

Which of the following compounds is insoluble in water?
 (a) $(\text{NH}_4)_2\text{S}$ (b) CaCO_3 (c) NaOH (d) Ag_2SO_4 (e) $\text{Pb}(\text{CH}_3\text{COO})_2$


Sample Exercise 4.3
Predicting a Metathesis Reaction


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

SOLUTION

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

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

Solve

(a) The reactants contain Ba^{2+} , Cl^- , K^+ , and SO_4^{2-} ions. Exchanging the anions gives us BaSO_4 and KCl . According to Table 4.1,

most compounds of SO_4^{2-} are soluble but those of Ba^{2+} are not. Thus, BaSO_4 is insoluble and will precipitate from solution. KCl is soluble.

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

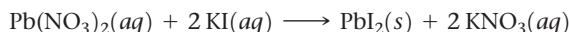


Practice Exercise

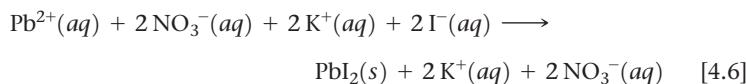
(a) What compound precipitates when aqueous solutions of $\text{Fe}_2(\text{SO}_4)_3$ and LiOH are mixed? (b) Write a balanced equation for the reaction.

Ionic Equations and Spectator Ions

In writing equations for reactions in aqueous solution, it is often useful to indicate whether the dissolved substances are present predominantly as ions or as molecules. Let's reconsider the precipitation reaction between $\text{Pb}(\text{NO}_3)_2$ and 2 KI (Eq. 4.3):

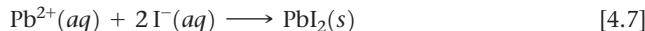


An equation written in this fashion, showing the complete chemical formulas of reactants and products, is called a **molecular equation** because it shows chemical formulas without indicating ionic character. Because $\text{Pb}(\text{NO}_3)_2$, KI , and KNO_3 are all water-soluble ionic compounds and therefore strong electrolytes, we can write the equation in a form that indicates which species exist as ions in the solution:



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

Notice that $\text{K}^+(aq)$ and $\text{NO}_3^-(aq)$ appear on both sides of Equation 4.6. Ions that appear in identical forms on both sides of a complete ionic equation, called **spectator ions**, play no direct role in the reaction. Spectator ions can be canceled, like algebraic quantities, on either side of the reaction arrow, since they are not reacting with anything. Once we cancel the spectator ions, we are left with the **net ionic equation**, which is one that includes only the ions and molecules directly involved in the reaction:



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

Net ionic equations illustrate the similarities between various reactions involving electrolytes. For example, Equation 4.7 expresses the essential feature of the precipitation reaction between any strong electrolyte containing $\text{Pb}^{2+}(aq)$ and any strong electrolyte containing $\text{I}^-(aq)$: The ions combine to form a precipitate of PbI_2 . Thus, a net ionic

equation demonstrates that more than one set of reactants can lead to the same net reaction. For example, aqueous solutions of KI and MgI₂ share many chemical similarities because both contain I⁻ ions. Either solution when mixed with a Pb(NO₃)₂ solution produces PbI₂(s). The complete ionic equation, however, identifies the actual reactants that participate in a reaction.

How to Write a Net Ionic Equation

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

Sample Exercise 4.4

Writing a Net Ionic Equation



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

SOLUTION

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

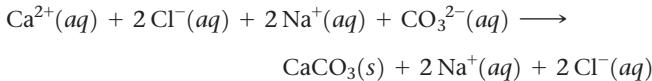
Plan We write the chemical formulas of the reactants and products and then determine which product is insoluble. We then write and balance the molecular equation. Next, we write each soluble strong electrolyte as separated ions to obtain the complete ionic equation. Finally, we eliminate the spectator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

Solve Calcium chloride is composed of calcium ions, Ca²⁺, and chloride ions, Cl⁻; hence, an aqueous solution of the substance is CaCl₂(aq). Sodium carbonate is composed of Na⁺ ions and CO₃²⁻ ions; hence, an aqueous solution of the compound is Na₂CO₃(aq). In the molecular equations for precipitation reactions, the anions and cations appear to exchange partners. Thus, we put Ca²⁺ and CO₃²⁻ together to give CaCO₃ and Na⁺ and Cl⁻ together to give NaCl. According to the solubility guidelines in Table 4.1, CaCO₃ is insoluble and NaCl is soluble. The balanced molecular equation is

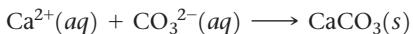


In a complete ionic equation, *only* dissolved strong electrolytes (such as soluble ionic compounds) are written as separate ions. As the (aq) designations remind us, CaCl₂, Na₂CO₃, and NaCl are all dissolved in the solution. Furthermore, they are all strong

electrolytes. CaCO₃ is an ionic compound, but it is not soluble. We do not write the formula of any insoluble compound as its component ions. Thus, the complete ionic equation is



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



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

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

► Practice Exercise

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

Self-Assessment Exercise

- 4.6** Which combination of solutions will form a precipitate?

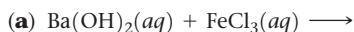
- (a) KOH(aq) and MgSO₄(aq)
- (b) NaOH(aq) and KNO₃(aq)
- (c) NH₄Cl(aq) and Rb₂CO₃(aq)

Exercises

4.7 Using solubility guidelines, predict whether each of the following compounds is soluble or insoluble in water: (a) Hg_2SO_4 , (b) NH_4OH , (c) $\text{Ni}(\text{CH}_3\text{COO})_2$, (d) AgNO_3 , (e) FeCO_3 .

4.8 Will precipitation occur when the following solutions are mixed? If so, write a balanced chemical equation for the reaction. (a) $\text{Ca}(\text{CH}_3\text{COO})_2$ and NaOH , (b) K_2CO_3 and NH_4NO_3 , (c) Na_2S and FeCl_3 .

4.9 Write balanced net ionic equations for the reactions that occur in each of the following cases. Identify the spectator ion or ions in each reaction.



4.10 Separate samples of a solution of an unknown salt are treated with dilute solutions of HBr , H_2SO_4 , and NaOH . A precipitate forms in all three cases. Which of the following cations could be present in the unknown salt solution: K^+ , Pb^{2+} , Ba^{2+} ?

4.11 You know that an unlabeled bottle contains an aqueous solution of one of the following: AgNO_3 , CaCl_2 , or $\text{Al}_2(\text{SO}_4)_3$. A friend suggests that you test a portion of the solution with $\text{Ba}(\text{NO}_3)_2$ and then with NaCl solutions. According to your friend's logic, which of these chemical reactions could occur, thus helping you identify the solution in the bottle? (a) Barium sulfate could precipitate. (b) Silver chloride could precipitate. (c) Silver sulfate could precipitate. (d) More than one, but not all, of the reactions described in answers a-c could occur. (e) All three reactions described in answers a-c could occur.

4.6 (a)

Answers to Self-Assessment Exercises



4.3 | Acids, Bases, and Neutralization Reactions



Many acids and bases are industrial and household substances, and some are important components of biological fluids. Hydrochloric acid, for example, is an important industrial chemical and the main constituent of gastric juice in your stomach. Vinegar and lemon juice are common household acids. Ammonia and baking soda (sodium hydrogen carbonate) are common household bases. Acids and bases are also common electrolytes.

By the end of this section, you should be able to

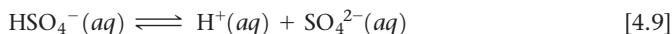
- Recognize the common types of reaction that acids and bases undergo

Acids

As noted in Section 2.8, **acids** are substances that ionize in aqueous solution to form hydrogen ions $\text{H}^+(aq)$. Because a hydrogen atom consists of a proton and an electron, H^+ is simply a proton. Thus, acids are often called *proton donors*. Molecular models of four common acids are shown in **Figure 4.4**.

Protons in aqueous solution are solvated by water molecules, just as other cations are [Figure 4.2(a)]. In writing chemical equations involving protons in water, therefore, we write $\text{H}^+(aq)$.

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



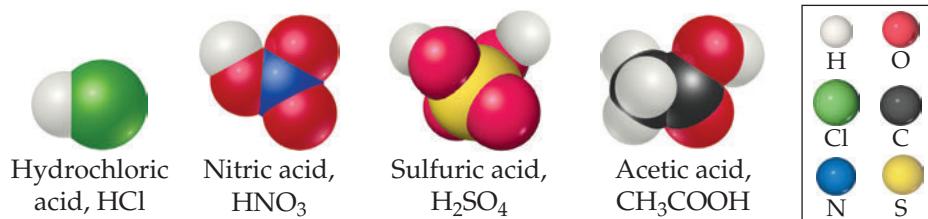
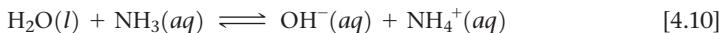
Although H_2SO_4 is a strong electrolyte, only the first ionization (Equation 4.8) is complete. Thus, aqueous solutions of sulfuric acid contain a mixture of $\text{H}^+(aq)$, $\text{HSO}_4^-(aq)$, and $\text{SO}_4^{2-}(aq)$.

The molecule CH_3COOH (acetic acid) that we have mentioned previously is the primary component in vinegar. Acetic acid has four hydrogens, as Figure 4.4 shows, but only one of them, the H that is bonded to an oxygen in the $-\text{COOH}$ group, is ionized in water. Thus, the H in the COOH group breaks its O—H bond in water. The three other hydrogens in acetic acid are bound to carbon and do not break their C—H bonds in water. The reasons for this difference are very interesting and will be discussed in Chapter 16.

Bases

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

Compounds that do not contain OH^- ions can also be bases. For example, ammonia (NH_3) is a common base. When added to water, it accepts an H^+ ion from a water molecule and thereby produces an OH^- ion (**Figure 4.5**):



► **Figure 4.4** Molecular models of four common acids.

► **Figure 4.5 Proton transfer.** An H_2O molecule acts as a proton donor (acid), and NH_3 acts as a proton acceptor (base). In aqueous solutions, only a fraction of the NH_3 molecules react with H_2O . Consequently, NH_3 is a weak electrolyte.

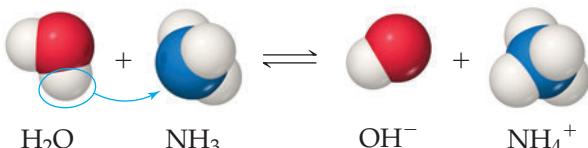


TABLE 4.2 Common Strong Acids and Bases

Strong Acids	Strong Bases
Hydrochloric acid, HCl	Group 1 metal hydroxides [LiOH, NaOH, KOH, RbOH, CsOH]
Hydrobromic acid, HBr	Some Group 2 metal hydroxides [Ca(OH) ₂ , Sr(OH) ₂ , Ba(OH) ₂]
Hydroiodic acid, HI	
Chloric acid, HClO ₃	
Perchloric acid, HClO ₄	
Nitric acid, HNO ₃	
Sulfuric acid (first proton), H ₂ SO ₄	

Ammonia is a weak electrolyte because only about 1% of the NH₃ forms NH₄⁺ and OH⁻ ions.

Strong and Weak Acids and Bases

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

Table 4.2 lists the strong acids and bases we are most likely to encounter. You need to commit this information to memory in order to correctly identify strong electrolytes and write net ionic equations. The brevity of this list tells us that most acids are weak. (For H₂SO₄, as we noted earlier, only the first proton completely ionizes.) The only common strong bases are the common soluble metal hydroxides. The most common weak base is NH₃, which reacts with water to form OH⁻ ions (Equation 4.10).

Identifying Strong and Weak Electrolytes

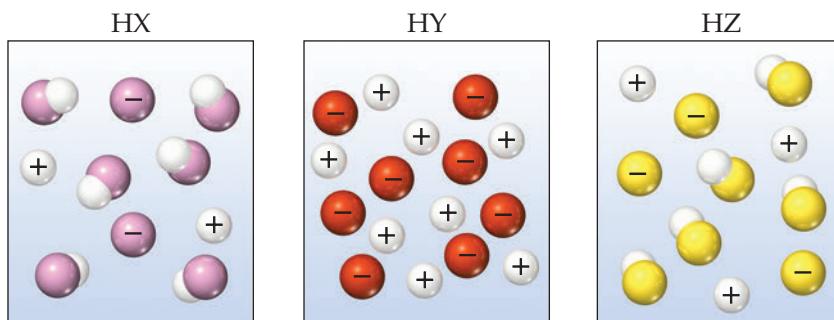
If we remember the common strong acids and bases (Table 4.2) and also remember that NH₃ is a weak base, we can make reasonable predictions about the electrolytic strength of



Sample Exercise 4.5

Comparing Acid Strengths

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



SOLUTION

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

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

Solve The order is $HY > HZ > HX$. HY is a strong acid because it is totally ionized (no HY molecules in solution), whereas both HX and HZ are weak acids, whose solutions consist of a mixture

of molecules and ions. Because HZ contains more H^+ ions and fewer molecules than HX , it is a stronger acid.

► Practice Exercise

A set of aqueous solutions are prepared containing different acids at the same concentration: acetic acid, chloric acid, and hydrobromic acid. Which solution(s) are the most electrically conductive? (a) chloric acid (b) hydrobromic acid (c) acetic acid (d) both chloric acid and hydrobromic acid (e) all three solutions have the same electrical conductivity

a great number of *water-soluble* substances. **Table 4.3** summarizes our observations about electrolytes. We first ask whether the substance is ionic or molecular. If it is ionic, it is a strong electrolyte. If the substance is molecular, we ask whether it is an acid or a base. (It is an acid if it either has H first in the chemical formula or contains a COOH group.) If it is an acid, we use Table 4.2 to determine whether it is a strong or weak electrolyte: All strong acids are strong electrolytes, and all weak acids are weak electrolytes. If an acid is not listed in Table 4.2, it is probably a weak acid and therefore a weak electrolyte.

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

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

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



Sample Exercise 4.6

Identifying Strong, Weak, and Nonelectrolytes

Classify these dissolved substances as a strong electrolyte, weak electrolyte, or nonelectrolyte: $CaCl_2$, HNO_3 , C_2H_5OH (ethanol), $HCOOH$ (formic acid), KOH .

SOLUTION

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

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

Solve Two compounds fit the criteria for ionic compounds: $CaCl_2$ and KOH . Because Table 4.3 tells us that all ionic compounds are strong electrolytes, that is how we classify these two substances. The three remaining compounds are molecular. Two of these molecular substances, HNO_3 and $HCOOH$, are acids. Nitric acid, HNO_3 , is a common strong acid, as shown in Table 4.2, and therefore is a strong electrolyte. Because most acids are weak acids, our

best guess would be that $HCOOH$ is a weak acid (weak electrolyte), which is in fact the case. The remaining molecular compound, C_2H_5OH , is neither an acid nor a base, so it is a nonelectrolyte.

Comment Although ethanol, C_2H_5OH , has an OH group, it is not a metal hydroxide and therefore not a base. Rather, ethanol is a member of a class of organic compounds that have C—OH bonds, which are known as alcohols. Organic compounds containing the COOH group are called carboxylic acids (Chapter 16). Molecules that have this group are weak acids.

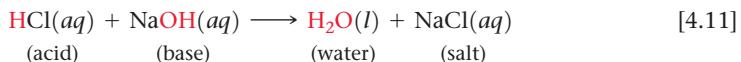
► Practice Exercise

Which of these substances, when dissolved in water, is a strong electrolyte? (a) ammonia (b) hydrofluoric acid (c) folic acid (d) sodium nitrate (e) sucrose

Neutralization Reactions and Salts

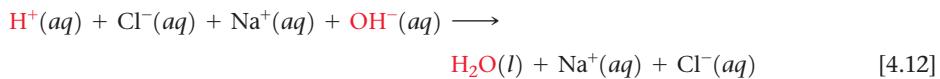
The properties of acidic solutions are quite different from those of basic solutions. Acids have a sour taste, whereas bases have a bitter taste.* Acids change the colors of certain dyes in a way that differs from the way bases affect the same dyes. This is the principle behind the indicator known as litmus paper (**Figure 4.6**). Acid–base chemistry is an important theme throughout all of chemistry that we begin to explore here.

