3

Calculations with Chemical Formulas and Equations

Zinc and iodine react to produce zinc iodide, a solution used to find flaws in composite airplane wings. Zinc iodide solution sprayed on a wing will fill a crack, if present, which shows up on an x ray as an opaque area (from the absorption of x rays by iodine atoms).

Contents and Concepts

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Here we will establish a critical relationship between the mass of a chemical substance and the quantity of that substance (in moles).

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3.3 Mass Percentages from the Formula
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Explore how the percentage composition and mass percentage of the elements in a chemical substance can be used to determine the chemical formula.

Stoichiometry: Quantitative Relations in Chemical Reactions

3.6 Molar Interpretation of a Chemical Equation
3.7 Amounts of Substances in a Chemical Reaction
3.8 Limiting Reactant; Theoretical and Percentage Yields

Develop a molar interpretation of chemical equations, which then allows for calculation of the quantities of reactants and products.

Acetic acid (ah-see′-tik acid) is a colorless liquid with a sharp, vinegary odor. In fact, vinegar contains acetic acid, which accounts for vinegar's odor and sour taste. The name *vinegar* derives from the French word *vinaigre,* meaning "sour wine." Vinegar results from the fermentation of wine or cider by certain bacteria. These bacteria require oxygen, and the overall chemical change is the reaction of ethanol (alcohol) in wine with oxygen to give acetic acid (Figure 3.1).

Laboratory preparation of acetic acid may also start from ethanol, which reacts with oxygen in two steps. First, ethanol reacts with oxygen to yield a compound called acetaldehyde, in addition to water. In the second step, the acetaldehyde reacts with more oxygen to produce acetic acid. (The human body also produces acetaldehyde and then acetic acid from alcohol, as it attempts to eliminate alcohol from the system.)

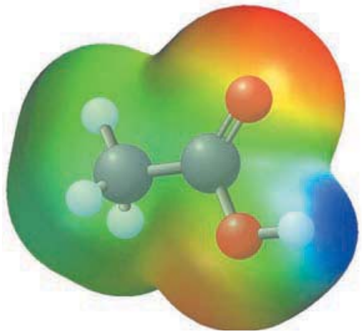


FIGURE 3.1

Electrostatic potential map of acetic acid molecule (CH_3COOH)
Acetic acid is the compound responsible for the sour taste and smell of vinegar.

This chapter focuses on two basic questions, which we can illustrate using these compounds: How do you determine the chemical formula of a substance such as acetic acid (or acetaldehyde)? How much acetic acid can you prepare from a given quantity of ethanol (or a given quantity of acetaldehyde)? These types of questions are very important in chemistry. You must know the formulas of all the substances involved in a reaction before you can write the chemical equation, and you need the balanced chemical equation to determine the quantitative relationships among the different substances in the reaction. We begin by discussing how you relate number of atoms or molecules to grams of substance, because this is the key to answering both questions.

■ See page 113 for the Media Summary.

Mass and Moles of Substance

You buy a quantity of groceries in several ways. You often purchase items such as oranges and lemons by counting out a particular number. Some things, such as eggs and soda, can be purchased in a "package" that represents a known quantity—for example, a dozen or a case. Bulk foods, such as peanuts or hard candy, are usually purchased by mass, because it is too tedious to count them out, and because we know that a given mass yields a certain quantity of the item. All three of these methods are used by chemists to determine the quantity of matter: counting, using a package that represents a quantity, and measuring the mass. For a chemist, it is a relatively easy matter to weigh a substance to obtain the mass. However, the number of atoms or molecules in even a seemingly minute amount is much too large to count. (You may recall from Section 2.6 that a billionth of a drop of water contains 2×10^{12} H_2O molecules.) Nevertheless, chemists are interested in knowing such numbers. How many atoms of carbon are there in one molecule of acetic acid? How many molecules of acetic acid can be obtained from one molecule of ethanol? Before we look at how chemists solve this problem of measuring numbers of atoms, molecules, and ions, we must look at the concept of molecular mass (or molecular weight) and formula mass (or formula weight) and introduce the package chemists call the mole.

3.1 Molecular Mass and Formula Mass

In Chapter 2 (Section 2.4), we discussed the concept of atomic mass. We can easily extend this idea to include molecular mass. The **molecular mass** (MM) of a substance is *the sum of the atomic masses of all the atoms in a molecule of the substance.* It is, therefore, the average mass of a molecule of that substance, expressed in atomic mass units. For example, the molecular mass of water, H_2O, is 18.0 amu (2 × 1.0 amu from two H atoms plus 16.0 amu from one O atom). If the molecular formula for the substance is not known, you can determine the molecular mass experimentally by means of a mass spectrometer. In later chapters we will discuss simple, inexpensive methods for determining molecular mass.

Some chemists use the term molecular mass *in a less strict sense for ionic as well as molecular compounds.*

The **formula mass** (FM) of a substance is *the sum of the atomic masses of all atoms in a formula unit of the compound,* whether molecular or not. Sodium chloride, with the formula unit NaCl, has a formula mass of 58.44 amu (22.99 amu from Na plus 35.45 amu from Cl). NaCl is ionic, so strictly speaking the expression "molecular mass of NaCl" has no meaning. On the other hand, the molecular mass and the formula mass calculated from the molecular formula of a substance are identical. <

Example 3.1 Calculating the Formula Mass from a Formula

Calculate the formula mass of each of the following to three significant figures, using a table of atomic masses (AM): a. chloroform, $CHCl_3$; b. iron(III) sulfate, $Fe_2(SO_4)_3$.

Problem Strategy Identify the number and type of atoms in the chemical formula. Use the periodic table to obtain the atomic mass of each of the elements present in the compounds. Taking into account the number of each atom present in the formula, sum the masses. If atoms in the formula are enclosed within parentheses as in part b, the number of each element within the parentheses should be multiplied by the subscript that follows the final, or closing, parenthesis.

Solution a. The calculation is

$$\begin{aligned} 1 \times \text{AM of C} &= & 12.0\ \text{amu} \\ 1 \times \text{AM of H} &= & 1.0\ \text{amu} \\ 3 \times \text{AM of Cl} &= 3 \times 35.45\ \text{amu} = & \underline{106.4\ \text{amu}} \\ \text{FM of } CHCl_3 &= & 119.4\ \text{amu} \end{aligned}$$

The answer rounded to three significant figures is **119 amu.**

b. The calculation is

$$\begin{aligned} 2 \times \text{AM of Fe} &= 2 \times 55.8\ \text{amu} = & 111.6\ \text{amu} \\ 3 \times \text{AM of S} &= 3 \times 32.1\ \text{amu} = & 96.3\ \text{amu} \\ 3 \times 4 \times \text{AM of O} &= 12 \times 16.00\ \text{amu} = & \underline{192.0\ \text{amu}} \\ \text{FM of } Fe_2(SO_4)_3 &= & 399.9\ \text{amu} \end{aligned}$$

The answer rounded to three significant figures is **4.00×10^2 amu.**

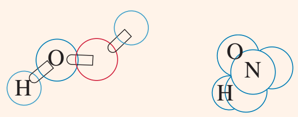
Answer Check The most common error when calculating formula masses is not correctly accounting for those atoms that are enclosed in parentheses.