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



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

Because HCl, NaOH, and NaCl are all water-soluble strong electrolytes, the complete ionic equation associated with Equation 4.11 is



Therefore, the net ionic equation is



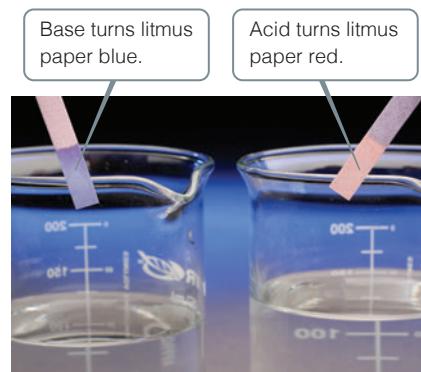
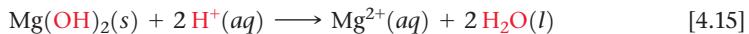
Equation 4.13 summarizes the main feature of the neutralization reaction between any strong acid and any strong base: $\text{H}^+(aq)$ and $\text{OH}^-(aq)$ ions combine to form $\text{H}_2\text{O}(l)$.

Figure 4.7 shows the neutralization reaction between hydrochloric acid and the water-insoluble base $\text{Mg}(\text{OH})_2$:

Molecular equation:



Net ionic equation:



▲ **Figure 4.6** **Litmus paper.** Litmus paper is coated with dyes that change color in response to exposure to either acids or bases.

Sample Exercise 4.7

Writing Chemical Equations for a Neutralization Reaction

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

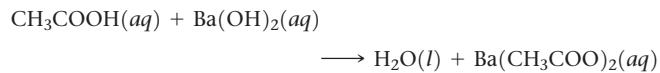
SOLUTION

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

Plan As Equation 4.11 and the italicized statement that follows it indicate, neutralization reactions form two products, H_2O and a salt. We examine the cation of the base and the anion of the acid to determine the composition of the salt.

Solve

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

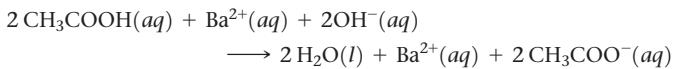
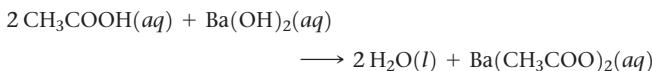


*Tasting chemical solutions is not a good practice. However, we have all had acids such as ascorbic acid (vitamin C), acetylsalicylic acid (aspirin), and citric acid (in citrus fruits) in our mouths, and we are familiar with their characteristic sour taste. Soaps, which are basic, have the characteristic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

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

- (b) To write the complete ionic equation, we identify the strong electrolytes and break them into ions. In this case $\text{Ba}(\text{OH})_2$ and $\text{Ba}(\text{CH}_3\text{COO})_2$ are both water-soluble ionic compounds and hence strong electrolytes. Thus, the complete ionic equation is:
- (c) Eliminating the spectator ion, Ba^{2+} , and simplifying coefficients give the net ionic equation:

Check We can determine whether the molecular equation is balanced by counting the number of atoms of each kind on both sides of the arrow (10 H, 6 O, 4 C, and 1 Ba on each side). However, it is often easier to check equations by counting groups: There are 2 CH_3COO groups, as well as 1 Ba, and 4 additional H atoms and 2 additional O atoms on each side of the equation. The net ionic equation checks out because the numbers of each kind of element and the net charge are the same on both sides of the equation.



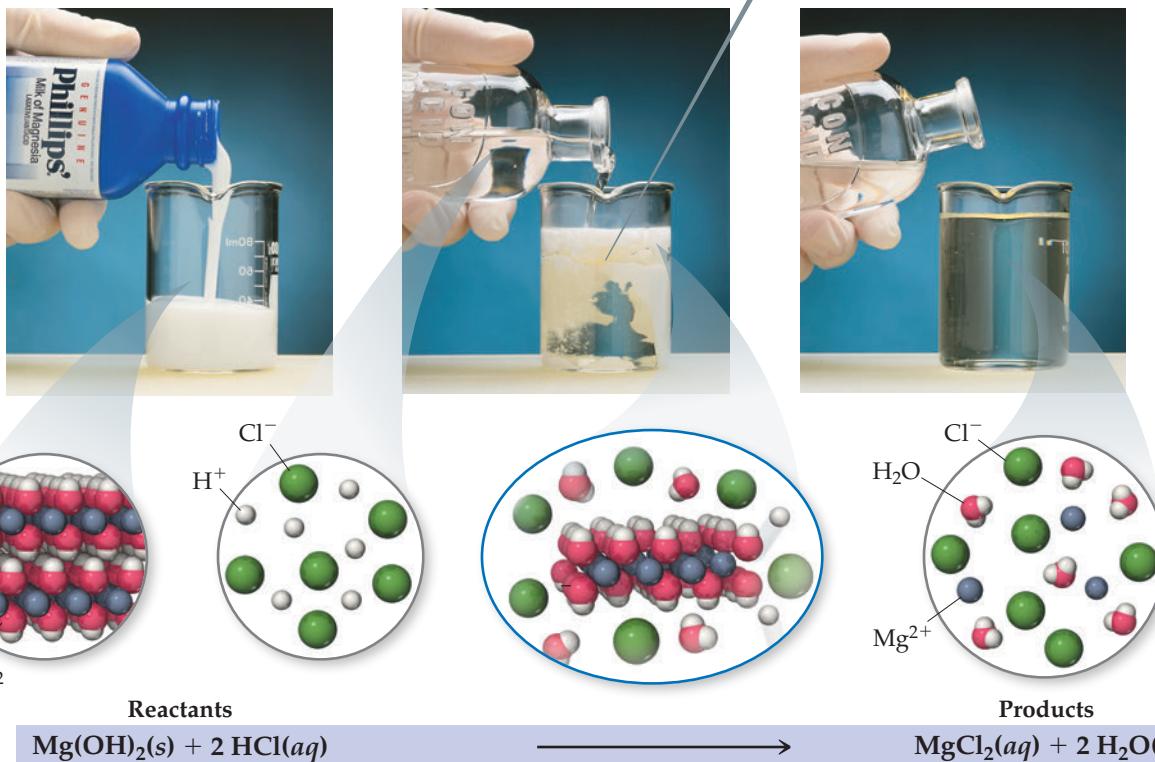
► Practice Exercise

Which is the correct net ionic equation for the reaction of aqueous ammonia with nitric acid?

- (a) $\text{NH}_4^+(aq) + \text{H}^+(aq) \longrightarrow \text{NH}_5^{2+}(aq)$
- (b) $\text{NH}_3(aq) + \text{NO}_3^-(aq) \longrightarrow \text{NH}_2^-(aq) + \text{HNO}_3(aq)$
- (c) $\text{NH}_2^-(aq) + \text{H}^+(aq) \longrightarrow \text{NH}_3(aq)$
- (d) $\text{NH}_3(aq) + \text{H}^+(aq) \longrightarrow \text{NH}_4^+(aq)$
- (e) $\text{NH}_4^+(aq) + \text{NO}_3^-(aq) \longrightarrow \text{NH}_4\text{NO}_3(aq)$

Go Figure

If you used nitric acid instead of hydrochloric acid in this reaction, what products would form?



▲ **Figure 4.7** Neutralization reaction between $\text{Mg}(\text{OH})_2(s)$ and hydrochloric acid. Milk of magnesia is a suspension of water-insoluble magnesium hydroxide, $\text{Mg}(\text{OH})_2(s)$, in water. When sufficient hydrochloric acid, $\text{HCl}(aq)$, is added, a reaction ensues that leads to an aqueous solution containing $\text{Mg}^{2+}(aq)$ and $\text{Cl}^-(aq)$ ions.

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

Neutralization Reactions with Gas Formation

Many bases besides OH^- react with H^+ to form molecular compounds. Two of these that you might encounter in the laboratory are the sulfide ion and the carbonate ion. Both of these anions react with acids to form gases that have low solubilities in water.

Hydrogen sulfide (H_2S), the substance that gives rotten eggs their foul odor, forms when an acid such as $\text{HCl}(aq)$ reacts with a metal sulfide such as Na_2S :

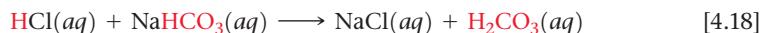
Molecular equation:



Net ionic equation:



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

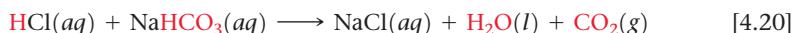


Carbonic acid is unstable. If present in solution in sufficient concentrations, it decomposes to H_2O and CO_2 , which escapes from the solution as a gas:



The overall reaction is summarized by the following equations:

Molecular equation:



Net ionic equation:



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

CHEMISTRY PUT TO WORK | Antacids

Your stomach secretes acids to help digest foods. These acids, which include hydrochloric acid, contain about 0.1 mol of H^+ per liter of solution. The stomach and digestive tract are normally protected from the corrosive effects of stomach acid by a mucosal lining. Holes can develop in this lining, however, allowing the acid to attack the underlying tissue, causing painful damage. These holes, known as ulcers, can be caused by the secretion of excess acids and/or by a weakness in the digestive lining. Many peptic ulcers are caused by infection by the bacterium *Helicobacter pylori*. Many people suffer from ulcers at some point in their lives. Many others experience occasional

indigestion, heartburn, or reflux due to digestive acids entering the esophagus.

The problem of excess stomach acid can be addressed by (1) removing the excess acid or (2) decreasing the production of acid. Substances that remove excess acid are called *antacids*, whereas those that decrease acid production are called *acid inhibitors*. Figure 4.8 shows several common over-the-counter antacids, which usually contain hydroxide, carbonate, or bicarbonate ions (Table 4.4). Antilulcer drugs, such as Tagamet® and Zantac®, are acid inhibitors. They act on acid-producing cells in the lining of the stomach. Formulations that control acid in this way are now available as over-the-counter drugs.

Related Exercise: 4.99



▲ Figure 4.8 Antacids. These products all serve as acid-neutralizing agents in the stomach.

TABLE 4.4 Some Common Antacids

Commercial Name	Acid-Neutralizing Agents
Alka-Seltzer®	NaHCO ₃
Amphojel®	Al(OH) ₃
Di-Gel®	Mg(OH) ₂ and CaCO ₃
Milk of Magnesia	Mg(OH) ₂
Maalox®	Mg(OH) ₂ and Al(OH) ₃
Mylanta®	Mg(OH) ₂ and Al(OH) ₃
Rolaids®	Mg(OH) ₂ and CaCO ₃
Tums®	CaCO ₃

Self-Assessment Exercise

4.12 What is the net ionic equation for the reaction between stomach acid and an antacid containing Al(OH)₃?

- (a) HCl(*aq*) + Al(OH)₃(*s*) → H₂O(*l*) + AlCl₃(*aq*)
- (b) 3HCl(*aq*) + Al(OH)₃(*s*) → 3H₂O(*l*) + AlCl₃(*aq*)
- (c) 3H⁺(*aq*) + Al(OH)₃(*s*) → 3H₂O(*l*) + Al³⁺(*aq*)

Exercises

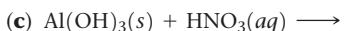
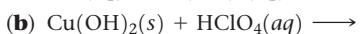
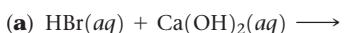
4.13 State whether each of the following statements is true or false. Justify your answer in each case.

- (a) Sulfuric acid is a monoprotic acid.
- (b) HCl is a weak acid.
- (c) Methanol is a base.

4.14 Label each of the following substances as an acid, base, salt, or none of these. Indicate whether the substance exists in aqueous solution entirely in molecular form, entirely as ions, or as a mixture of molecules and ions. (a) HF, (b) acetonitrile, CH₃CN, (c) NaClO₄, (d) Ba(OH)₂.

4.15 Classify each of the following substances as a nonelectrolyte, weak electrolyte, or strong electrolyte in water: (a) HF, (b) C₆H₅COOH (benzoic acid), (c) C₆H₆ (benzene), (d) CoCl₃, (e) AgNO₃.

4.16 Complete and balance the following molecular equations, and then write the net ionic equation for each:



4.17 Write balanced molecular and net ionic equations for the following reactions, and identify the gas formed in each:

(a) solid cadmium sulfide reacts with an aqueous solution of sulfuric acid; (b) solid magnesium carbonate reacts with an aqueous solution of perchloric acid.

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

4.12 (c)

Answers to Self-Assessment Exercises



4.4 | Oxidation–Reduction Reactions



Almost all metals will corrode when exposed to the atmosphere, a process in which the metal reacts to form a compound and loses its characteristic luster. Gold and platinum are exceptions, making these metals highly prized for jewelry. In a few cases, a surface coating of corrosion is just unsightly, but in many cases, it is associated with an undesirable economic impact. Forming a compound from a metal is nearly always accompanied by an increase in volume that can compromise the integrity of a structure. In extreme situations, this has resulted in the catastrophic failure of the structure: the collapse of the Morandi bridge in Genoa, Italy on 14 August 2018 resulted in 43 fatalities.

By the end of this section, you should be able to

- Understand the processes involved in redox reactions

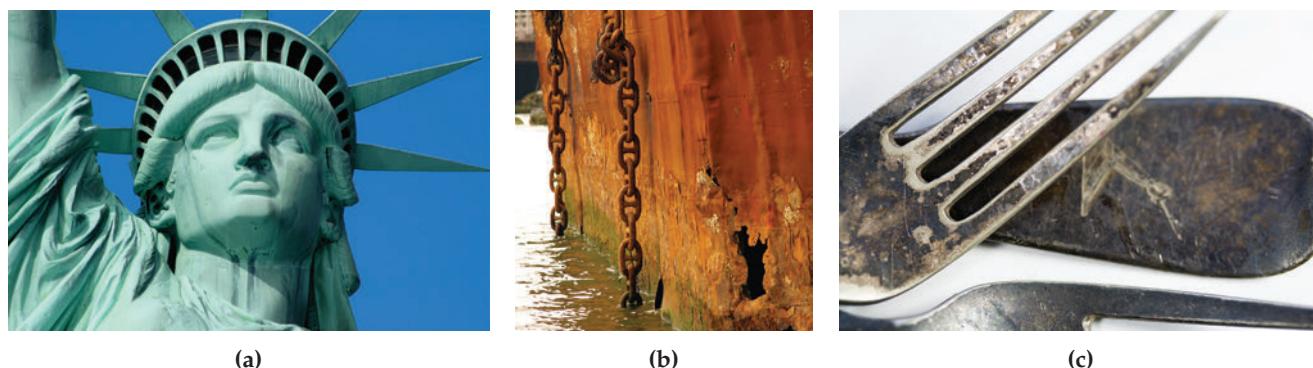
In precipitation reactions, cations and anions come together to form an insoluble ionic compound. In neutralization reactions, protons are transferred from one reactant to another. Now let's consider a third kind of reaction, one in which electrons are transferred from one reactant to another. Such reactions are called either **oxidation-reduction reactions** or **redox reactions**. In this section, we concentrate on redox reactions where one of the reactants is a metal in its elemental form. Redox reactions are critical in understanding many biological and geological processes in the world around us; they also form the basis for energy-related technologies such as batteries and fuel cells (Chapter 20).

Oxidation and Reduction

One of the most familiar redox reactions is *corrosion* of a metal (Figure 4.9). In some instances, corrosion is limited to the surface of the metal, as is the case with the green coating that forms on copper roofs and statues. In other instances, the corrosion goes deeper, eventually compromising the structural integrity of the metal, as happens with the rusting of iron.

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

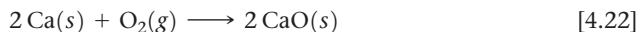
When an atom, ion, or molecule becomes more positively charged (that is, when it loses electrons), we say that it has been *oxidized*. Loss of electrons by a substance is called **oxidation**. The term *oxidation* is used because the first reactions of this sort to be studied were reactions with oxygen. Many metals react directly with O_2 in air to form metal oxides. In these reactions, the metal loses electrons to oxygen, forming an ionic



▲ **Figure 4.9** Familiar corrosion products. (a) A green coating forms when copper is oxidized. (b) Rust forms when iron corrodes. (c) A black tarnish forms as silver corrodes.

compound of the metal ion and oxide ion. The familiar example of rusting involves the reaction between iron metal and oxygen in the presence of water. In this process, Fe is *oxidized* (loses electrons) to form Fe^{3+} .

The reaction between iron and oxygen tends to be relatively slow, but other metals, such as the alkali and alkaline earth metals, react quickly upon exposure to air. **Figure 4.10** shows how the bright metallic surface of calcium tarnishes as CaO forms in the reaction



In this reaction, Ca is oxidized to Ca^{2+} and neutral O_2 is transformed to O^{2-} ions. In Equation 4.22, the oxidation involves transfer of electrons from the calcium metal to the O_2 , leading to formation of CaO . When an atom, ion, or molecule becomes more negatively charged (gains electrons), we say that it is *reduced*. The gain of electrons by a substance is called **reduction**. When one reactant loses electrons (that is, when it is oxidized), another reactant must gain them. In other words, oxidation of one substance must be accompanied by reduction of some other substance. In Equation 4.22, then, molecular oxygen is reduced to oxide (O^{2-}) ions.

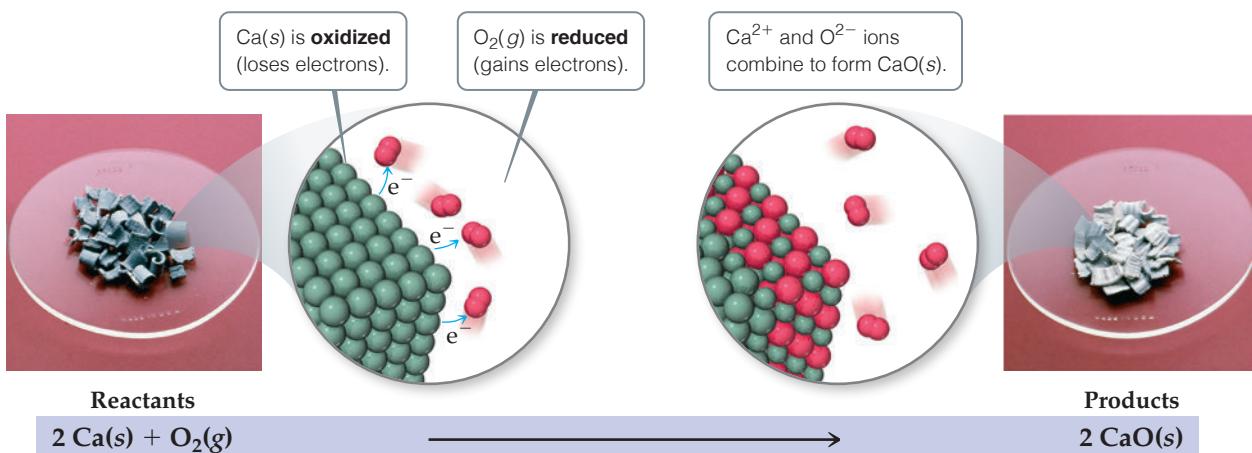
Oxidation Numbers

Before we can identify an oxidation-reduction reaction, we must have a bookkeeping system—a way of keeping track of electrons gained by the substance being reduced and electrons lost by the substance being oxidized. The concept of oxidation numbers (also called *oxidation states*) was devised as a way of doing this. Each atom in a neutral substance or ion is assigned an **oxidation number** (also known as an **oxidation state**). For monatomic ions, the oxidation number is the same as the charge. For neutral molecules



Go Figure

How many electrons does each oxygen atom gain during the course of this reaction?



▲ **Figure 4.10** Oxidation of calcium metal by molecular oxygen.

and polyatomic ions, the oxidation number of a given atom is a hypothetical charge. This charge is assigned by artificially dividing up the electrons among the atoms in the molecule or ion. We use the following rules for assigning oxidation numbers:

1. *For an atom in its elemental form, the oxidation number is always zero.* Thus, each H atom in the H₂ molecule has an oxidation number of 0, and each P atom in the P₄ molecule has an oxidation number of 0.

2. *For any monatomic ion, the oxidation number equals the ionic charge.* Thus, K⁺ has an oxidation number of +1, S²⁻ has an oxidation number of -2, and so forth.

In ionic compounds the alkali metal ions (Group 1) always have a 1+ charge and therefore an oxidation number of +1. The alkaline earth metals (Group 2) are always +2, and aluminum (Group 13) is always +3 in ionic compounds. (In writing oxidation numbers, we will write the sign before the number to distinguish them from the actual electronic charges, which we write with the number first.)

3. Nonmetals usually have negative oxidation numbers, although they can sometimes be positive:

(a) *The oxidation number of oxygen is usually -2 in both ionic and molecular compounds.* The major exception is in compounds called peroxides, which contain the O₂²⁻ ion, giving each oxygen an oxidation number of -1.

(b) *The oxidation number of hydrogen is usually +1 when bonded to nonmetals and -1 when bonded to metals* (for example, metal hydrides such as sodium hydride, NaH).

(c) *The oxidation number of fluorine is -1 in all compounds.* The other **halogens** have an oxidation number of -1 in most binary compounds. When combined with oxygen, as in oxyanions, however, they have positive oxidation states.

4. The sum of the oxidation numbers of all atoms in a neutral compound is zero. *The sum of the oxidation numbers in a polyatomic ion equals the charge of the ion.* For example, in the hydronium ion H₃O⁺, which is a more accurate description of H⁺(aq), the oxidation number of each hydrogen is +1 and that of oxygen is -2. Thus, the sum of the oxidation numbers is 3(+1) + (-2) = +1, which equals the net charge of the ion. This rule is useful in obtaining the oxidation number of one atom in a compound or ion if you know the oxidation numbers of the other atoms, as illustrated in Sample Exercise 4.8.



Sample Exercise 4.8

Determining Oxidation Numbers

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

SOLUTION

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

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

Solve

- (a) When bonded to a nonmetal, hydrogen has an oxidation number of +1. Because the H₂S molecule is neutral, the sum of the oxidation numbers must equal zero. Letting x equal the oxidation number of S, we have 2(+1) + x = 0. Thus, S has an oxidation number of -2.
- (b) Because S₈ is an elemental form of sulfur, the oxidation number of S is 0.
- (c) Because SCl₂ is a binary compound, we expect chlorine to have an oxidation number of -1. The sum of the oxidation numbers must equal zero. Letting x equal the oxidation number of S, we have x + 2(-1) = 0. Consequently, the oxidation number of S must be +2.

(d) Sodium, an alkali metal, always has an oxidation number of +1 in its compounds. Oxygen commonly has an oxidation number of -2. Letting x equal the oxidation number of S, we have 2(+1) + x + 3(-2) = 0. Therefore, the oxidation number of S in this compound (Na₂SO₃) is +4.

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

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

► Practice Exercise

In which compound is the oxidation state of oxygen -1?

- (a) O₂ (b) H₂O (c) H₂SO₄ (d) H₂O₂ (e) KCH₃COO

Oxidation of Metals by Acids and Salts

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

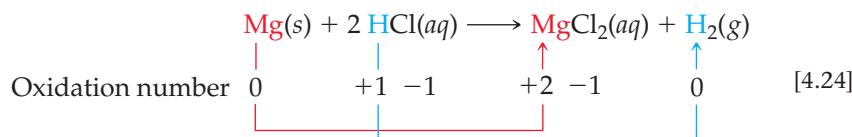


Examples:



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

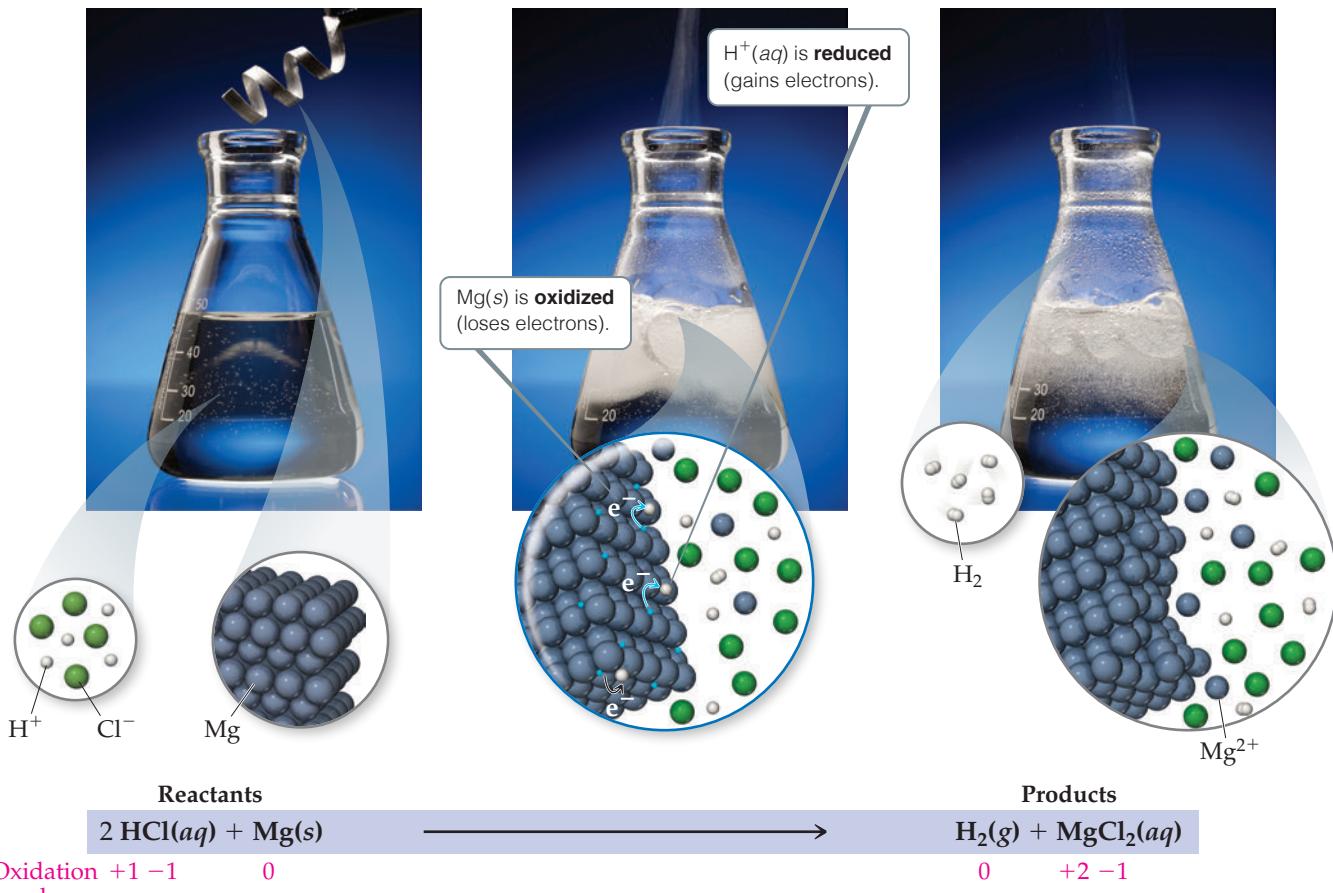
Many metals undergo displacement reactions with acids, producing salts and hydrogen gas. For example, magnesium metal reacts with hydrochloric acid to form magnesium chloride and hydrogen gas (Figure 4.11):



The oxidation number of Mg changes from 0 to +2, an increase that indicates the atom has lost electrons and has therefore been oxidized. The oxidation number of H⁺ in the acid decreases from +1 to 0, indicating that this ion has gained electrons and has therefore

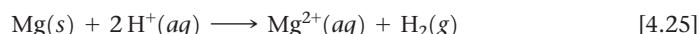
Go Figure

How many moles of hydrogen gas would be produced for every mole of magnesium added into the HCl solution?

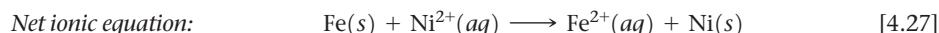
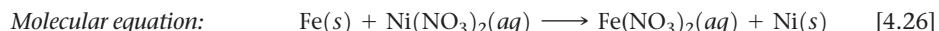


▲ Figure 4.11 Reaction of magnesium metal with hydrochloric acid. The metal is readily oxidized by the acid, producing hydrogen gas, H₂(g), and MgCl₂(aq).

been reduced. Chlorine has an oxidation number of -1 both before and after the reaction, indicating that it is neither oxidized nor reduced. In fact, the Cl^- ions are spectator ions, dropping out of the net ionic equation:



Metals can also be oxidized by aqueous solutions of various salts. Iron metal, for example, is oxidized to Fe^{2+} by aqueous solutions of Ni^{2+} such as $\text{Ni}(\text{NO}_3)_2(aq)$:



The oxidation of Fe to Fe^{2+} in this reaction is accompanied by the reduction of Ni^{2+} to Ni.

Remember: *Whenever one substance is oxidized, another substance must be reduced.*



Sample Exercise 4.9

Writing Equations for Oxidation-Reduction Reactions

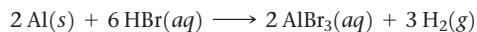
Write the balanced molecular and net ionic equations for the reaction of aluminum with hydrobromic acid.

SOLUTION

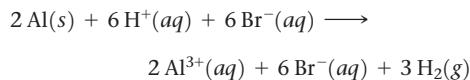
Analyze We must write two equations—molecular and net ionic—for the redox reaction between a metal and an acid.

Plan Metals react with acids to form salts and H_2 gas. To write the balanced equations, we must write the chemical formulas for the two reactants and then determine the formula of the salt, which is composed of the cation formed by the metal and the anion of the acid.

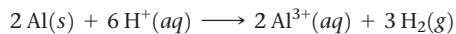
Solve The reactants are Al and HBr. The cation formed by Al is Al^{3+} , and the anion from hydrobromic acid is Br^- . Thus, the salt formed in the reaction is AlBr_3 . Writing the reactants and products and then balancing the equation gives the molecular equation:



Both HBr and AlBr_3 are soluble strong electrolytes. Thus, the complete ionic equation is



Because Br^- is a spectator ion, the net ionic equation is



Comment The substance oxidized is the aluminum metal because its oxidation state changes from 0 in the metal to +3 in the cation, thereby increasing in oxidation number. The H^+ is reduced because its oxidation state changes from +1 in the acid to 0 in H_2 .

► Practice Exercise

Which of the following statements is true about the reaction between zinc and copper sulfate? (a) Zinc is oxidized, and copper ion is reduced. (b) Zinc is reduced, and copper ion is oxidized. (c) All reactants and products are soluble strong electrolytes. (d) The oxidation state of copper in copper sulfate is 0. (e) More than one of the previous choices are true.

The Activity Series

Can we predict whether a certain metal will be oxidized either by an acid or by a particular salt? This question is of practical importance as well as chemical interest. According to Equation 4.26, for example, it would be unwise to store a solution of nickel nitrate in an iron container because the solution would dissolve the container. When a metal is oxidized, it forms various compounds. Extensive oxidation can lead to the failure of metal machinery parts or the deterioration of metal structures.

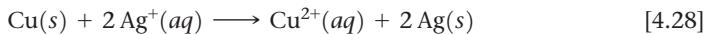
Different metals vary in the ease with which they are oxidized. Zn is oxidized by aqueous solutions of Cu^{2+} , for example, but Ag is not. Zn, therefore, loses electrons more readily than Ag; that is, Zn is easier to oxidize than Ag.