Exercise 3.1 Calculate the formula masses of the following compounds, using a table of atomic masses. Give the answers to three significant figures. a. nitrogen dioxide, NO_2; b. glucose, $C_6H_{12}O_6$; c. sodium hydroxide, NaOH; d. magnesium hydroxide, $Mg(OH)_2$.

■ See Problems 3.27 and 3.28.

Example 3.2 Calculating the Formula Mass from Molecular Models

For the following two compounds, write the molecular formula and calculate the formula mass to four significant figures:



(a) (b)

(continued)

(continued)

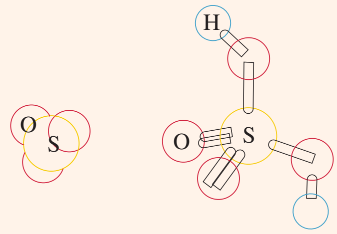
Problem Strategy In order to calculate the formula mass, you need to have the total number of each type of atom present in the structure, so look at the structure and keep a tally of all the atoms present.

Solution a. This molecular model is of a molecule that is composed of two O and two H atoms. For inorganic compounds, the elements in a chemical formula are written in order such that the most metallic element is listed first. (Even though H is not metallic, it is positioned in the periodic table in such a way that it is considered to be a metal when writing formulas.) Hence, the chemical formula is $\mathbf{H_2O_2}$. Using the same approach as Example 3.1, calculating the formula mass yields **34.02 amu.**

b. This molecular model represents a molecule made up of one N atom, three O atoms, and one H atom. The chemical formula is then $\mathbf{HNO_3}$. The formula mass is **63.01 amu.**

Answer Check Always make sure that your answer is reasonable. If you obtain a molecular mass of more than 200 amu for a simple molecular compound (this is possible but not typical), it is advisable to check your work closely.

Exercise 3.2 For the following compounds, write the molecular formula and calculate the formula mass to three significant figures.



(a) (b)

■ See Problems 3.29 and 3.30.

3.2 The Mole Concept

When we prepare a compound industrially or even study a reaction in the laboratory, we deal with tremendous numbers of molecules or ions. Suppose you wish to prepare acetic acid, starting from 10.0 g of ethanol. This small sample (less than 3 teaspoonsful) contains 1.31×10^{23} molecules, a truly staggering number. Imagine a device that counts molecules at the rate of one million per second. It would take more than four billion years—nearly the age of the earth—for this device to count that many molecules! Chemists have adopted the *mole concept* as a convenient way to deal with the enormous numbers of molecules or ions in the samples they work with.

Definition of Mole and Molar Mass

A **mole** (symbol **mol**) is defined as *the quantity of a given substance that contains as many molecules or formula units as the number of atoms in exactly 12 g of carbon-12.* One mole of ethanol, for example, contains the same number of ethanol molecules as there are carbon atoms in 12 g of carbon-12.

The number of atoms in a 12-g sample of carbon-12 is called **Avogadro's number** (to which we give the symbol N_A). Recent measurements of this number give the value 6.0221367×10^{23}, which to three significant figures is 6.02×10^{23}.

A mole of a substance contains Avogadro's number (6.02×10^{23}) of molecules (or formula units). The term *mole,* like a dozen or a gross, thus refers to a particular number of things. A dozen eggs equals 12 eggs, a gross of pencils equals 144 pencils, and a mole of ethanol equals 6.02×10^{23} ethanol molecules.

Sodium carbonate, Na_2CO_3, is a white, crystalline solid known commercially as soda ash. Large amounts of soda ash are used in the manufacture of glass. The hydrated compound, $Na_2CO_3 \cdot 10H_2O$, is known as washing soda.

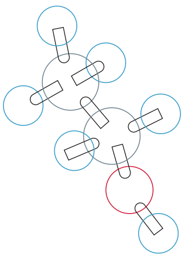
In using the term *mole* for ionic substances, we mean the number of formula units of the substance. For example, a mole of sodium carbonate, Na_2CO_3, is a quantity containing 6.02×10^{23} Na_2CO_3 units. But each formula unit of Na_2CO_3 contains two Na^+ ions and one CO_3^{2-} ion. Therefore, a mole of Na_2CO_3 also contains $2 \times 6.02 \times 10^{23}$ Na^+ ions and $1 \times 6.02 \times 10^{23}$ CO_3^{2-} ions. <

FIGURE 3.2 **One mole each of various substances**
Clockwise from top left: 1-octanol ($C_8H_{17}OH$); mercury(II) iodide (HgI_2); methanol (CH_3OH); sulfur (S_8).

When using the term *mole,* it is important to specify the formula of the unit to avoid any misunderstanding. For example, a mole of oxygen atoms (with the formula O) contains 6.02×10^{23} O atoms. A mole of oxygen molecules (formula O_2) contains 6.02×10^{23} O_2 molecules—that is, $2 \times 6.02 \times 10^{23}$ O atoms.

The **molar mass** of a substance is *the mass of one mole of the substance.* Carbon-12 has a molar mass of exactly 12 g/mol, by definition.

For all substances, the molar mass in grams per mole is numerically equal to the formula mass in atomic mass units.



Ethanol
C_2H_5OH

Ethanol, whose molecular formula is C_2H_6O (frequently written as the condensed structural formula C_2H_5OH), has a molecular mass of 46.1 amu and a molar mass of 46.1 g/mol. Figure 3.2 shows molar amounts of different substances.

Example 3.3 Calculating the Mass of an Atom or Molecule

a. What is the mass in grams of a chlorine atom, Cl?

b. What is the mass in grams of a hydrogen chloride molecule, HCl?

Problem Strategy In order to solve this type of problem, we need to consider using molar mass and the relationship between the number of atoms or molecules and the molar mass.

Solution a. The atomic mass of Cl is 35.5 amu, so the molar mass of Cl is 35.5 g/mol. Dividing 35.5 g (per mole) by 6.02×10^{23} (Avogadro's number) gives the mass of one atom.

$$\text{Mass of a Cl atom} = \frac{35.5\ \text{g}}{6.02 \times 10^{23}} = \mathbf{5.90 \times 10^{-23}\ g}$$

b. The molecular mass of HCl equals the AM of H plus the AM of Cl, or 1.01 amu + 35.5 amu = 36.5 amu. Therefore, 1 mol HCl contains 36.5 g HCl and

$$\text{Mass of an HCl molecule} = \frac{36.5\ \text{g}}{6.02 \times 10^{23}} = \mathbf{6.06 \times 10^{-23}\ g}$$

Answer Check As you know, individual atoms and molecules are incredibly small. Therefore, whenever you are asked to calculate the mass of a few atoms or molecules, you should expect a very small mass.

Exercise 3.3 a. What is the mass in grams of a calcium atom, Ca? b. What is the mass in grams of an ethanol molecule, C_2H_5OH?

■ See Problems 3.33, 3.34, 3.35, and 3.36.