A list of metals arranged in order of decreasing ease of oxidation, such as in **Table 4.5**, is called an **activity series**. The metals at the top of the table, such as the alkali metals and the alkaline earth metals, are most easily oxidized; that is, they react most readily to form compounds. They are called the *active metals*. The metals at the bottom of the activity series, such as the transition elements from Groups 8 to 11, are very stable and form compounds less readily. These metals, which are used to make coins and jewelry, are called *noble metals* because of their low reactivity.

TABLE 4.5 Activity Series of Metals in Aqueous Solution

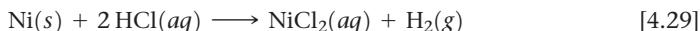
Metal	Oxidation Reaction	Ease of oxidation increases
Lithium	$\text{Li}(s) \longrightarrow \text{Li}^+(aq) + \text{e}^-$	
Potassium	$\text{K}(s) \longrightarrow \text{K}^+(aq) + \text{e}^-$	
Barium	$\text{Ba}(s) \longrightarrow \text{Ba}^{2+}(aq) + 2\text{e}^-$	
Calcium	$\text{Ca}(s) \longrightarrow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

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

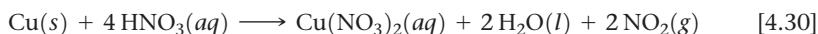


The oxidation of copper to copper ions is accompanied by the reduction of silver ions to silver metal. The silver metal is evident on the surface of the copper wire in **Figure 4.12**. The copper(II) nitrate produces a blue color in the solution, as can be seen most clearly in the photograph on the right of Figure 4.12.

Only metals above hydrogen in the activity series are able to react with acids to form H₂. For example, Ni reacts with HCl(aq) to form H₂:



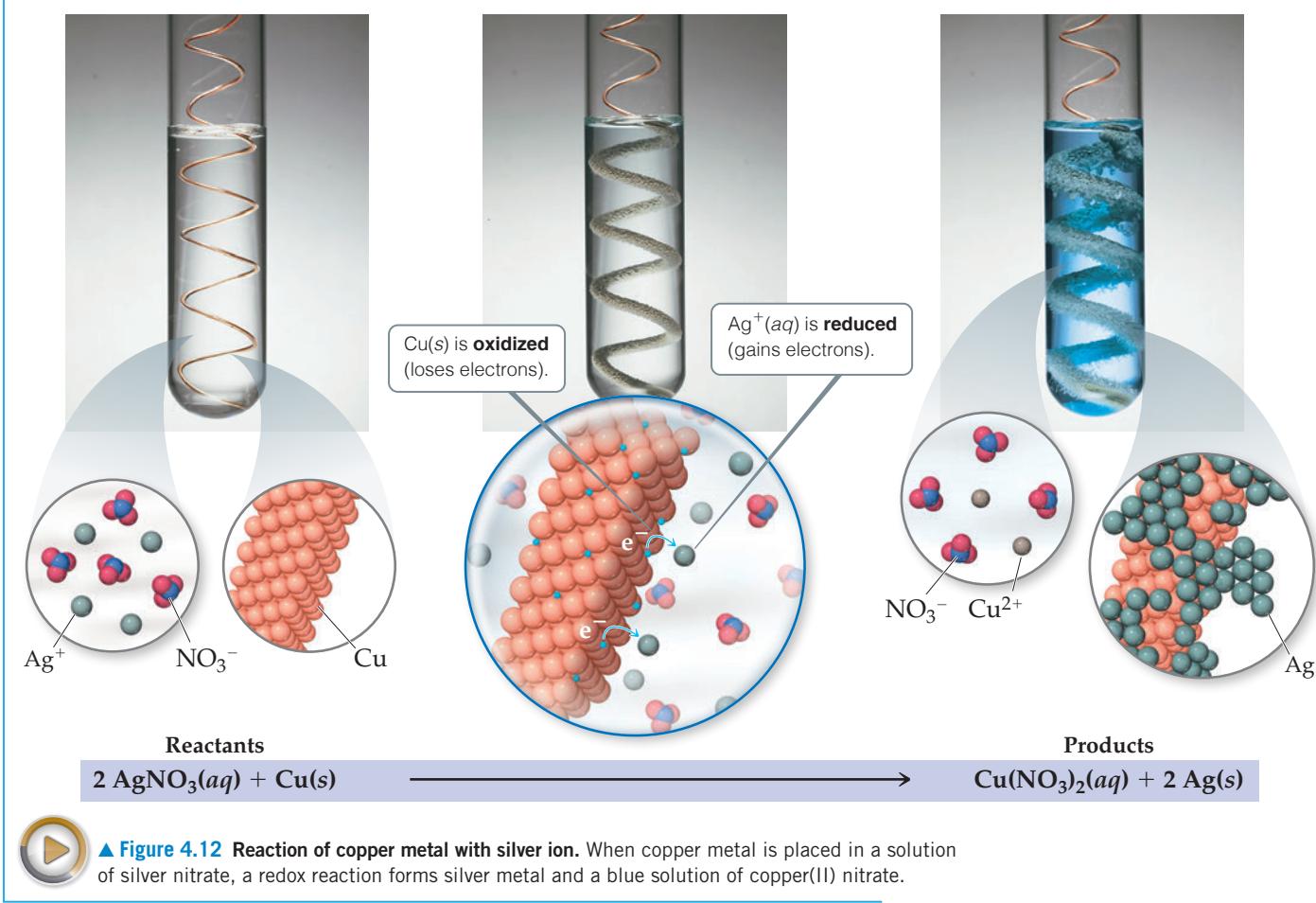
Because elements below hydrogen in the activity series are not oxidized by H⁺, Cu does not react with HCl(aq). Interestingly, copper does react with nitric acid, as shown in Figure 1.11, but the reaction is not oxidation of Cu by H⁺ ions. Instead, the metal is oxidized to Cu²⁺ by the nitrate ion, accompanied by the formation of brown nitrogen dioxide, NO₂(g):



As the copper is oxidized in this reaction, NO₃⁻, where the oxidation number of nitrogen is +5, is reduced to NO₂, where the oxidation number of nitrogen is +4. We will examine reactions of this type in Chapter 20.

**Go Figure**

Why does this solution turn blue?



▲ **Figure 4.12** Reaction of copper metal with silver ion. When copper metal is placed in a solution of silver nitrate, a redox reaction forms silver metal and a blue solution of copper(II) nitrate.

**Sample Exercise 4.10****Determining If an Oxidation-Reduction Reaction Will Occur**

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

SOLUTION

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

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

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



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



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

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

► Practice Exercise

Which of these metals is the easiest to oxidize?

- (a) gold (b) lithium (c) iron (d) sodium (e) aluminum

STRATEGIES FOR SUCCESS Analyzing Chemical Reactions

In this chapter, you have been introduced to a great number of chemical reactions. It's not easy to get a "feel" for what happens when chemicals react. One goal of this textbook is to help you become more adept at predicting the outcomes of reactions. The key to gaining this "chemical intuition" is to learn how to categorize reactions.

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

- What are the reactants?
- Are they electrolytes or nonelectrolytes?
- Are they acids or bases?
- If the reactants are electrolytes, will metathesis produce a precipitate? Water? A gas?

- If metathesis cannot occur, can the reactants engage in an oxidation-reduction reaction? This requires that there be both a reactant that can be oxidized and a reactant that can be reduced.

Being able to predict what happens during a reaction follows from asking basic questions like these. Each question narrows the set of possible outcomes, steering you ever closer to a likely outcome. Your prediction might not always be entirely correct, but if you keep your wits about you, you will not be far off. As you gain experience, you will begin to look for reactants that might not be immediately obvious, such as water from the solution or oxygen from the atmosphere. Because proton transfer (acid-base) and electron transfer (oxidation-reduction) are involved in a huge number of chemical reactions, knowing the hallmarks of such reactions will mean you are well on your way to becoming an excellent chemist!

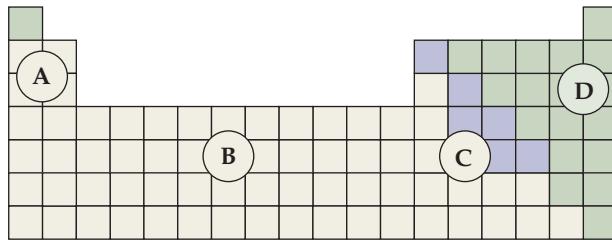
Self-Assessment Exercise

- 4.19** Which combination of metal and metal ion do you expect to undergo a redox reaction?

- Ca(s) and K⁺(aq)
- Fe(s) and Al³⁺(aq)
- Ag(s) and Cu²⁺(aq)
- Fe(s) and Pb²⁺(aq)

Exercises

- 4.20** (a) Which region of the periodic table shown here contains elements that are easiest to oxidize? (b) Which region contains the least readily oxidized elements?



- 4.21** Determine the oxidation number of sulfur in each of the following substances: (a) barium sulfate, BaSO₄, (b) sulfurous acid, H₂SO₃, (c) strontium sulfide, SrS, (d) hydrogen sulfide, H₂S. (e) Locate sulfur in the periodic table in Exercise 4.20; what region is it in? (f) Which region(s) of the periodic table contains elements that can adopt both positive and negative oxidation numbers?

- 4.22** Determine the oxidation number for the indicated element in each of the following substances: (a) S in SO₃,

- (b) Ti in TiCl₄, (c) P in AgPF₆, (d) N in HNO₃, (e) S in H₂SO₃, (f) O in OF₂.

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

- N₂(g) + 3 H₂(g) → 2 NH₃(g)
- 3 Fe(NO₃)₂(aq) + 2 Al(s) → 3 Fe(s) + 2 Al(NO₃)₃(aq)
- Cl₂(aq) + 2 NaI(aq) → I₂(aq) + 2 NaCl(aq)
- PbS(s) + 4 H₂O₂(aq) → PbSO₄(s) + 4 H₂O(l)

- 4.24** Write balanced molecular and net ionic equations for the reactions of (a) manganese with dilute sulfuric acid, (b) chromium with hydrobromic acid, (c) tin with hydrochloric acid, (d) aluminum with formic acid, HCOOH.

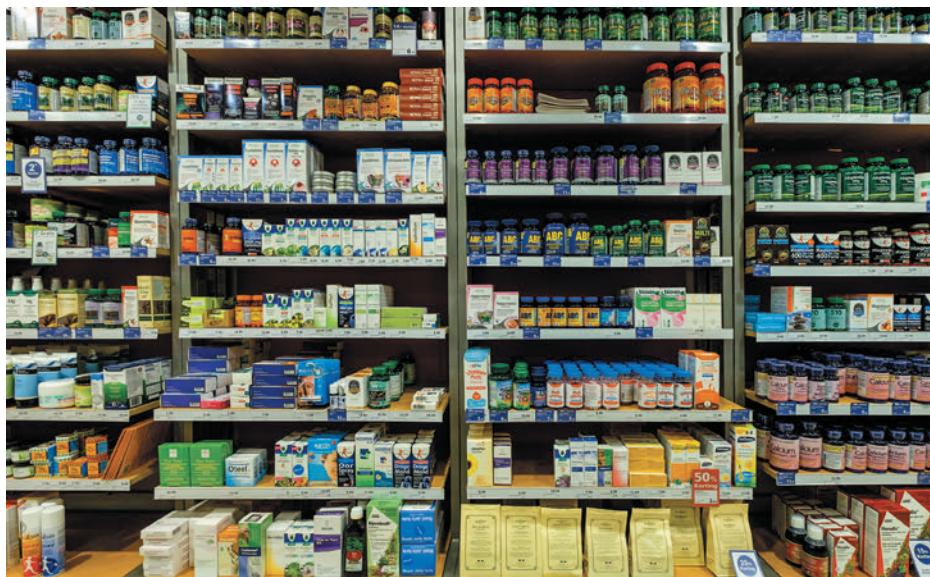
- 4.25** Using the activity series (Table 4.5), write balanced chemical equations for the following reactions. If no reaction occurs, write NR. (a) Iron metal is added to a solution of copper(II) nitrate, (b) zinc metal is added to a solution of magnesium sulfate, (c) hydrobromic acid is added to tin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

4.19 (d)

Answers to Self-Assessment Exercises



4.5 | Concentrations of Solutions



In recent years, we have seen an explosion in the marketing of dietary supplements. Many of these involve “trace elements”—substances we require in small quantities for the healthy functioning of our bodies. While a diet deficient in such essential elements can cause undesirable physiological effects, so too can an excess of the element. For example, there is around 2.3 g of iron in the body of an adult woman and 3.8 g in an adult man. A deficiency of iron can lead to conditions such as anemia, characterized by fatigue among other symptoms, while too much iron can lead to stomach pain and metabolic acidosis. Body chemistry is essentially solution chemistry and an ability to quantify the amount of substance in a solution is essential to its understanding.

By the end of this section, you should be able to

- Convert between mass, moles, and concentration of a soluble substance

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

Molarity

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

$$\text{Molarity} = \frac{\text{moles solute}}{\text{volume of solution in liters}} \quad [4.31]$$

A 1.00 molar solution (written $1.00 M$) contains 1.00 mol of solute in every liter of solution. [Figure 4.13](#) shows the preparation of 0.250 L of a $1.00 M$ solution of CuSO_4 . The molarity of the solution is $(0.250 \text{ mol CuSO}_4)/(0.250 \text{ L soln}) = 1.00 M$. Note that we use the abbreviation “soln” for “solution.”

Expressing the Concentration of an Electrolyte

In biology, the total concentration of ions in solution is very important in metabolic and cellular processes. When an ionic compound dissolves, the relative concentrations of the ions in the solution depend on the chemical formula of the compound. For example, a $1.0 M$ solution of NaCl is $1.0 M$ in Na^+ ions and $1.0 M$ in Cl^- ions, and a $1.0 M$ solution of



▲ Figure 4.13 Preparing 0.250 L of a 1.00 M solution of CuSO_4 .

Sample Exercise 4.11

Calculating Molarity

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

SOLUTION

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

Plan We can calculate molarity using Equation 4.31. To do so, we must convert the number of grams of solute to moles and the volume of the solution from milliliters to liters.

Solve

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

$$\text{Moles Na}_2\text{SO}_4 = (23.4 \text{ g Na}_2\text{SO}_4) \left(\frac{1 \text{ mol Na}_2\text{SO}_4}{142.1 \text{ g Na}_2\text{SO}_4} \right) = 0.165 \text{ mol Na}_2\text{SO}_4$$

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

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

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

► Practice Exercise

What is the molarity of a solution that is made by dissolving 3.68 g of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) in sufficient water to form 275.0 mL of solution? (a) 13.4 M (b) $7.43 \times 10^{-2} \text{ M}$ (c) $3.91 \times 10^{-2} \text{ M}$ (d) $7.43 \times 10^{-5} \text{ M}$ (e) $3.91 \times 10^{-5} \text{ M}$



Sample Exercise 4.12

Calculating Molar Concentrations of Ions

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

SOLUTION

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

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

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

Thus, a solution that is 0.025 M in $\text{Ca}(\text{NO}_3)_2$ is 0.025 M in Ca^{2+} and $2 \times 0.025 \text{ } M = 0.050 \text{ } M$ in NO_3^- :

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

► Practice Exercise

What is the ratio of the concentration of potassium ions to the concentration of carbonate ions in a 0.015 M solution of potassium carbonate? (a) 1:0.015 (b) 0.015:1 (c) 1:1 (d) 1:2 (e) 2:1

Na_2SO_4 is 2.0 M in Na^+ ions and 1.0 M in SO_4^{2-} ions. Thus, the concentration of an electrolyte solution can be specified either in terms of the compound used to make the solution (1.0 M Na_2SO_4) or in terms of the ions in the solution (2.0 M Na^+ and 1.0 M SO_4^{2-}).