Mole Calculations

Now that you know how to find the mass of one mole of substance, there are two important questions to ask. First, how much does a given number of moles of a substance weigh? Second, how many moles of a given formula unit does a given mass of substance contain? Both questions are easily answered using dimensional analysis, or the conversion-factor method. <

Alternatively, because the molar mass is the mass per mole, you can relate mass and moles by means of the formula

Molar mass = mass/moles

To illustrate, consider the conversion of grams of ethanol, C_2H_5OH, to moles of ethanol. The molar mass of ethanol is 46.1 g/mol, so we write

$$1 \text{ mol } C_2H_5OH = 46.1 \text{ g } C_2H_5OH$$

Thus, the factor converting grams of ethanol to moles of ethanol is 1 mol C_2H_5OH/46.1 g C_2H_5OH. To convert moles of ethanol to grams of ethanol, we simply invert the conversion factor (46.1 g C_2H_5OH/1 mol C_2H_5OH). Note that the unit you are converting *from* is on the bottom of the conversion factor; the unit you are converting *to* is on the top.

Again, suppose you are going to prepare acetic acid from 10.0 g of ethanol, C_2H_5OH. How many moles of C_2H_5OH is this? You convert 10.0 g C_2H_5OH to moles C_2H_5OH by multiplying by the appropriate conversion factor.

$$10.0 \cancel{\text{ g } C_2H_5OH} \times \frac{1 \text{ mol } C_2H_5OH}{46.1 \cancel{\text{ g } C_2H_5OH}} = 0.217 \text{ mol } C_2H_5OH$$

The following examples further illustrate this conversion-factor technique.

Example 3.4 Converting Moles of Substance to Grams

Zinc iodide, ZnI_2, can be prepared by the direct combination of elements (Figure 3.3). A chemist determines from the amounts of elements that 0.0654 mol ZnI_2 can form. How many grams of zinc iodide is this?

Problem Strategy Use the formula mass to write the factor that converts from mol ZnI_2 to g ZnI_2. Note that the unit you are converting from (mol ZnI_2) is on the bottom of the conversion factor, and the unit you are converting to (g ZnI_2) is on the top.

Solution The molar mass of ZnI_2 is 319 g/mol. (The formula mass is 319 amu, which is obtained by summing the atomic masses in the formula.) Therefore,

$$0.0654 \cancel{\text{ mol } ZnI_2} \times \frac{319 \text{ g } ZnI_2}{1 \cancel{\text{ mol } ZnI_2}} = \mathbf{20.9 \text{ g } ZnI_2}$$

Answer Check Whenever you solve a problem of this type, be sure to write all units, making certain that they will cancel. This "built-in" feature of dimensional analysis ensures that you are correctly using the conversion factors.

FIGURE 3.3

Reaction of zinc and iodine

Heat from the reaction of the elements causes some iodine to vaporize (violet vapor).

Exercise 3.4 Hydrogen peroxide, H_2O_2, is a colorless liquid. A concentrated solution of it is used as a source of oxygen for rocket propellant fuels. Dilute aqueous solutions are used as a bleach. Analysis of a solution shows that it contains 0.909 mol H_2O_2 in 1.00 L of solution. What is the mass of hydrogen peroxide in this volume of solution?

■ See Problems 3.37, 3.38, 3.39, and 3.40.

Example 3.5 Converting Grams of Substance to Moles

Lead(II) chromate, $PbCrO_4$, is a yellow paint pigment (called chrome yellow) prepared by a precipitation reaction (Figure 3.4). In a preparation, 45.6 g of lead(II) chromate is obtained as a precipitate. How many moles of $PbCrO_4$ is this?

Problem Strategy Since we are starting with a mass of $PbCrO_4$, we need the conversion factor for grams of $PbCrO_4$ to moles of $PbCrO_4$. The molar mass of $PbCrO_4$ will provide this information.

Solution The molar mass of $PbCrO_4$ is 323 g/mol. That is,

$$1 \text{ mol } PbCrO_4 = 323 \text{ g } PbCrO_4$$

Therefore,

$$45.6 \text{ g } \cancel{PbCrO_4} \times \frac{1 \text{ mol } PbCrO_4}{323 \text{ g } \cancel{PbCrO_4}} = \mathbf{0.141 \text{ mol } PbCrO_4}$$

Answer Check Note that the given amount of material in this problem (45.6 g $PbCrO_4$) is much less than its molar mass (323 g/mol). Therefore, we would expect the number of moles of $PbCrO_4$ to be much less than 1, which is the case here. Quick, alert comparisons such as this can be very valuable in checking for calculation errors.

FIGURE 3.4 **Preparation of lead(II) chromate**
When lead(II) nitrate solution (colorless) is added to potassium chromate solution (clear yellow), bright yellow solid lead(II) chromate forms (giving a cloudlike formation of fine crystals).

Exercise 3.5 Nitric acid, HNO_3, is a colorless, corrosive liquid used in the manufacture of nitrogen fertilizers and explosives. In an experiment to develop new explosives for mining operations, a sample containing 28.5 g of nitric acid was poured into a beaker. How many moles of HNO_3 are there in this sample of nitric acid?

■ See Problems 3.41 and 3.42.

Example 3.6 Calculating the Number of Molecules in a Given Mass

How many molecules are there in a 3.46-g sample of hydrogen chloride, HCl?

Problem Strategy The number of molecules in a sample is related to moles of compound (1 mol HCl = 6.02×10^{23} HCl molecules). Therefore, if you first convert grams HCl to moles, then you can convert moles to number of molecules.

Solution Here is the calculation:

$$3.46 \text{ g } \cancel{HCl} \times \frac{1 \cancel{\text{ mol HCl}}}{36.5 \text{ g } \cancel{HCl}} \times \frac{6.02 \times 10^{23} \text{ HCl molecules}}{1 \cancel{\text{ mol HCl}}}$$
$$= \mathbf{5.71 \times 10^{22} \text{ HCl molecules}}$$

Note how the units in the numerator of a factor are canceled by the units in the denominator of the following factor.

Answer Check A very common mistake made when solving this type of problem is to use an incorrect conversion factor, such as 1 mol HCl = 6.02×10^{23} g HCl. If this statement

(*continued*)

(*continued*)

were true, the mass of HCl contained in a mole would be far more than the mass of all the matter in the Milky Way galaxy! Therefore, if you end up with a gigantic mass for an answer, or get stuck on how to use the quantity 6.02×10^{23} as a conversion factor, improper unit assignment is a likely culprit.

Exercise 3.6 Hydrogen cyanide, HCN, is a volatile, colorless liquid with the odor of certain fruit pits (such as peach and cherry pits). The compound is highly poisonous. How many molecules are there in 56 mg HCN, the average toxic dose?

■ See Problems 3.45, 3.46, 3.47, and 3.48.

Concept Check 3.1

You have 1.5 moles of tricycles.

a. How many moles of seats do you have?

b. How many moles of tires do you have?

c. How could you use parts a and b as an analogy to teach a friend about the number of moles of OH^- ions in 1.5 moles of $Mg(OH)_2$?

Determining Chemical Formulas

When a chemist has discovered a new compound, the first question to answer is, What is the formula? To answer, you begin by analyzing the compound to determine amounts of the elements for a given amount of compound. This is conveniently expressed as **percentage composition**—that is, as *the mass percentages of each element in the compound.* You then determine the formula from this percentage composition. If the compound is a molecular substance, you must also find the molecular mass of the compound in order to determine the molecular formula.

The next section describes the calculation of mass percentages. Then, in two following sections, we describe how to determine a chemical formula.

3.3 Mass Percentages from the Formula

Suppose that A is a part of something—that is, part of a whole. It could be an element in a compound or one substance in a mixture. We define the **mass percentage** of A *as the parts of* A *per hundred parts of the total, by mass.* That is,

$$\text{Mass \% } A = \frac{\text{mass of } A \text{ in the whole}}{\text{mass of the whole}} \times 100\%$$

You can look at the mass percentage of A as the number of grams of A in 100 g of the whole.

The next example will provide practice with the concept of mass percentage. In this example we will start with a compound (formaldehyde, CH_2O) whose formula is given and obtain the percentage composition.

Example 3.7 Calculating the Percentage Composition from the Formula

Formaldehyde, CH_2O, is a toxic gas with a pungent odor. Large quantities are consumed in the manufacture of plastics (Figure 3.5), and a water solution of the compound is used to preserve biological specimens. Calculate the mass percentages of the elements in formaldehyde (give answers to three significant figures).

Problem Strategy To calculate mass percentage, you need the mass of an element in a given mass of compound. You can get this information by interpreting the formula in molar terms and then converting moles to masses, using a table of atomic masses. Thus, 1 mol CH_2O has a mass of 30.0 g and contains 1 mol C (12.0 g), 2 mol H (2×1.01 g), and 1 mol O (16.0 g). You divide each mass of element by the molar mass, then multiply by 100, to obtain the mass percentage.

Solution Here are the calculations:

$$\textbf{\% C} = \frac{12.0\text{ g}}{30.0\text{ g}} \times 100\% = \mathbf{40.0\%}$$

$$\textbf{\% H} = \frac{2 \times 1.01\text{ g}}{30.0\text{ g}} \times 100\% = \mathbf{6.73\%}$$

You can calculate the percentage of O in the same way, but it can also be found by subtracting the percentages of C and H from 100%:

$$\textbf{\% O} = 100\% - (40.0\% + 6.73\%) = \mathbf{53.3\%}$$

Answer Check A typical mistake when working a mass percentage problem is to forget to account for the number of moles of each element given in the chemical formula. An example would be to answer this question as though the formula were CHO instead of CH_2O.

FIGURE 3.5 **Preparing resorcinol-formaldehyde plastic**
Top: The clear solution contains formaldehyde, CH_2O, and resorcinol, $C_6H_4(OH)_2$. The formation of the plastic is started by adding several drops of potassium hydroxide. *Bottom:* The red plastic has formed in the beaker.

Exercise 3.7 Ammonium nitrate, NH_4NO_3, which is prepared from nitric acid, is used as a nitrogen fertilizer. Calculate the mass percentages of the elements in ammonium nitrate (to three significant figures).

■ See Problems 3.57, 3.58, 3.59, and 3.60.

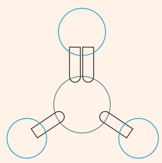
Example 3.8 Calculating the Mass of an Element in a Given Mass of Compound

How many grams of carbon are there in 83.5 g of formaldehyde, CH_2O? Use the percentage composition obtained in the previous example (40.0% C, 6.73% H, 53.3% O).

Problem Strategy Solving this type of problem requires that you first calculate the mass percentage of the element of interest, carbon in this case (as noted in the problem, this was done in Example 3.7). Multiplication of this percentage, expressed as a decimal, times the mass of formaldehyde in the sample, will yield the mass of carbon present.

Solution CH_2O is 40.0% C, so the mass of carbon in 83.5 g CH_2O is

$$83.5\text{ g} \times 0.400 = \mathbf{33.4\text{ g}}$$



Formaldehyde
CH_2O

(*continued*)

(continued)

Answer Check Make sure that you have converted the percent to a decimal prior to multiplication. An answer that is more than the starting mass of material is an indication that you probably made this mistake.

Exercise 3.8 How many grams of nitrogen, N, are there in a fertilizer containing 48.5 g of ammonium nitrate and no other nitrogen-containing compound? See Exercise 3.7 for the percentage composition of NH_4NO_3.

■ See Problems 3.61 and 3.62.

3.4 Elemental Analysis: Percentages of Carbon, Hydrogen, and Oxygen

Suppose you have a newly discovered compound whose formula you wish to determine. The first step is to obtain its percentage composition. As an example, consider the determination of the percentages of carbon, hydrogen, and oxygen in compounds containing only these three elements. The basic idea is this: You burn a sample of the compound of known mass and get CO_2 and H_2O. Next you relate the masses of CO_2 and H_2O to the masses of carbon and hydrogen. Then you calculate the mass percentages of C and H. You find the mass percentage of O by subtracting the mass percentages of C and H from 100.

Figure 3.6 shows an apparatus used to find the amount of carbon and hydrogen in a compound. The compound is burned in a stream of oxygen gas. The vapor of the compound and its combustion products pass over copper pellets coated with copper(II) oxide, CuO, which supplies additional oxygen and ensures that the compound is completely burned. As a result of the combustion, every mole of carbon (C) in the compound ends up as a mole of carbon dioxide (CO_2), and every mole of hydrogen (H) ends up as one-half mole of water (H_2O). The water is collected by a drying agent, a substance that has a strong affinity for water. The carbon dioxide is collected by chemical reaction with sodium hydroxide, NaOH. < By weighing the U-tubes containing the drying agent and the sodium hydroxide before and after combustion, it is possible to determine the masses of water and carbon dioxide produced. From these data, you can calculate the percentage composition of the compound.

Sodium hydroxide reacts with carbon dioxide according to the following equations:

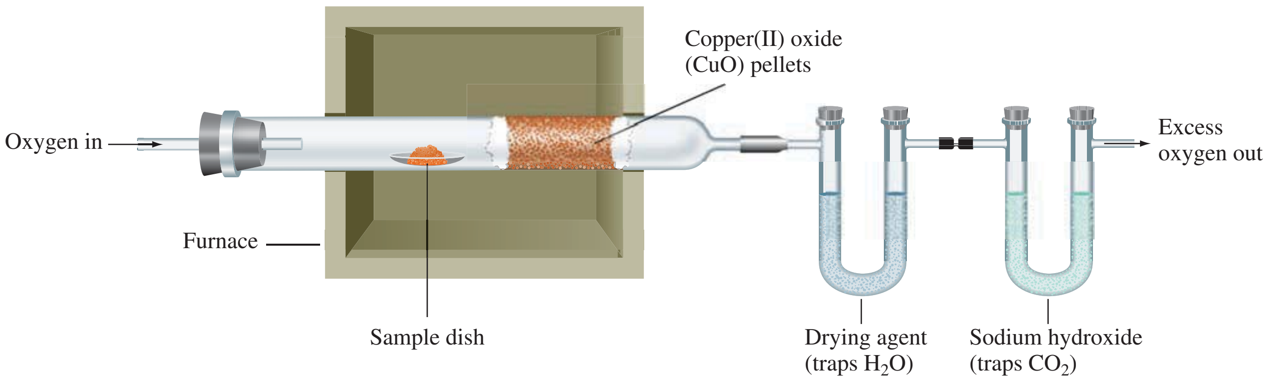
$NaOH + CO_2 \longrightarrow NaHCO_3$
$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$

The chapter opened with a discussion of acetic acid. The next example shows how to determine the percentage composition of this substance from combustion data. We will use this percentage composition later in Example 3.12 to determine the formula of acetic acid.