Interconverting Molarity, Moles, and Volume

If we know any two of the three quantities in the definition of molarity (Equation 4.31), we can calculate the third. For example, if we know the molarity of an HNO_3 solution to be 0.200 M , which means 0.200 mol of HNO_3 per liter of solution, we can calculate the number of moles of solute in a given volume, say 2.0 L. Molarity therefore is a conversion factor between volume of solution and moles of solute:

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

To illustrate the conversion of moles to volume, let's calculate the volume of 0.30 M HNO_3 solution required to supply 2.0 mol of HNO_3 :

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

Note that in this case we used the reciprocal of molarity in the conversion:

$$\text{Liters} = \text{mol} \times 1/M = \text{mol} \times \text{liters/mol}$$

If one of the solutes is a liquid, we can use its density to convert its mass to volume and vice versa. For example, a typical American beer contains 5.0% ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) by volume in water (along with other components). The density of ethanol is 0.789 g/mL. Therefore, if we wanted to calculate the molarity of ethanol (usually just called "alcohol" in everyday language) in beer, we would first consider 1.00 L of beer.

This 1.00 L of beer contains 0.950 L of water and 0.050 L of ethanol:

$$5\% = 5/100 = 0.050$$

Then we can calculate the moles of ethanol by proper cancellation of units, taking into account the density of ethanol and its molar mass (46.0 g/mol):

$$\text{Moles ethanol} = (0.050 \text{ L}) \left(\frac{1000 \text{ mL}}{\text{L}} \right) \left(\frac{0.789 \text{ g}}{\text{mL}} \right) \left(\frac{1 \text{ mol}}{46.0 \text{ g}} \right) = 0.858 \text{ mol}$$

Because there are 0.858 moles of ethanol in 1.00 L of beer, the concentration of ethanol in beer is 0.86 M (taking into account significant figures).



Sample Exercise 4.13

Using Molarity to Calculate Grams of Solute



How many grams of Na_2SO_4 are required to make 0.350 L of 0.500 M Na_2SO_4 ?

SOLUTION

Analyze We are given the volume of the solution (0.350 L), its concentration (0.500 M), and the identity of the solute Na_2SO_4 and asked to calculate the number of grams of the solute in the solution.

Plan We can use the definition of molarity (Equation 4.31) to determine the number of moles of solute, and then convert moles to grams using the molar mass of the solute.

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

Solve Calculating the moles of Na_2SO_4 using the molarity and volume of solution gives

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

Because each mole of Na_2SO_4 has a mass of 142.1 g, the required number of grams of Na_2SO_4 is

$$\begin{aligned} \text{Grams Na}_2\text{SO}_4 &= (0.175 \text{ mol Na}_2\text{SO}_4) \left(\frac{142.1 \text{ g Na}_2\text{SO}_4}{1 \text{ mol Na}_2\text{SO}_4} \right) \\ &= 24.9 \text{ g Na}_2\text{SO}_4 \end{aligned}$$

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

► Practice Exercise

- (a) How many grams of Na_2SO_4 are there in 15 mL of 0.50 M Na_2SO_4 ? (b) How many milliliters of 0.50 M Na_2SO_4 solution are needed to provide 0.038 mol of this salt?

Dilution

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

Let's see how we can prepare a dilute solution from a concentrated one. Suppose we want to prepare 250.0 mL (that is, 0.2500 L) of 0.100 M CuSO_4 solution by diluting a 1.00 M CuSO_4 stock solution. The main point to remember is that when solvent is added to a solution, the number of moles of solute remains unchanged:

$$\text{Moles solute before dilution} = \text{moles solute after dilution} \quad [4.32]$$

Because we know both the volume (250.0 mL) and the concentration (0.100 mol/L) of the dilute solution, we can calculate the number of moles of CuSO_4 it contains:

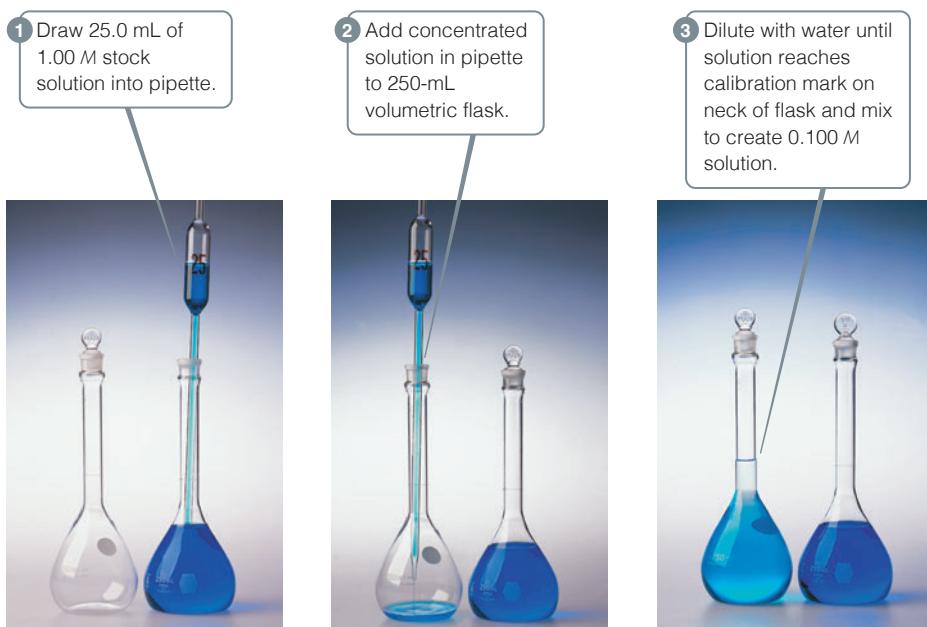
$$\begin{aligned} \text{Moles CuSO}_4 \text{ in dilute soln} &= (0.2500 \text{ L soln}) \left(\frac{0.100 \text{ mol CuSO}_4}{1 \text{ L soln}} \right) \\ &= 0.0250 \text{ mol CuSO}_4 \end{aligned}$$

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

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

Figure 4.14 shows the dilution carried out in the laboratory. Notice that the diluted solution is less intensely colored than the concentrated one.

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



▲ Figure 4.14 Preparing 250.0 mL of 0.100 M CuSO₄ by dilution of 1.00 M CuSO₄.

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

$$\text{Moles solute in conc soln} = \text{moles solute in dilute soln}$$

$$M_{\text{conc}} \times V_{\text{conc}} = M_{\text{dil}} \times V_{\text{dil}} \quad [4.33]$$

Although we derived Equation 4.33 in terms of liters, any volume unit can be used as long as it is used on both sides of the equation. For example, in the calculation we did for the CuSO₄ solution, we have

$$(1.00 \text{ M})(V_{\text{conc}}) = (0.100 \text{ M})(250.0 \text{ mL})$$

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



Sample Exercise 4.14

Preparing a Solution by Dilution

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

SOLUTION

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

Solve

Calculate the moles of H₂SO₄ in the dilute solution:

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

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

Converting liters to milliliters gives 15 mL.

If we apply Equation 4.33, we get the same result:

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

$$(3.0 \text{ M})(V_{\text{conc}}) = (0.10 \text{ M})(450 \text{ mL})$$

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

Either way, we see that if we start with 15 mL of 3.0 M H_2SO_4 and dilute it to a total volume of 450 mL, the desired 0.10 M solution will be obtained.

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

Comment The first approach can also be used to find the final concentration when two solutions of different concentrations are mixed, whereas the second approach, using Equation 4.33,

can be used only for diluting a concentrated solution with pure solvent.

► Practice Exercise

What volume of a 1.00 M stock solution of glucose must be used to make 500.0 mL of a 1.75×10^{-2} M glucose solution in water?

- (a) 1.75 mL (b) 8.75 mL (c) 48.6 mL (d) 57.1 mL (e) 28,570 mL

Self-Assessment Exercise

4.26 Which solution has the greatest number of molecules or ions present?

- (a) 1.00 M FeCl_3
- (b) 1.50 M HCl
- (c) 2.00 M $\text{C}_6\text{H}_{12}\text{O}_6$

Exercises

4.27 (a) Calculate the molarity of a solution that contains 0.175 mol ZnCl_2 in exactly 150 mL of solution. (b) How many moles of protons are present in 35.0 mL of a 4.50 M solution of nitric acid? (c) How many milliliters of a 6.00 M NaOH solution are needed to provide 0.350 mol of NaOH?

4.28 The average adult human male has a total blood volume of 5.0 L. If the concentration of sodium ion in this average individual is 0.135 M, what is the mass of sodium ion circulating in the blood?

4.29 The concentration of alcohol ($\text{CH}_3\text{CH}_2\text{OH}$) in blood, called the “blood alcohol concentration” or BAC, is given in units of grams of alcohol per 100 mL of blood. What is the concentration of alcohol, in terms of molarity, in blood if the BAC is 0.08?

4.30 (a) Which will have the highest concentration of sodium ions: 0.25 M NaCl , 0.15 M Na_2CO_3 , or 0.075 M Na_3PO_4 ? (b) Which will contain the greater number of moles of sodium ion: 20.0 mL of 0.15 M NaHCO_3 or 15.0 mL of 0.04 M Na_2S ?

4.31 Ignoring protolysis reactions, indicate the concentration of each ion or molecule present in the following

solutions: (a) 0.35 M K_3PO_4 , (b) 5×10^{-4} M CuCl_2 , (c) 0.0184 M $\text{CH}_3\text{CH}_2\text{OH}$ (d) a mixture of 35.0 mL of 0.010 M Na_2CO_3 and 50.0 mL of 0.200 M K_2SO_4 . Assume the volumes are additive.

4.32 (a) You have a stock solution of 14.8 M NH_3 . How many milliliters of this solution should you dilute to make 1000.0 mL of 0.250 M NH_3 ? (b) If you take a 10.0-mL portion of the stock solution and dilute it to a total volume of 0.500 L, what will be the concentration of the final solution?

4.33 A medical lab is testing a new anticancer drug on cancer cells. The drug stock solution concentration is 1.5×10^{-9} M, and 1.00 mL of this solution will be delivered to a dish containing 2.0×10^5 cancer cells in 5.00 mL of aqueous fluid. What is the ratio of drug molecules to the number of cancer cells in the dish?

4.34 Pure acetic acid, known as glacial acetic acid, is a liquid with a density of 1.049 g/mL at 25 °C. Calculate the molarity of a solution of acetic acid made by dissolving 20.00 mL of glacial acetic acid at 25 °C in enough water to make 250.0 mL of solution.

4.26 (a)

Answers to Self-Assessment Exercises



4.6 | Solution Stoichiometry and Chemical Analysis

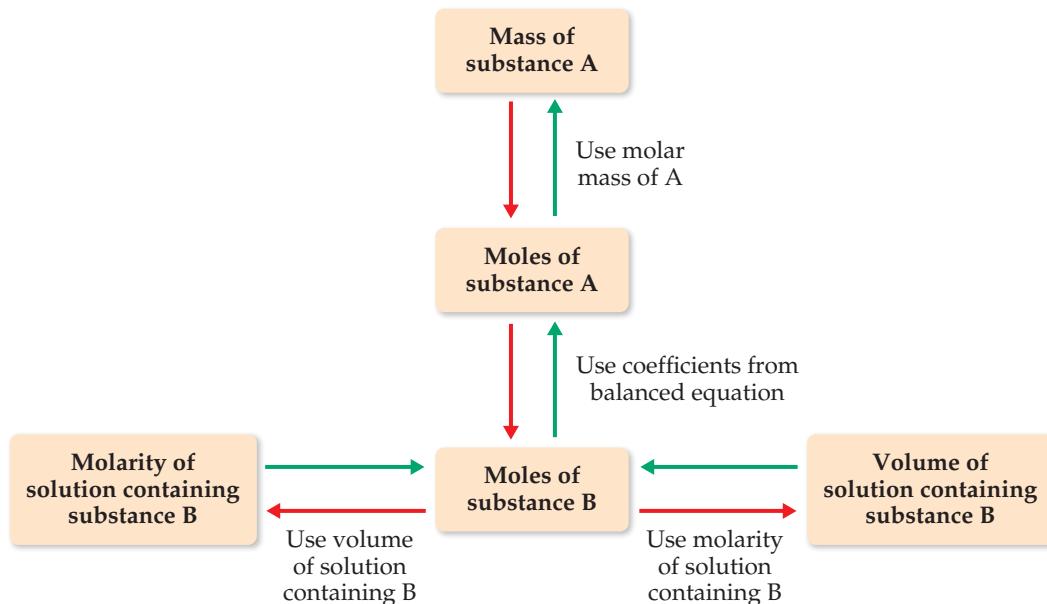


Many reactions occur in solution form. In Chapter 3, we learned that given the chemical equation for a reaction and the amount of one reactant consumed in the reaction, you can calculate the quantities of other reactants and products. In this section we extend this concept to reactions involving solutions.

By the end of this section, you should be able to

- Perform stoichiometric calculations involving solutions.

Recall that the coefficients in a balanced equation give the relative number of moles of reactants and products. To use this information, we must convert the masses of substances involved in a reaction into moles. When dealing with pure substances, as we did in Chapter 3, we use molar mass to convert between grams and moles of the substances. This conversion is not valid when working with a solution because both solute and solvent contribute to its mass. However, if we know the solute concentration, we can use molarity and volume to determine the number of moles (moles solute = $M \times V$). **Figure 4.15** summarizes this approach to using stoichiometry for the reaction between a pure substance and a solution.



▲ Figure 4.15 Procedure for solving stoichiometry problems involving reactions between a pure substance A and a solution containing a known concentration of substance B. Starting from a known mass of substance A, we follow the red arrows to determine either the volume of the solution containing B (if the molarity of B is known) or the molarity of the solution containing B (if the volume of B is known). Starting from either a known volume or a known molarity of the solution containing B, we follow the green arrows to determine the mass of substance A.



Sample Exercise 4.15

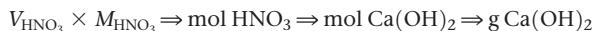
Using Mass Relations in a Neutralization Reaction

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

SOLUTION

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

Plan Following the steps outlined by the green arrows in Figure 4.15, we use the molarity and volume of the HNO_3 solution (substance B in Figure 4.15) to calculate the number of moles of HNO_3 . We then use the balanced equation to relate moles of HNO_3 to moles of $\text{Ca}(\text{OH})_2$ (substance A). Finally, we use the molar mass to convert moles to grams of $\text{Ca}(\text{OH})_2$:



Solve

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

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

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



Thus, 2 mol $\text{HNO}_3 \approx 1$ mol $\text{Ca}(\text{OH})_2$. Therefore, Grams $\text{Ca}(\text{OH})_2 = (2.50 \times 10^{-3} \text{ mol HNO}_3) \times \left(\frac{1 \text{ mol Ca}(\text{OH})_2}{2 \text{ mol HNO}_3} \right) \left(\frac{74.1 \text{ g Ca}(\text{OH})_2}{1 \text{ mol Ca}(\text{OH})_2} \right) = 0.0926 \text{ g Ca}(\text{OH})_2$

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

► Practice Exercise

How many milligrams of sodium sulfide are needed to completely react with 25.00 mL of a 0.0100 M aqueous solution of cadmium nitrate, to form a precipitate of $\text{CdS}(s)$?

- (a) 13.8 mg (b) 19.5 mg (c) 23.5 mg (d) 32.1 mg (e) 39.0 mg

Titrations

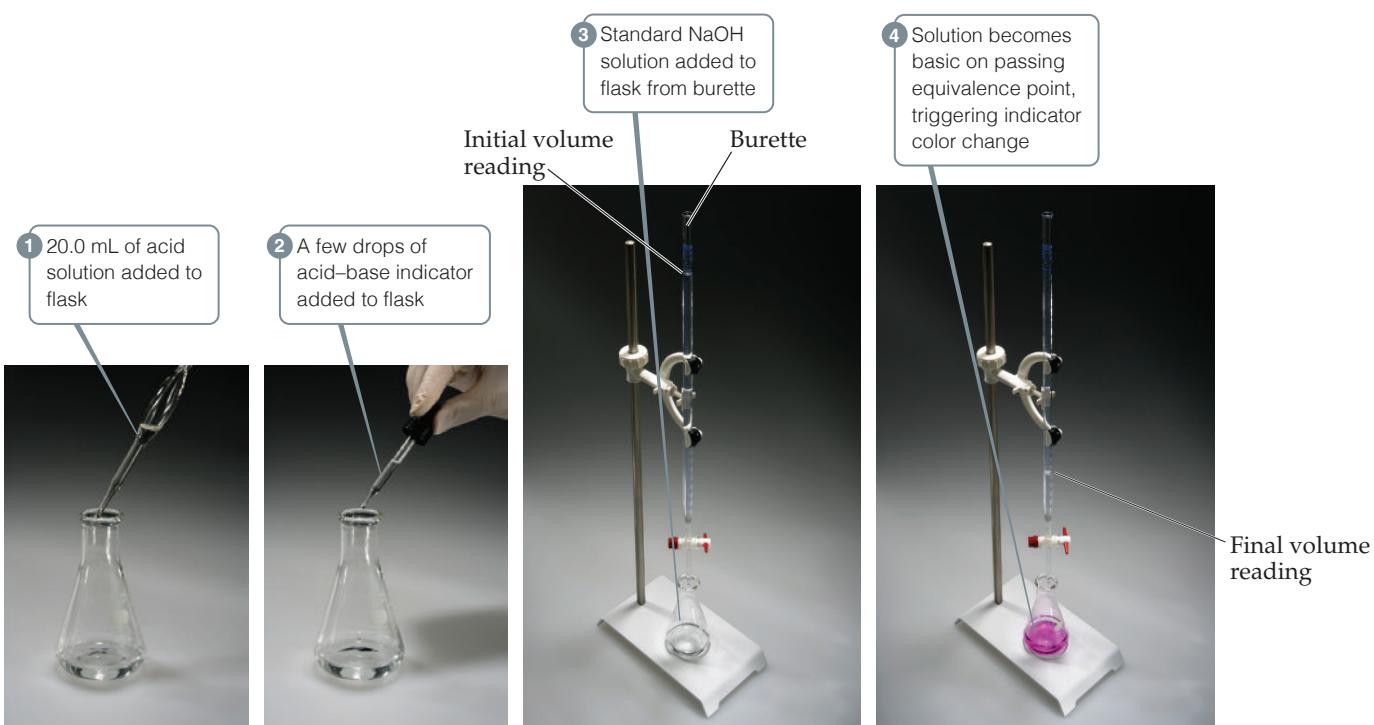
To determine the concentration of a particular solute in a solution, chemists often carry out a **titration**, which involves combining a solution where the solute concentration is not known with a reagent solution of known concentration, called a **standard solution**. Just enough standard solution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

Titration can be conducted using neutralization, precipitation, or oxidation-reduction reactions. Figure 4.16 illustrates a typical neutralization titration, one between an HCl solution of unknown concentration and a standard NaOH solution. To determine the HCl concentration, we first add a specific volume of the HCl solution, 20.0 mL in this example, to a flask. Next we add a few drops of an acid-base **indicator**. The acid-base indicator is a dye that changes color on passing the equivalence point.* For example, the dye phenolphthalein is colorless in acidic solution but pink in basic solution. The standard solution is then slowly added until the solution turns pink, telling us that the neutralization reaction between HCl and NaOH is complete. The standard solution is added from a *burette* so that we can accurately determine the added volume of NaOH solution. Knowing the volumes of both solutions and the concentration of the standard solution, we can calculate the concentration of the unknown solution as diagrammed in Figure 4.17.

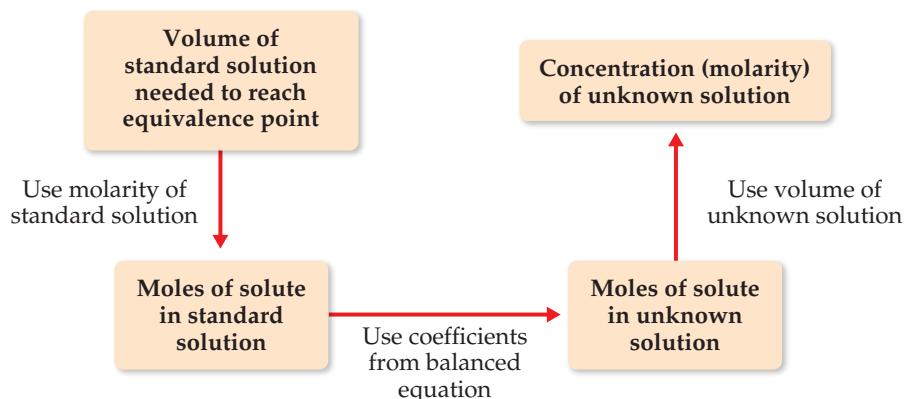
*More precisely, the color change of an indicator signals the end point of the titration, which if the proper indicator is chosen lies very near the equivalence point. Acid-base titrations are discussed in more detail in Section 17.3.

Go Figure

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



▲ **Figure 4.16** Procedure for titrating an acid against a standard solution of NaOH . The acid–base indicator, phenolphthalein, is colorless in acidic solution but takes on a pink color in basic solution.



◀ **Figure 4.17** Procedure for determining the concentration of a solution from titration with a standard solution.

Sample Exercise 4.16**Determining Solution Concentration by an Acid–Base Titration**

One commercial method used to peel potatoes is to soak them in a NaOH solution for a short time and then remove the potatoes and spray off the peel. The NaOH concentration is normally 3 to 6 M , and the solution must be analyzed periodically. In one such analysis, 45.7 mL of 0.500 M H_2SO_4 is required to neutralize 20.0 mL of NaOH solution. What is the concentration of the NaOH solution?

SOLUTION

Analyze We are given the volume (45.7 mL) and molarity (0.500 M) of an H_2SO_4 solution (the standard solution) that reacts completely with 20.0 mL of NaOH solution. We are asked to calculate the molarity of the NaOH solution.

Plan Following the steps given in Figure 4.17, we use the H_2SO_4 volume and molarity to calculate the number of moles of H_2SO_4 . Then we can use this quantity and the balanced equation for the reaction to calculate moles of NaOH . Finally, we can use moles of NaOH and the NaOH volume to calculate NaOH molarity.

Solve

The number of moles of H_2SO_4 is the product of the volume and molarity of this solution:

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

Acids react with metal hydroxides to form water and a salt.

Thus, the balanced equation for the neutralization reaction is:



According to the balanced equation,
 $1 \text{ mol H}_2\text{SO}_4 \approx 2 \text{ mol NaOH}$. Therefore,

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

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

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

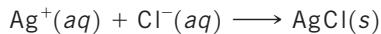
► Practice Exercises

What is the molarity of an HCl solution if 27.3 mL of it neutralizes 134.5 mL of 0.0165 M $\text{Ba}(\text{OH})_2$?

- (a) 0.0444 M (b) 0.0813 M (c) 0.163 M (d) 0.325 M
(e) 3.35 M

**Sample Exercise 4.17****Determining the Quantity of Solute by Titration**

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



- (a) How many grams of chloride ion are in a sample of the water if 20.2 mL of 0.100 M Ag^+ is needed to react with all the chloride in the sample? (b) If the sample has a mass of 10.0 g, what percentage of Cl^- does it contain?

SOLUTION

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

Plan (a) We can use the procedure outlined by the green arrows in Figure 4.15. We begin by using the volume and molarity of Ag^+ to calculate the number of moles of Ag^+ used in the titration. We then use the balanced equation to determine the moles of Cl^- in the sample and from that the grams of Cl^- . (b) To calculate the percentage of Cl^- in the sample, we compare the number of grams of Cl^- in the sample with the original mass of the sample, 10.0 g.

Solve

- (a) Calculate the number of moles of Ag^+ used in the titration.

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

From the balanced equation we see that

$1 \text{ mol Ag}^+ \approx 1 \text{ mol Cl}^-$. Using this information and the molar mass of Cl, we have:

- (b) Calculate the percentage of Cl^- used in the sample.

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

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

► Practice Exercise

A mysterious white powder is found at a crime scene. A simple chemical analysis concludes that the powder is a mixture of sugar and morphine ($C_{17}H_{19}NO_3$), a weak base similar to ammonia. The crime lab takes 10.00 mg of the mysterious white powder, dissolves it in 100.00 mL water, and titrates it to the equivalence

point with 2.84 mL of a standard 0.0100 M HCl solution. What is the percentage of morphine in the white powder?
(a) 8.10%
(b) 17.3%
(c) 32.6%
(d) 49.7%
(e) 81.0%

**Sample Integrative Exercise****Putting Concepts Together**

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

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

SOLUTION

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



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

$$(70.5 \text{ mg } K_3PO_4) \left(\frac{10^{-3} \text{ g } K_3PO_4}{1 \text{ mg } K_3PO_4} \right) \left(\frac{1 \text{ mol } K_3PO_4}{212.3 \text{ g } K_3PO_4} \right)$$

$$= 3.32 \times 10^{-4} \text{ mol } K_3PO_4$$

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

$$(15.0 \text{ mL}) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left(\frac{0.050 \text{ mol } AgNO_3}{\text{L}} \right)$$

$$= 7.5 \times 10^{-4} \text{ mol } AgNO_3$$

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

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

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

$$(7.5 \times 10^{-4} \text{ mol } AgNO_3) \left(\frac{1 \text{ mol } Ag_3PO_4}{3 \text{ mol } AgNO_3} \right) \left(\frac{418.7 \text{ g } Ag_3PO_4}{1 \text{ mol } Ag_3PO_4} \right)$$

$$= 0.10 \text{ g } Ag_3PO_4$$

Self-Assessment Exercise

4.35 Hard water contains Ca^{2+} , Mg^{2+} , and Fe^{2+} ions, which form a scum with soap. Water softeners replace these ions with Na^+ . If 1500 L of hard water contains 0.020 M Ca^{2+} and 0.0040 M Mg^{2+} , how many grams of NaCl are needed to replace these ions? Keep in mind charge balance must be maintained.

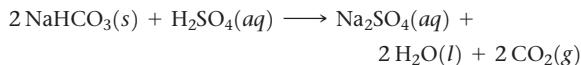
- (a) 1800 g
- (b) 2100 g
- (c) 3500 g
- (d) 4200 g

Exercises

4.36 You want to analyze a silver nitrate solution. (a) You could add $\text{HCl}(aq)$ to the solution to precipitate out $\text{AgCl}(s)$. What volume of a 0.150 M $\text{HCl}(aq)$ solution is needed to precipitate the silver ions from 15.0 mL of a 0.200 M AgNO_3 solution? (b) You could add solid KCl to the solution to precipitate out $\text{AgCl}(s)$. What mass of KCl is needed to precipitate the silver ions from 15.0 mL of 0.200 M AgNO_3 solution? (c) Given that a 0.150 M $\text{HCl}(aq)$ solution costs \$39.95 for 500 mL and that KCl costs \$10/ton, which analysis procedure is more cost-effective?

4.37 (a) What volume of 0.115 M HClO_4 solution is needed to neutralize 50.00 mL of 0.0875 M NaOH ? (b) What volume of 0.128 M HCl is needed to neutralize 2.87 g of $\text{Mg}(\text{OH})_2$? (c) If 25.8 mL of an AgNO_3 solution is needed to precipitate all the Cl^- ions in a 785-mg sample of KCl (forming AgCl), what is the molarity of the AgNO_3 solution? (d) If 45.3 mL of a 0.108 M HCl solution is needed to neutralize a solution of KOH, how many grams of KOH must be present in the solution?

4.38 Some sulfuric acid is spilled on a lab bench. You can neutralize the acid by sprinkling sodium hydrogen carbonate on it and then mopping up the resulting solution. The sodium hydrogen carbonate reacts with sulfuric acid according to:



Sodium hydrogen carbonate is added until the fizzing due to the formation of $\text{CO}_2(g)$ stops. If 27 mL of 6.0 M H_2SO_4 was spilled, what is the minimum mass of NaHCO_3 that must be added to the spill to neutralize the acid?

4.39 A 4.36 g sample of an unknown alkali metal hydroxide is dissolved in 100.0 mL of water. An acid-base indicator is added, and the resulting solution is titrated with 2.50 M $\text{HCl}(aq)$ solution. The indicator changes color, signaling that the equivalence point has been reached, after 17.0 mL of the hydrochloric acid solution has been added. (a) What is the molar mass of the metal hydroxide? (b) What is the identity of the alkali metal cation: Li^+ , Na^+ , K^+ , Rb^+ , or Cs^+ ?

4.40 A solution of 105.0 mL of 0.300 M NaOH is mixed with a solution of 150.0 mL of 0.060 M AlCl_3 . (a) Write the balanced chemical equation for the reaction that occurs. (b) What precipitate forms? (c) What is the limiting reactant? (d) How many grams of this precipitate form? (e) What is the concentration of each ion that remains in solution?

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

4.35 (d)

Answers to Self-Assessment Exercises

Chapter Summary and Key Terms

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

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

PRECIPITATION REACTIONS (SECTION 4.2) Precipitation reactions are those in which an insoluble product, called a **precipitate**, forms. Solubility guidelines help determine whether an ionic compound

will be soluble in water. (The **solubility** of a substance is the amount that dissolves in a given quantity of solvent.) Reactions such as precipitation reactions, in which cations and anions appear to exchange partners, are called **exchange reactions**, or **metathesis reactions**.

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

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

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

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

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

CONCENTRATIONS OF SOLUTIONS (SECTION 4.5) The **concentration** of a solution expresses the amount of a solute dissolved in the

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

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

Learning Outcomes After studying this chapter, you should be able to:

- Identify compounds as acids or bases, and as strong, weak, or nonelectrolytes. (Sections 4.1 and 4.3) *Related Exercises: 4.13–4.15, 4.63–4.65*
- Recognize reactions by type and be able to predict the products of simple acid-base, precipitation, and redox reactions. (Sections 4.2–4.4) *Related Exercises: 4.16–4.18, 4.24–4.25, 4.43–4.45, 4.66–4.68, 4.73–4.76*
- Calculate molarity and use it to convert between moles of a substance in solution and volume of the solution. (Section 4.5) *Related Exercises: 4.27–4.31, 4.79–4.85*

- Describe how to carry out a dilution to achieve a desired solution concentration. (Section 4.5) *Related Exercises: 4.32–4.34, 4.86–4.88*
- Describe how to perform and interpret the results of a titration. (Section 4.6) *Related Exercises: 4.38–4.41, 4.91–4.94*

Key Equations

$$\bullet \text{ Molarity} = \frac{\text{moles solute}}{\text{volume of solution in liters}} \quad [4.31]$$

$$\bullet M_{\text{conc}} \times V_{\text{conc}} = M_{\text{dil}} \times V_{\text{dil}} \quad [4.33]$$

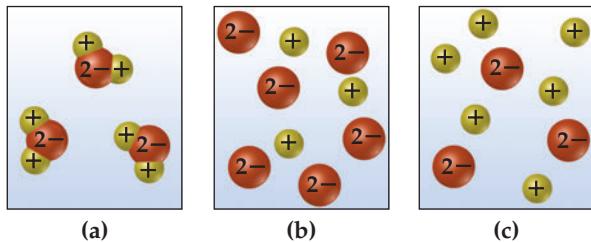
Molarity is the most commonly used unit of concentration in chemistry.