FIGURE 3.6

Combustion method for determining the percentages of carbon and hydrogen in a compound

The compound is placed in the sample dish and is heated by the furnace. Vapor of the compound burns in O_2 in the presence of CuO pellets, giving CO_2 and H_2O. The water vapor is collected by a drying agent, and CO_2 combines with the sodium hydroxide. Amounts of CO_2 and H_2O are obtained by weighing the U-tubes before and after combustion.



Example 3.9 Calculating the Percentages of C and H by Combustion

Acetic acid contains only C, H, and O. A 4.24-mg sample of acetic acid is completely burned. It gives 6.21 mg of carbon dioxide and 2.54 mg of water. What is the mass percentage of each element in acetic acid?

Problem Strategy Note that in the products of the combustion, all of the carbon from the sample ends up in the CO_2, all of the hydrogen ends up in the H_2O, and the oxygen is in both compounds. Because of this, you should concentrate first on the carbon and hydrogen and worry about the oxygen last. If we can determine the mass of carbon and hydrogen in the original sample, we should then be able to determine the percentage of each of these elements present in the compound. Once we know the mass percentages of carbon and hydrogen in the original compound, the remaining mass percentage (100% total) must be due to oxygen. Let's start by determining the mass of carbon that was originally contained in the compound. You first convert the mass of CO_2 to moles of CO_2. Then you convert this to moles of C, noting that 1 mol C produces 1 mol CO_2. Finally, you convert to mass of C. Similarly, for hydrogen, you convert the mass of H_2O to mol H_2O, then to mol H, and finally to mass of H. (Remember that 1 mol H_2O produces 2 mol H.) Once you have the masses of C and H, you can calculate the mass percentages. Subtract from 100% to get % O.

Solution Following is the calculation of grams C:

$$6.21 \times 10^{-3}\ \cancel{\text{g CO}_2} \times \frac{1\ \cancel{\text{mol CO}_2}}{44.0\ \cancel{\text{g CO}_2}} \times \frac{1\ \cancel{\text{mol C}}}{1\ \cancel{\text{mol CO}_2}} \times \frac{12.0\ \text{g C}}{1\ \cancel{\text{mol C}}}$$
$$= 1.69 \times 10^{-3}\ \text{g C (or 1.69 mg C)}$$

For hydrogen, you note that 1 mol H_2O yields 2 mol H, so you write

$$2.54 \times 10^{-3}\ \cancel{\text{g H}_2\text{O}} \times \frac{1\ \cancel{\text{mol H}_2\text{O}}}{18.0\ \cancel{\text{g H}_2\text{O}}} \times \frac{2\ \cancel{\text{mol H}}}{1\ \cancel{\text{mol H}_2\text{O}}} \times \frac{1.01\ \text{g H}}{1\ \cancel{\text{mol H}}}$$
$$= 2.85 \times 10^{-4}\ \text{g H (or 0.285 mg H)}$$

You can now calculate the mass percentages of C and H in acetic acid.

$$\text{Mass \% C} = \frac{1.69\ \text{mg}}{4.24\ \text{mg}} \times 100\% = 39.9\%$$

$$\text{Mass \% H} = \frac{0.285\ \text{mg}}{4.24\ \text{mg}} \times 100\% = 6.72\%$$

You find the mass percentage of oxygen by subtracting the sum of these percentages from 100%:

$$\text{Mass \% O} = 100\% - (39.9\% + 6.72\%) = 53.4\%$$

Thus, the percentage composition of acetic acid is **39.9% C, 6.7% H, and 53.4% O.**

Answer Check The most common error for this type of problem is not taking into account the fact that each mole of water contains two moles of hydrogen.

Exercise 3.9 A 3.87-mg sample of ascorbic acid (vitamin C) gives 5.80 mg CO_2 and 1.58 mg H_2O on combustion. What is the percentage composition of this compound (the mass percentage of each element)? Ascorbic acid contains only C, H, and O.

■ See Problems 3.63 and 3.64.

Concept Check 3.2

You perform combustion analysis on a compound that contains only C and H.

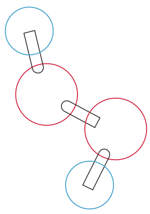
a. Considering the fact that the combustion products CO_2 and H_2O are colorless, how can you tell if some of the product got trapped in the CuO pellets (see Figure 3.6)?

b. Would your calculated results of mass percentage of C and H be affected if some of the combustion products got trapped in the CuO pellets? If your answer is yes, how might your results differ from the expected values for the compound?

3.5 Determining Formulas

The percentage composition of a compound leads directly to its empirical formula. An **empirical formula** (or **simplest formula**) for a compound is *the formula of a substance written with the smallest integer (whole number) subscripts.* For most ionic substances, the empirical formula is the formula of the compound. < This is often not the case for molecular substances. For example, hydrogen peroxide has the molecular formula H_2O_2. The molecular formula, you may recall, tells you the precise number of atoms of different elements in a molecule of the substance. The empirical formula, however, merely tells you the ratio of numbers of atoms in the compound. The empirical formula of hydrogen peroxide (H_2O_2) is HO (Figure 3.7).

The formula of sodium peroxide, an ionic compound of Na^+ and $O_2{}^{2-}$, is Na_2O_2. Its empirical formula is NaO.



H_2O_2

FIGURE 3.7

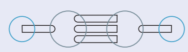
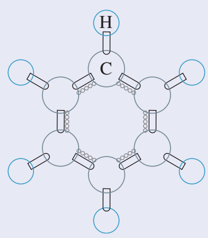
Molecular model of hydrogen peroxide (H_2O_2)
Hydrogen peroxide has the empirical formula HO and the molecular formula H_2O_2. In order to arrive at the correct structure of molecular compounds like H_2O_2 shown here, chemists must have the molecular formula.

Compounds with different molecular formulas can have the same empirical formula, and such substances will have the same percentage composition. An example is acetylene, C_2H_2, and benzene, C_6H_6. Acetylene is a gas used as a fuel and also in welding. Benzene, in contrast, is a liquid that is used in the manufacture of plastics and is a component of gasoline. Table 3.1 illustrates how these two compounds, with the same empirical formula, but different molecular formulas, also have different chemical structures. Because the empirical formulas of acetylene and benzene are the same, they have the same percentage composition: 92.3% C and 7.7% H, by mass.

To obtain the molecular formula of a substance, you need two pieces of information: (1) as in the previous section, the percentage composition, from which the empirical formula can be determined; and (2) the molecular mass. The molecular mass allows you to choose the correct multiple of the empirical formula for the molecular formula. We will illustrate these steps in the next three examples.