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

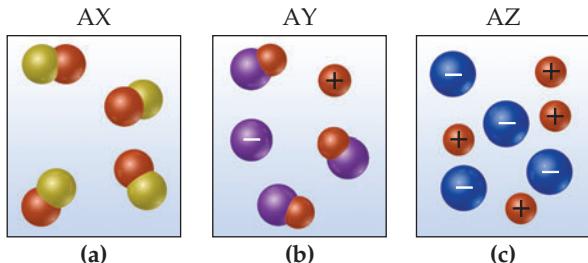
Exercises

Visualizing Concepts

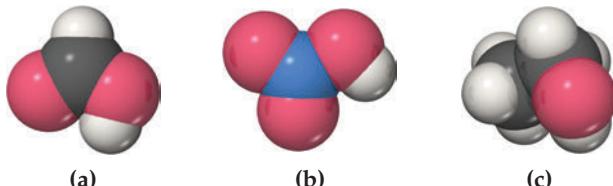
- 4.42** Which of the following schematic drawings best describes a solution of Li_2SO_4 in water (water molecules not shown for simplicity)? [Section 4.1]



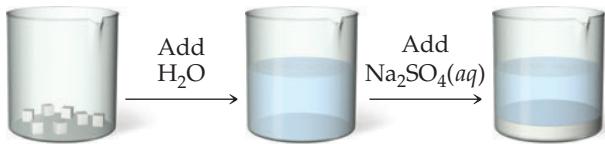
- 4.43** Aqueous solutions of three different substances, AX, AY, and AZ, are represented by the three accompanying diagrams. Identify each substance as a strong electrolyte, a weak electrolyte, or a nonelectrolyte. [Section 4.1]



- 4.44** Use the molecular representations shown here to classify each compound as a nonelectrolyte, a weak electrolyte, or a strong electrolyte (see Figure 4.4 for the element color scheme). [Sections 4.1 and 4.3]



- 4.45** The concept of chemical equilibrium is very important. Which one of the following statements is the most correct way to think about equilibrium?
- If a system is at equilibrium, nothing is happening.
 - If a system is at equilibrium, the rate of the forward reaction is equal to the rate of the back reaction.
 - If a system is at equilibrium, the product concentration is changing over time. [Section 4.1]
- 4.46** You are presented with a white solid and told that due to careless labeling it is not clear if the substance is barium chloride, lead chloride, or zinc chloride. When you transfer the solid to a beaker and add water, the solid dissolves to give a clear solution. Next an $\text{Na}_2\text{SO}_4(aq)$ solution is added and a white precipitate forms. What is the identity of the unknown white solid? [Section 4.2]

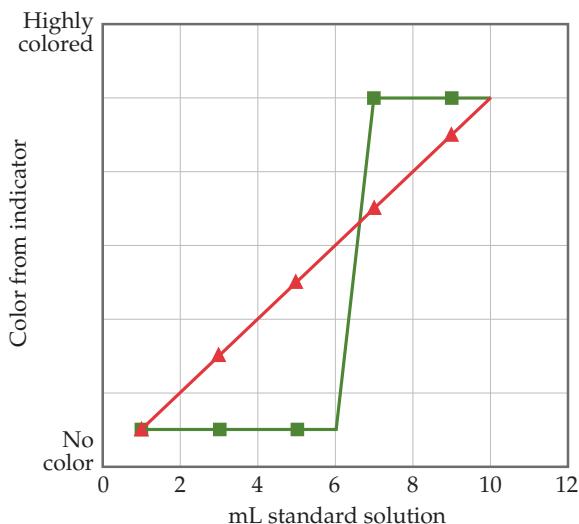


- 4.47** Which of the following ions will *always* be a spectator ion in a precipitation reaction? (a) Cl^- , (b) NO_3^- , (c) NH_4^+ , (d) S^{2-} , (e) SO_4^{2-} . [Section 4.2]
- 4.48** The labels have fallen off three bottles containing powdered samples of metals; one contains zinc, one lead, and the other platinum. You have three solutions at your disposal: 1 M sodium nitrate, 1 M nitric acid, and 1 M nickel nitrate. How could you use these solutions to determine the identities of each metal powder? [Section 4.4]
- 4.49** Explain how a redox reaction involves electrons in the same way that a neutralization reaction involves protons. [Sections 4.3 and 4.4]

- 4.50** What kind of reaction is the “water-splitting” reaction?
 $\text{H}_2\text{O(l)} \longrightarrow \text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)}$
- an acid-base reaction
 - a metathesis reaction
 - a redox reaction
 - a precipitation reaction [Section 4.4]

- 4.51** An aqueous solution contains 1.2 mM of total ions. (a) If the solution is $\text{NaCl}(aq)$, what is the concentration of chloride ion? (b) If the solution is $\text{FeCl}_3(aq)$, what is the concentration of chloride ion? [Section 4.5]

- 4.52** Which data set, of the two graphed here, would you expect to observe from a titration like that shown in Figure 4.16? [Section 4.6]



- 4.53** You are titrating an acidic solution with a basic one, and just realized you forgot to add the indicator that tells you when the equivalence point is reached. In this titration, the indicator turns blue at the equivalence point from an initially colorless solution. You quickly grab a bottle of indicator and add some to your titration beaker, and the whole solution turns dark blue. What do you do now? [Section 4.6]

General Properties of Aqueous Solutions (Section 4.1)

- 4.54** State whether each of the following statements is true or false. Justify your answer in each case.
- When acetone, CH_3COCH_3 , is dissolved in water, a conducting solution results.
 - When ammonium nitrate, NH_4NO_3 , dissolves in water, the solution is weakly conducting and basic in nature.
- 4.55** Would you expect that an anion would be physically closer to the oxygen or to the hydrogens of water molecules that surround it in solution?
- 4.56** Specify what ions are present upon dissolving each of the following substances in water: (a) HIO_3 , (b) Ba(OH)_2 , (c) HCN , (d) CuSO_4 .
- 4.57** Acetone, CH_3COCH_3 , is a nonelectrolyte; hypochlorous acid, HClO , is a weak electrolyte; and ammonium chloride, NH_4Cl , is a strong electrolyte. (a) What are the solutes present in aqueous solutions of each compound? (b) If 0.1 mol of each compound is dissolved in solution, which one contains 0.2 mol of solute particles, which contains 0.1 mol of solute particles, and which contains somewhere between 0.1 and 0.2 mol of solute particles?

Precipitation Reactions (Section 4.2)

- 4.58** Predict whether each of the following compounds is soluble in water: (a) MgS , (b) Cr(OH)_3 , (c) ZnCl_2 , (d) $\text{Pb}_3(\text{PO}_4)_2$, (e) $\text{Sr}(\text{CH}_3\text{COO})_2$.
- 4.59** Identify the precipitate (if any) that forms when the following solutions are mixed, and write a balanced equation for each reaction. (a) NH_4I and CuCl_2 , (b) LiOH and MnCl_2 , (c) K_3PO_4 and CoSO_4 .
- 4.60** Which ions remain in solution, unreacted, after each of the following pairs of solutions is mixed?
- potassium carbonate and magnesium sulfate
 - lead nitrate and lithium sulfide
 - ammonium phosphate and calcium chloride
- 4.61** Separate samples of a solution of an unknown ionic compound are treated with dilute AgNO_3 , $\text{Pb}(\text{NO}_3)_2$, and BaCl_2 . Precipitates form in all three cases. Which of the following could be the anion of the unknown salt: Br^- , CO_3^{2-} , NO_3^- ?
- 4.62** Three solutions are mixed together to form a single solution; in the final solution, there are 0.2 mol $\text{Pb}(\text{CH}_3\text{COO})_2$, 0.1 mol Na_2S , and 0.1 mol CaCl_2 present. What solid(s) will precipitate?

Acids, Bases, and Neutralization Reactions (Section 4.3)

- 4.63** State whether each of the following statements is true or false. Justify your answer in each case.
- NH_3 contains no OH^- ions, and yet its aqueous solutions are basic.
 - HF is a strong acid.
 - Although sulfuric acid is a strong electrolyte, an aqueous solution of H_2SO_4 contains more HSO_4^- ions than SO_4^{2-} ions.

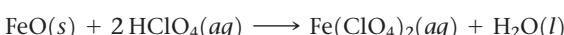
4.64 An aqueous solution of an unknown solute is tested with litmus paper and found to be acidic. The solution is weakly conducting compared with a solution of NaCl of the same concentration. Which of the following substances could the unknown be: KOH, NH₃, HNO₃, KClO₂, H₃PO₃, CH₃COCH₃ (acetone)?

4.65 Classify each of the following aqueous solutions as a non-electrolyte, weak electrolyte, or strong electrolyte: (a) PbCl₂, (b) N(CH₃)₃, (c) CsOH, (d) H₂S, (e) CrCl₂, (f) Ni(CH₃COO)₂.

4.66 Write the balanced molecular and net ionic equations for each of the following neutralization reactions:

- (a) Aqueous acetic acid is neutralized by aqueous barium hydroxide.
- (b) Solid chromium(III) hydroxide reacts with nitrous acid.
- (c) Aqueous nitric acid and aqueous ammonia react.

4.67 Because the oxide ion is basic, metal oxides react readily with acids. (a) Write the net ionic equation for the following reaction:



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

4.68 As K₂O dissolves in water, the oxide ion reacts with water molecules to form hydroxide ions. (a) Write the molecular and net ionic equations for this reaction. (b) Based on the definitions of acid and base, what ion is the base in this reaction? (c) What is the acid in the reaction? (d) What is the spectator ion in the reaction?

Oxidation-Reduction Reactions (Section 4.4)

4.69 True or false:

- (a) If a substance is oxidized, there must be more oxygen in the substance.
- (b) If a substance is oxidized, it must lose at least one electron and form an anion.

4.70 True or false:

- (a) Reduction occurs if the oxidation number of an element increases.
- (b) Oxidation and reduction must occur together in a reaction.

4.71 Determine the oxidation number for the indicated element in each of the following substances: (a) N in N₂H₄, (b) N in NO₂, (c) Mn in MnCl₃, (d) Fe in FeSO₄, (e) Pt in PtCl₄, (f) Cl in NaClO₄.

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

- (a) P₄(s) + 10 HClO(aq) + 6 H₂O(l) \longrightarrow 4 H₃PO₄(aq) + 10 HCl(aq)
- (b) Br₂(l) + 2 K(s) \longrightarrow 2 KBr(s)
- (c) CH₃CH₂OH(l) + 3 O₂(g) \longrightarrow 3 H₂O(l) + 2 CO₂(g)
- (d) ZnCl₂(aq) + 2 NaOH(aq) \longrightarrow Zn(OH)₂(s) + 2 NaCl(aq)

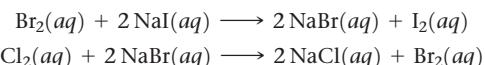
4.73 Write balanced molecular and net ionic equations for the reactions of (a) hydrochloric acid with nickel, (b) dilute sulfuric acid with iron, (c) hydrobromic acid with magnesium, (d) acetic acid, CH₃COOH, with zinc.

4.74 Using the activity series (Table 4.5), write balanced chemical equations for the following reactions. If no reaction occurs, write NR. (a) Nickel metal is added to a solution of copper(II) nitrate, (b) a solution of zinc nitrate is added to

a solution of magnesium sulfate, (c) hydrochloric acid is added to gold metal, (d) chromium metal is immersed in an aqueous solution of cobalt(II) chloride, (e) hydrogen gas is bubbled through a solution of silver nitrate.

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

4.76 The following reactions (note that the arrows are pointing only one direction) can be used to prepare an activity series for the halogens:



- (a) Which elemental halogen would you predict is the most stable, upon mixing with other halides? (b) Predict whether a reaction will occur when elemental chlorine and potassium iodide are mixed. (c) Predict whether a reaction will occur when elemental bromine and lithium chloride are mixed.

Concentrations of Solutions (Section 4.5)

4.77 (a) Is the number of moles of ions present in a solution an intensive or an extensive property? (b) Can you identify which one between 0.10 mol ZnCl₂ and 0.1M ZnCl₂ contains more Zn²⁺ ion? Why?

4.78 You make 1.000 L of an aqueous solution that contains 35.0 g of sucrose (C₁₂H₂₂O₁₁). (a) What is the molarity of sucrose in this solution? (b) How many liters of water would you have to add to this solution to reduce the molarity you calculated in part (a) by a factor of two?

4.79 (a) Calculate the molarity of a solution made by dissolving 12.5 grams of Na₂CrO₄ in enough water to form exactly 750 mL of solution. (b) How many moles of KBr are present in 150 mL of a 0.112 M solution? (c) How many milliliters of 6.1 M HCl solution are needed to obtain 0.150 mol of HCl?

4.80 A person suffering from hyponatremia has a sodium ion concentration in the blood of 0.118 M and a total blood volume of 4.6 L. What mass of sodium chloride would need to be added to the blood to bring the sodium ion concentration up to 0.138 M, assuming no change in blood volume?

4.81 The average adult male has a total blood volume of 5.0 L. After drinking a few beers, he has the “blood alcohol concentration” or BAC of 0.10 (BAC, is given in units of grams of alcohol per 100 mL of blood). What mass of alcohol is circulating in his blood?

4.82 (a) How many grams of ethanol, CH₃CH₂OH, should you dissolve in water to make 1.00 L of vodka (which is an aqueous solution that is 6.86 M ethanol)? (b) Using the density of ethanol (0.789 g/mL), calculate the volume of ethanol you need to make 1.00 L of vodka.

4.83 In a sugar tolerance test, a patient needs to drink a glucose (C₆H₁₂O₆) solution containing 100 g glucose. Given that one cup = 350 mL, calculate the molarity of glucose in the glucose solution.

4.84 In each of the following pairs, indicate which has the higher concentration of Cl⁻ ion: (a) 0.10 M AlCl₃ solution or a 0.25 M LiCl solution, (b) 150 mL of a 0.05 M MnCl₃ solution or 200 mL of 0.10 M KCl solution, (c) a 2.8 M HCl solution or a solution made by dissolving 23.5 g of KCl in water to make 100 mL of solution.

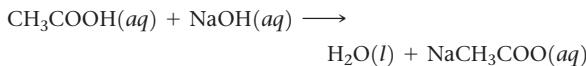
- 4.85** Calculate the concentration of each ion in the following solutions obtained by mixing: **(a)** 32.0 mL of 0.30 M KMnO_4 with 15.0 mL of 0.60 M KMnO_4 , **(b)** 60.0 mL of 0.100 M ZnCl_2 with 5.0 mL of 0.200 M $\text{Zn}(\text{NO}_3)_2$, **(c)** 4.2 g of CaCl_2 in 150.0 mL of 0.02 M KCl solution. Assume that the volumes are additive.
- 4.86** **(a)** How many milliliters of a stock solution of 6.0 M HNO_3 would you have to use to prepare 110 mL of 0.500 M HNO_3 ? **(b)** If you dilute 10.0 mL of the stock solution to a final volume of 0.250 L, what will be the concentration of the diluted solution?
- 4.87** Calicheamicin gamma-1, $\text{C}_{55}\text{H}_{74}\text{IN}_3\text{O}_{21}\text{S}_4$, is one of the most potent antibiotics known: one molecule kills one bacterial cell. Describe how you would (carefully!) prepare 25.00 mL of an aqueous calicheamicin gamma-1 solution that could kill 1.0×10^8 bacteria, starting from a 5.00×10^{-9} M stock solution of the antibiotic.
- 4.88** Glycerol, $\text{C}_3\text{H}_8\text{O}_3$, is a substance used extensively in the manufacture of cosmetics, foodstuffs, antifreeze, and plastics. Glycerol is a water-soluble liquid with a density of 1.2656 g/mL at 15 °C. Calculate the molarity of a solution of glycerol made by dissolving 50.000 mL glycerol at 15 °C in enough water to make 250.00 mL of solution.

Solution Stoichiometry and Chemical Analysis (Section 4.6)

- 4.89** You want to analyze a silver nitrate solution. What mass of NaCl is needed to precipitate Ag^+ ions from 45.0 mL of 0.2500 M AgNO_3 solution?
- 4.90** **(a)** How many milliliters of 0.120 M HCl are needed to completely neutralize 50.0 mL of 0.101 M $\text{Ba}(\text{OH})_2$ solution? **(b)** How many milliliters of 0.125 M H_2SO_4 are needed to neutralize 0.200 g of NaOH? **(c)** If 55.8 mL of a BaCl_2 solution

is needed to precipitate all the sulfate ion in a 752-mg sample of Na_2SO_4 , what is the molarity of the BaCl_2 solution? **(d)** If 42.7 mL of 0.208 M HCl solution is needed to neutralize a solution of $\text{Ca}(\text{OH})_2$, how many grams of $\text{Ca}(\text{OH})_2$ must be in the solution?

- 4.91** The distinctive odor of vinegar is due to acetic acid, CH_3COOH , which reacts with sodium hydroxide according to:



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

- 4.92** An 8.65 g sample of an unknown Group 2 metal hydroxide is dissolved in 85.0 mL of water. An acid-base indicator is added and the resulting solution is titrated with 2.50 M $\text{HCl}(aq)$ solution. The indicator changes color, signaling that the equivalence point has been reached, after 56.9 mL of the hydrochloric acid solution has been added. **(a)** What is the molar mass of the metal hydroxide? **(b)** What is the identity of the metal cation: Ca^{2+} , Sr^{2+} , or Ba^{2+} ?

- 4.93** A solution is made by mixing 1.5 g of LiOH and 23.5 mL of 1.000 M HNO_3 . **(a)** Write a balanced equation for the reaction that occurs between the solutes. **(b)** Calculate the concentration of each ion remaining in solution. **(c)** Is the resulting solution acidic or basic?

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

Additional Exercises

- 4.95** Uranium hexafluoride, UF_6 , is processed to produce fuel for nuclear reactors and nuclear weapons. UF_6 can be produced in a two-step reaction. Solid uranium (IV) oxide, UO_2 , is first made to react with hydrofluoric acid (HF) solution to form solid UF_4 with water as a by-product. UF_4 further reacts with fluorine gas to form UF_6 .
- (a)** Write the balanced molecular equations for the conversion of UO_2 into UF_4 and the conversion of UF_4 to UF_6 .
- (b)** Which step is an acid-base reaction?
- (c)** Which step is a redox reaction?
- 4.96** The accompanying photo shows the reaction between a solution of $\text{Cd}(\text{NO}_3)_2$ and one of Na_2S . **(a)** What is the identity of the precipitate? **(b)** What ions remain in solution? **(c)** Write the net ionic equation for the reaction. **(d)** Is this a redox reaction?



- 4.97** Suppose you have a solution that might contain any or all of the following cations: Ni^{2+} , Ag^+ , Sr^{2+} , and Mn^{2+} . Addition of HCl solution causes a precipitate to form. After filtering off the precipitate, H_2SO_4 solution is added to the resulting solution and another precipitate forms. This is filtered off, and a solution of NaOH is added to the resulting solution. No precipitate is observed. Which ions are present in each of the precipitates? Which of the four ions listed here must be absent from the original solution?

- 4.98** You choose to investigate some of the solubility guidelines for two ions not listed in Table 4.1, the chromate ion (CrO_4^{2-}) and the oxalate ion ($\text{C}_2\text{O}_4^{2-}$). You are given 0.01 M solutions (A, B, C, D) of four water-soluble salts:

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

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

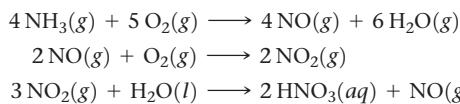
Experiment Number	Solutions Mixed	Result
1	A + B	No precipitate, yellow solution
2	A + C	Red precipitate forms
3	A + D	Yellow precipitate forms

Experiment Number	Solutions Mixed	Result
4	B + C	White precipitate forms
5	B + D	White precipitate forms
6	C + D	White precipitate forms

(a) Write a net ionic equation for the reaction that occurs in each of the experiments. (b) Identify the precipitate formed, if any, in each of the experiments.

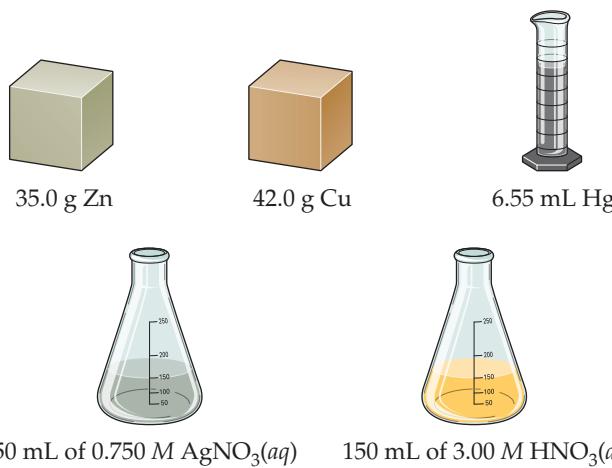
- 4.99** Antacids are often used to relieve pain and promote healing in the treatment of mild ulcers. Write balanced net ionic equations for the reactions between the aqueous HCl in the stomach and each of the following substances used in various antacids: (a) $\text{Al}(\text{OH})_3(s)$, (b) $\text{Mg}(\text{OH})_2(s)$, (c) $\text{MgCO}_3(s)$, (d) $\text{NaAl}(\text{CO}_3)(\text{OH})_2(s)$, (e) $\text{CaCO}_3(s)$.

- 4.100** The commercial production of nitric acid involves the following chemical reactions:



(a) Which of these reactions are redox reactions? (b) In each redox reaction identify the element undergoing oxidation and the element undergoing reduction. (c) How many grams of ammonia must you start with to make 1000.0 L of a 0.150 M aqueous solution of nitric acid? Assume all the reactions give 100% yield.

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

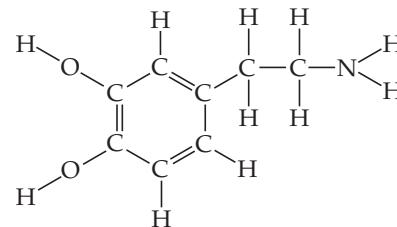


- 4.102** Bronze is a *solid solution* of $\text{Cu}(s)$ and $\text{Sn}(s)$; solutions of metals like this that are solids are called *alloys*. There is a range of compositions over which the solution is considered a bronze. Bronzes are stronger and harder than either copper or

tin alone. (a) A 100.0-g sample of a certain bronze is 90.0% copper by mass and 10.0% tin. Which metal can be called the solvent, and which the solute? (b) Based on part (a), calculate the concentration of the solute metal in the alloy in units of molarity, assuming a density of 7.9 g/cm³. (c) Suggest a reaction that you could do to remove all the tin from this bronze to leave a pure copper sample. Justify your reasoning.

- 4.103** A 35.0 mL sample of 1.00 M $\text{Co}(\text{NO})_3$ and an 80.0-mL sample of 0.600 M $\text{Co}(\text{NO})_3$ are mixed. The solution is then heated to evaporate water until the total volume is 50.0 mL. Calculate the volume, in mL, of 0.20 M H_3PO_4 that is required to precipitate out cobalt (III) phosphate in the final solution.

- 4.104** Neurotransmitters are molecules that are released by nerve cells to other cells in our bodies, and are needed for muscle motion, thinking, feeling, and memory. Dopamine is a common neurotransmitter in the human brain.



(a) Predict what kind of reaction dopamine is most likely to undergo in water: redox, acid-base, precipitation, or metathesis? Explain your reasoning. (b) Patients with Parkinson's disease suffer from a shortage of dopamine and may need to take it to reduce symptoms. An IV (intravenous fluid) bag is filled with a solution that contains 400.0 mg dopamine per 250.0 mL of solution. What is the concentration of dopamine in the IV bag in units of molarity? (c) Experiments with rats show that if rats are dosed with 3.0 mg/kg of cocaine (that is, 3.0 mg cocaine per kg of animal mass), the concentration of dopamine in their brains increases by 0.75 μM after 60 seconds. Calculate how many molecules of dopamine would be produced in a rat (average brain volume 5.00 mm³) after 60 seconds of a 3.0 mg/kg dose of cocaine.

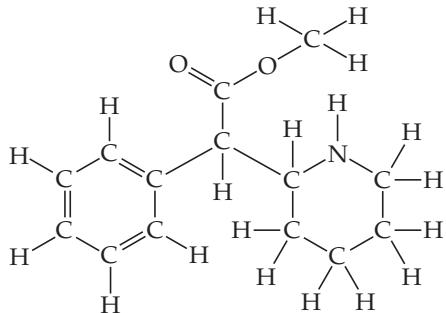
- 4.105** Citric acid, $\text{C}_6\text{H}_8\text{O}_7$, is a triprotic acid. It occurs naturally in citrus fruits like lemons and has applications in food flavouring and preservatives. A solution containing an unknown concentration of the acid is titrated with KOH. It requires 23.20 mL of 0.500 M KOH solution to titrate all three acidic protons in 100.00 mL of the citric acid solution. Write a balanced net ionic equation for the neutralization reaction, and calculate the molarity of the citric acid solution.

- 4.106** (a) A caesium hydroxide solution is prepared by dissolving 3.20 g of CsOH in water to make 25.00 mL of solution. What is the molarity of this solution? (b) Then, the caesium hydroxide solution prepared in part (a) is used to titrate a hydroiodic acid solution of unknown concentration. Write a balanced chemical equation to represent the reaction between the caesium hydroxide and hydroiodic acid solutions. (c) If 18.65 mL of the caesium hydroxide solution was needed to neutralize a 42.3 mL aliquot of the hydroiodic acid solution, what is the concentration (molarity) of the acid?

- 4.107** A solid sample of $\text{Fe}(\text{OH})_3$ is added to 0.500 L of 0.250 M aqueous H_2SO_4 . The solution that remains is still acidic. It is then titrated with 0.500 M NaOH solution, and it takes 12.5 mL of the NaOH solution to reach the equivalence point. What mass of $\text{Fe}(\text{OH})_3$ was added to the H_2SO_4 solution?

Integrative Exercises

- 4.108** Suppose you have 3.00 g of powdered zinc metal, 3.00 g of powdered silver metal and 500.0 mL of a 0.2 M copper(II) nitrate solution. (a) Which metal will react with the copper(II) nitrate solution? (b) What is the net ionic equation that describes this reaction? (c) Which is the limiting reagent in the reaction? (d) What is the molarity of Cu²⁺ ions in the resulting solution?
- 4.109** (a) By titration, 15.0 mL of 0.1008 M sodium hydroxide is needed to neutralize a 0.2053-g sample of a weak acid. What is the molar mass of the acid if it is monoprotic? (b) An elemental analysis of the acid indicates that it is composed of 5.89% H, 70.6% C, and 23.5% O by mass. What is its molecular formula?
- 4.110** Copper exists in the form of CuFeS₂ in copper ore. Copper is isolated in a two-step process. First, CuFeS₂ is heated with SiO₂ in the presence of oxygen to form copper(I) sulfide, Cu₂S: 2CuFeS₂ + 2SiO₂(s) + 4O₂(g) → Cu₂S(s) + 2FeSiO₃(s) + 3SO₂(g). Cu₂S is then heated with oxygen to form copper and SO₂(g). (a) Write the balanced chemical equation for the second reaction. (b) Which atoms from which compounds are being oxidized, and which atoms from which compounds are being reduced? (c) How many grams of copper would be isolated from 85.36 g of CuFeS₂ in copper ore?
- 4.111** A fertilizer rail car carrying 129,840 L of commercial aqueous ammonia (30% ammonia by mass) tips over and spills. The density of the aqueous ammonia solution is 0.88 g/cm³. What mass of citric acid, C(OH)(COOH)(CH₂COOH)₂, (which contains three acidic protons) is required to neutralize the spill?
- 4.112** A sample of 8.69 g of Zn(OH)₂ is added to 155.0 mL of 0.750 M H₂SO₄. (a) Write the chemical equation for the reaction that occurs. (b) Which is the limiting reactant in the reaction? (c) How many moles of Zn(OH)₂, H₂SO₄, and ZnSO₄ are present after the reaction is complete?
- 4.113** Ritalin is the trade name of a drug, methylphenidate, used to treat attention-deficit/hyperactivity disorder in young adults. The chemical structure of methylphenidate is

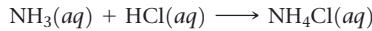


(a) Is Ritalin an acid or a base? An electrolyte or a nonelectrolyte? (b) A tablet contains a 10.0 mg dose of Ritalin. Assuming all the drug ends up in the bloodstream, and the average man has a total blood volume of 5.0 L, calculate the initial molarity of Ritalin in a man's bloodstream. (c) Ritalin has a half-life of 3 hours in the blood, which means that after 3 hours the concentration in the blood has decreased by half of its initial value. For the man in part (b), what is the concentration of Ritalin in his blood after 6 hours?

- 4.114** A 3.50 g of an alloy which contains only lead and tin is dissolved in hot HNO₃. Excess sulfuric acid is added to this solution and 1.57 g of PbSO₄(s) is obtained. (a) Write the net ionic equation for the formation of PbSO₄. (b) Assuming all the lead in the alloy reacted to form PbSO₄, what was the amount, in grams, of lead and tin in the alloy respectively?
- 4.115** The arsenic in a 1.22-g sample of a pesticide was converted to AsO₄³⁻ by suitable chemical treatment. It was then titrated using Ag⁺ to form Ag₃AsO₄ as a precipitate. (a) What is the oxidation state of As in AsO₄³⁻? (b) Name Ag₃AsO₄ by analogy to the corresponding compound containing phosphorus in place of arsenic. (c) If it took 25.0 mL of 0.102 M Ag⁺ to reach the equivalence point in this titration, what is the mass percentage of arsenic in the pesticide?
- 4.116** The U.S. standard for arsenate in drinking water requires that public water supplies must contain no greater than 10 parts per billion (ppb) arsenic. If this arsenic is present as arsenate, AsO₄³⁻, what mass of sodium arsenate would be present in a 1.00 L sample of drinking water that just meets the standard? Parts per billion is defined on a mass basis as

$$\text{ppb} = \frac{\text{g solute}}{\text{g solution}} \times 10^9$$

- 4.117** Federal regulations in the United States set an upper limit of 50 parts per million (ppm) of NH₃ in the air in a work environment [that is, 50 molecules of NH₃(g) for every million molecules in the air]. Air from a manufacturing operation was drawn through a solution containing 1.00 × 10⁻² mL of 0.0105 M HCl. The NH₃ reacts with HCl according to:



After drawing air through the acid solution for 10.0 min at a rate of 10.0 L/min, the acid was titrated. The remaining acid needed 13.1 mL of 0.0588 M NaOH to reach the equivalence point. (a) How many grams of NH₃ were drawn into the acid solution? (b) How many ppm of NH₃ were in the air? (Air has a density of 1.20 g/L and an average molar mass of 29.0 g/mol under the conditions of the experiment.) (c) Is this manufacturer in compliance with regulations?

Design an Experiment

You are cleaning out a chemistry lab and find three unlabeled bottles, each containing white powder. Near these bottles are three loose labels: "Sodium sulfide," "Sodium bicarbonate," and "Sodium chloride." Let's design an experiment to figure out which label goes with which bottle.

(a) You could try to use the physical properties of the three solids to distinguish among them. Using an Internet resource or the *CRC Handbook of Chemistry and Physics*, look up the melting points, aqueous solubilities, or other properties of these salts. Are the differences

among these properties for each salt large enough to distinguish among them? If so, design a set of experiments to distinguish each salt and therefore figure out which label goes on which bottle.

(b) You could use the chemical reactivity of each salt to distinguish it from the others. Which of these salts, if any, will act as an acid? A base? A strong electrolyte? Can any of these salts be easily oxidized or reduced? Can any of these salts react to produce a gas? Based on your answers to these questions, design a set of experiments to distinguish each salt and thus determine which label goes on which bottle.