TABLE 3.1 Molecular Models of Two Compounds That Have the Empirical Formula CH

Although benzene and acetylene have the same empirical formula, they do not have the same molecular formula or structure.

Compound	Empirical Formula	Molecular Formula	Molecular Model
Acetylene	CH	C_2H_2	
Benzene	CH	C_6H_6	

Instrumental Methods

Mass Spectrometry and Molecular Formula

Some very sophisticated instruments have become indispensable in modern chemical research. One such instrument is the mass spectrometer, which measures the masses of positive ions produced from a very small sample and displays the data as a *mass spectrum* (see Figure 3.8). This mass spectrum can be used to identify a substance or to obtain the molecular formula of a newly prepared compound.

Positive ions of molecules, like those of atoms, can be generated by bombarding the gas, or vapor of the substance, with electrons. The mass spectra of molecules, however, are usually much more complicated than those of atoms. One reason is that the molecular ions produced often break into fragments, giving several different kinds of positive ions. Consider the CH_2Cl_2 molecule (methylene chloride). When this molecule is struck by a high-energy electron, a positive ion $CH_2Cl_2^+$ may form.

$$CH_2Cl_2 + e^- \longrightarrow CH_2Cl_2^+ + 2e^-$$

The $CH_2Cl_2^+$ ion gains a great deal of energy from the collision of CH_2Cl_2 with the electron, and the ion frequently loses this energy by breaking into smaller pieces. One way is

$$CH_2Cl_2^+ \longrightarrow CH_2Cl^+ + Cl$$

Thus, the original molecule, even one as simple as CH_2Cl_2, can give rise to a number of ions.

The second reason for the complexity of the mass spectrum of a molecular substance is that many of the atoms in any ion can occur with different isotopic mass, so each ion often has many peaks. The mass spectrum of methylene chloride, CH_2Cl_2, is shown in Figure 3.8. Fourteen peaks are clearly visible. A larger molecule can give an even more complicated spectrum.

Because of the complexity of the mass spectrum, it can be used as a "fingerprint" in identifying a compound. Only methylene chloride has exactly the spectrum shown in Figure 3.8. Thus, by comparing the mass spectrum of an unknown substance with those in a catalog of mass spectra of known compounds, you can determine its identity. The more information you have about the compound, the shorter the search through the catalog of spectra.

The mass spectrum itself contains a wealth of information about molecular structure. Some experience is needed to analyze the spectrum of a compound, but you can get an idea of how it is done by looking at Figure 3.8. Suppose you do not know the identity of the compound.

Empirical Formula from the Composition

The empirical formula of a compound shows the ratios of numbers of atoms in the compound. You can find this formula from the composition of the compound by converting masses of the elements to moles. The next two examples show these calculations in detail.

Example 3.10 Determining the Empirical Formula from Masses of Elements (Binary Compound)

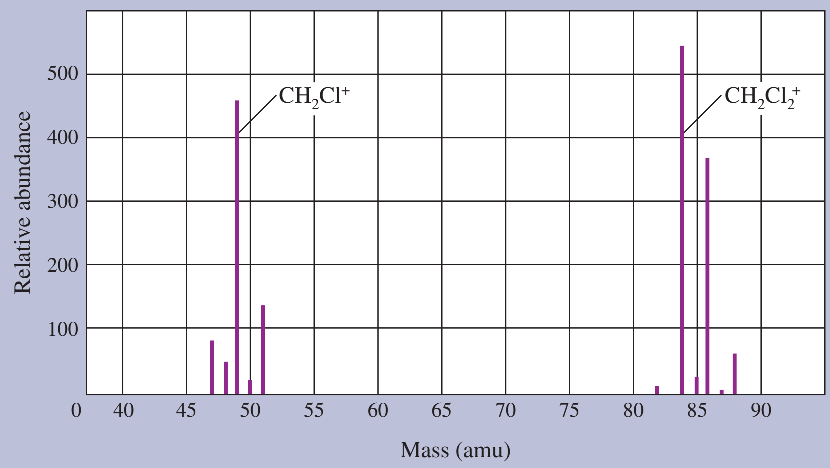
A compound of nitrogen and oxygen is analyzed, and a sample weighing 1.587 g is found to contain 0.483 g N and 1.104 g O. What is the empirical formula of the compound?

Problem Strategy This compound has the formula N_xO_y, where x and y are whole numbers that we need to determine. Masses of N and O are given in the problem. If we convert the masses of each of these elements to moles, they will be proportional to the subscripts in the empirical formula. The formula must be the smallest integer ratio of the elements. To obtain the smallest integers from the moles, we divide each by the smallest one. If the results are all whole numbers, they will be the subscripts in the formula. (Otherwise, you will need to multiply by some factor, as illustrated in Example 3.11.)

(*continued*)

FIGURE 3.8

Mass spectrum of methylene chloride, CH_2Cl_2
The lines at higher mass correspond to ions of the original molecule. Several lines occur because of the presence of different isotopes in the ion.



The most intense peaks at the greatest mass often correspond to the ion from the original molecule and give you the molecular mass. Thus, you would expect the peaks at mass 84 and mass 86 to be from the original molecular ion, so the molecular mass is approximately 84 to 86.

An elemental analysis is also possible. The two most intense peaks in Figure 3.8 are at 84 amu and 49 amu. They differ by 35 amu. Perhaps the original molecule that gives the peak at 84 amu contains a chlorine-35 atom, which is lost to give the peak at 49 amu. If this is true, you should expect a weaker peak at mass 86, corresponding to the original molecular ion with chlorine-37 in place of a chlorine-35 atom. This is indeed what you see.

The relative heights of the peaks, which depend on the natural abundances of atoms, are also important, because they give you additional information about the elements present. The relative heights can also tell you how many atoms of a given element are in the original molecule. Naturally occurring chlorine is 75.8% chlorine-35 and 24.2% chlorine-37. If the original molecule contained only one Cl atom, the peaks at 84 amu and 86 amu would be in the ratio 0.758 : 0.242. That is, the peak at 86 amu would be about one-third the height of the one at 84 amu. In fact, the relative height is twice this value. This means that the molecular ion contains two chlorine atoms, because the chance that any such ion contains one chlorine-37 atom is then twice as great. Thus, simply by comparing relative peak heights, you can both confirm the presence of particular elements and obtain the molecular formula.

■ See Problems 3.109 and 3.110.

(continued)

Solution You convert the masses to moles:

$$0.483\ \cancel{g\ N} \times \frac{1\ \text{mol N}}{14.0\ \cancel{g\ N}} = 0.0345\ \text{mol N}$$

$$1.104\ \cancel{g\ O} \times \frac{1\ \text{mol O}}{16.00\ \cancel{g\ O}} = 0.06900\ \text{mol O}$$

In order to obtain the smallest integers, you divide each mole number by the smaller one (0.0345 mol). For N, you get 1.00; for O, you get 2.00. Thus, the ratio of number of N atoms to the number of O atoms is 1 to 2. Hence, the empirical formula is $\mathbf{NO_2}$.

Answer Check Keep in mind that the empirical formula determined by this type of calculation is not necessarily the molecular formula of the compound. The only information that it provides is the smallest whole-number ratio of the elements.

Exercise 3.10 A sample of compound weighing 83.5 g contains 33.4 g of sulfur. The rest is oxygen. What is the empirical formula?

■ See Problems 3.65 and 3.66.

Example 3.11 Determining the Empirical Formula from Percentage Composition (General)

Chromium forms compounds of various colors. (The word *chromium* comes from the Greek *khroma,* meaning "color"; see Figure 3.9.) Sodium dichromate is the most important commercial chromium compound, from which many other chromium compounds are manufactured. It is a bright orange, crystalline substance. An analysis of sodium dichromate gives the following mass percentages: 17.5% Na, 39.7% Cr, and 42.8% O. What is the empirical formula of this compound? (Sodium dichromate is ionic, so it has no molecular formula.)

FIGURE 3.9

Chromium compounds of different colors *Clockwise from top:* Potassium chromate, K_2CrO_4; chromium(VI) oxide, CrO_3; chromium(III) sulfate, $Cr_2(SO_4)_3$; chromium metal; potassium dichromate, $K_2Cr_2O_7$; chromium(III) oxide, Cr_2O_3.

Problem Strategy Here we need to determine the whole-number values for x, y, and z in the compound $Na_xCr_yO_z$. The first task is to use the percent composition data to determine the moles of Na, Cr, and O in the compound. Then we can use mole ratios of these elements to determine the empirical formula. Assume for the purposes of this calculation that you have 100.0 g of substance. Then the mass of each element in the sample equals the numerical value of the percentage. For example, the quantity of sodium in sodium dichromate is 17.5 g, since the substance is 17.5% Na. Now convert the masses to moles and divide each mole number by the smallest. In this example, you do not obtain a series of integers, or whole numbers, from this division. You will need to find a whole-number factor to multiply these results by to obtain integers. Normally this factor will be 2 or 3, though it might be larger.

Solution Of the 100.0 g of sodium dichromate, 17.5 g is Na, 39.7 g is Cr, and 42.8 g is O. You convert these amounts to moles.

$$17.5\ \cancel{\text{g Na}} \times \frac{1\ \text{mol Na}}{23.0\ \cancel{\text{g Na}}} = 0.761\ \text{mol Na}$$

$$39.7\ \cancel{\text{g Cr}} \times \frac{1\ \text{mol Cr}}{52.0\ \cancel{\text{g Cr}}} = 0.763\ \text{mol Cr}$$

$$42.8\ \cancel{\text{g O}} \times \frac{1\ \text{mol O}}{16.0\ \cancel{\text{g O}}} = 2.68\ \text{mol O}$$

Now you divide all the mole numbers by the smallest one.

$$\text{For Na:}\ \frac{0.761\ \cancel{\text{mol}}}{0.761\ \cancel{\text{mol}}} = 1.00$$

$$\text{For Cr:}\ \frac{0.763\ \cancel{\text{mol}}}{0.761\ \cancel{\text{mol}}} = 1.00$$

$$\text{For O:}\ \frac{2.68\ \cancel{\text{mol}}}{0.761\ \cancel{\text{mol}}} = 3.52$$

You must decide whether these numbers are integers (whole numbers), within experimental error. If you round off the last digit, which is subject to experimental error, you get $Na_{1.0}Cr_{1.0}O_{3.5}$. In this case, the subscripts are not all integers. However, they can be made into integers by multiplying each one by 2; you get $Na_{2.0}Cr_{2.0}O_{7.0}$. Thus, the empirical formula is $\mathbf{Na_2Cr_2O_7}$.

Answer Check If you are working this type of problem and are not arriving at an answer that is readily converted to integers, it might be that you did not carry forward enough significant figures throughout the calculation and/or that you rounded intermediate calculations.

Exercise 3.11 Benzoic acid is a white, crystalline powder used as a food preservative. The compound contains 68.8% C, 5.0% H, and 26.2% O, by mass. What is its empirical formula?

■ See Problems 3.67, 3.68, 3.69, and 3.70.

Molecular Formula from Empirical Formula

The molecular formula of a compound is a multiple of its empirical formula. For example, the molecular formula of acetylene, C_2H_2, is equivalent to $(CH)_2$, and the molecular formula of benzene, C_6H_6, is equivalent to $(CH)_6$. Therefore, the molecular mass is some multiple of the empirical formula mass, which is obtained by summing the atomic masses of the atoms in the empirical formula. For any molecular compound, you can write

$$\text{Molecular mass} = n \times \text{empirical formula mass}$$

where n is the number of empirical formula units in the molecule. You get the molecular formula by multiplying the subscripts of the empirical formula by n, which you calculate from the equation

$$n = \frac{\text{molecular mass}}{\text{empirical formula mass}}$$

Once you determine the empirical formula for a compound, you can calculate its empirical formula mass. If you have an experimental determination of its molecular mass, you can calculate n and then the molecular formula. The next example illustrates how you use percentage composition and molecular mass to determine the molecular formula of acetic acid.

Example 3.12 Determining the Molecular Formula from Percentage Composition and Molecular Mass

In Example 3.9, we found the percentage composition of acetic acid to be 39.9% C, 6.7% H, and 53.4% O. Determine the empirical formula. The molecular mass of acetic acid was determined by experiment to be 60.0 amu. What is its molecular formula?

Problem Strategy This problem employs the same general strategy as Example 3.11, with a few additional steps. In this case the compound is composed of C, H, and O. After determining the empirical formula of the compound, you calculate the empirical formula mass. You then determine how many times more massive the molecular compound is than the empirical compound by dividing the molecular mass by the empirical formula mass. You now have a factor by which the subscripts of the empirical formula need to be multiplied to arrive at the molecular formula.

Solution A sample of 100.0 g of acetic acid contains 39.9 g C, 6.7 g H, and 53.4 g O. Converting these masses to moles gives 3.33 mol C, 6.6 mol H, and 3.34 mol O. Dividing the mole numbers by the smallest one gives 1.00 for C, 2.0 for H, and 1.00 for O. **The empirical formula of acetic acid is CH_2O.** (You may have noted that the percentage composition of acetic acid is, within experimental error, the same as that of formaldehyde—see Example 3.7—so they must have the same empirical formula.) The empirical formula mass is 30.0 amu. Dividing the empirical formula mass into the moecular mass gives the number by which the subscripts in CH_2O must be multiplied.

$$n = \frac{\text{molecular mass}}{\text{empirical formula mass}} = \frac{60.0\ \text{amu}}{30.0\ \text{amu}} = 2.00$$

The molecular formula of acetic acid is $(CH_2O)_2$, or $C_2H_4O_2$. (A molecular model of acetic acid is shown in Figure 3.10.)

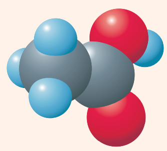


FIGURE 3.10 ▲ **Molecular model of acetic acid**

(continued)

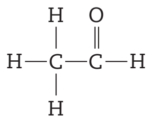
(continued)

Answer Check Calculate the molecular mass of your answer. It should agree with the molecular mass of the compound given in the problem.

Exercise 3.12 The percentage composition of acetaldehyde is 54.5% C, 9.2% H, and 36.3% O, and its molecular mass is 44 amu. Obtain the molecular formula of acetaldehyde.

■ See Problems 3.73, 3.74, 3.75, and 3.76.

The condensed structural formula for acetaldehyde is CH_3CHO. Its structural formula is



Determining this structural formula requires additional information.

The formula of acetic acid is often written $HC_2H_3O_2$ to indicate that one of the hydrogen atoms is acidic (lost easily), while the other three are not (Figure 3.10). Now that you know the formulas of acetic acid and acetaldehyde (determined from the data in Exercise 3.12 to be C_2H_4O), you can write the equations for the preparation of acetic acid described in the chapter opener. < The first step consists of reacting ethanol with oxygen to obtain acetaldehyde and water. If you write the chemical equation and balance it, you obtain

$$\underset{\text{ethanol}}{2C_2H_5OH} + O_2 \longrightarrow \underset{\text{acetaldehyde}}{2C_2H_4O} + 2H_2O$$

In practice, the reaction is carried out with the reactants as gases (gas phase) at about 400°C using silver as a catalyst.

The second step consists of reacting acetaldehyde with oxygen to obtain acetic acid. Acetaldehyde liquid is mixed with a catalyst—manganese(II) acetate—and air is bubbled through it. The balanced equation is

$$\underset{\text{acetaldehyde}}{2C_2H_4O} + O_2 \longrightarrow \underset{\text{acetic acid}}{2HC_2H_3O_2}$$

Once you have this balanced equation, you are in a position to answer quantitative questions such as, How much acetic acid can you obtain from a 10.0-g sample of acetaldehyde? You will see how to answer such questions in the next sections.

Concept Check 3.3

A friend has some questions about empirical formulas and molecular formulas. You can assume that he is good at performing the calculations.

a. For a problem that asked him to determine the empirical formula, he came up with the answer $C_2H_8O_2$. Is this a possible answer to the problem? If not, what guidance would you offer your friend?

b. For another problem he came up with the answer $C_{1.5}H_4$ as the empirical formula. Is this answer correct? Once again, if it isn't correct, what could you do to help your friend?

c. Since you have been a big help, your friend asks one more question. He completed a problem of the same type as Example 3.12. His answers indicate that the compound had an empirical formula of C_3H_8O and the molecular formula C_3H_8O. Is this result possible?

Stoichiometry: Quantitative Relations in Chemical Reactions

In Chapter 2, we described a chemical equation as a representation of what occurs when molecules react. We will now study chemical equations more closely to answer questions about the stoichiometry of reactions. **Stoichiometry** (pronounced "stoy-key-om′-e-tree") is *the calculation of the quantities of reactants and products involved in a chemical reaction.* It is based on the chemical equation and on the relationship between mass and moles. Such calculations are fundamental to most quantitative work in chemistry. In the next sections, we will use the industrial Haber process for the production of ammonia to illustrate stoichiometric calculations.

3.6 Molar Interpretation of a Chemical Equation

In the Haber process for producing ammonia, NH_3, nitrogen (from the atmosphere) reacts with hydrogen at high temperature and pressure.

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

Hydrogen is usually obtained from natural gas or petroleum and so is relatively expensive. For this reason, the price of hydrogen partly determines the price of ammonia. Thus, an important question to answer is, How much hydrogen is required to give a particular quantity of ammonia? For example, how much hydrogen would be needed to produce one ton (907 kg) of ammonia? Similar kinds of questions arise throughout chemical research and industry.

To answer such quantitative questions, you must first look at the balanced chemical equation: one N_2 molecule and three H_2 molecules react to produce two NH_3 molecules (see models above). A similar statement involving multiples of these numbers of molecules is also correct. For example, 6.02×10^{23} N_2 molecules react with $3 \times 6.02 \times 10^{23}$ H_2 molecules, giving $2 \times 6.02 \times 10^{23}$ NH_3 molecules. This last statement can be put in molar terminology: one mole of N_2 reacts with three moles of H_2 to give two moles of NH_3.

You may interpret a chemical equation either in terms of numbers of molecules (or ions or formula units) or in terms of numbers of moles, depending on your needs.

Because moles can be converted to mass, you can also give a mass interpretation of a chemical equation. The molar masses of N_2, H_2, and NH_3 are 28.0, 2.02, and 17.0 g/mol, respectively. Therefore, 28.0 g of N_2 reacts with 3×2.02 g of H_2 to yield 2×17.0 g of NH_3.

We summarize these three interpretations as follows:

N_2	+	$3H_2$	$\longrightarrow$	$2NH_3$	
1 molecule N_2	+	3 molecules H_2	$\longrightarrow$	2 molecules NH_3	(molecular interpretation)
1 mol N_2	+	3 mol H_2	$\longrightarrow$	2 mol NH_3	(molar interpretation)
28.0 g N_2	+	3×2.02 g H_2	$\longrightarrow$	2×17.0 g NH_3	(mass interpretation)

Suppose you ask how many grams of atmospheric nitrogen will react with 6.06 g (3×2.02 g) of hydrogen. You see from the last equation that the answer is 28.0 g N_2. We formulated this question for one mole of atmospheric nitrogen. Recalling the question posed earlier, you may ask how much hydrogen (in kg) is needed to yield 907 kg of ammonia in the Haber process. The solution to this problem depends on the fact that *the number of moles involved in a reaction is proportional to the coefficients in the balanced chemical equation.* In the next section, we will describe a procedure for solving such problems.

Exercise 3.13 In an industrial process, hydrogen chloride, HCl, is prepared by burning hydrogen gas, H_2, in an atmosphere of chlorine, Cl_2. Write the chemical equation for the reaction. Below the equation, give the molecular, molar, and mass interpretations.

■ See Problems 3.77 and 3.78.

3.7 Amounts of Substances in a Chemical Reaction

You see from the preceding discussion that a balanced chemical equation relates the amounts of substances in a reaction. The coefficients in the equation can be given a molar interpretation, and using this interpretation you can, for example, calculate the moles of product obtained from any given moles of reactant. Also, you can extend this type of calculation to answer questions about masses of reactants and products.

Again consider the Haber process for producing ammonia gas. Suppose you have a mixture of H_2 and N_2, and 4.8 mol H_2 in this mixture reacts with N_2 to produce NH_3. How many moles of NH_3 can you produce from this quantity of H_2? In asking questions like this, you assume that the mixture contains a sufficient quantity of the other reactant (N_2, in this case).

This conversion factor simply expresses the fact that the mole ratio of NH_3 to H_2 in the reaction is 2 to 3.

The balanced chemical equation for the Haber process tells you that 3 mol H_2 produce 2 mol NH_3. You can express this as a conversion factor: <

$$\underbrace{\frac{2 \text{ mol } NH_3}{3 \text{ mol } H_2}}_{\substack{\text{Converts from} \\ \text{mol } H_2 \text{ to mol } NH_3}}$$

Multiplying any quantity of H_2 by this conversion factor mathematically converts that quantity of H_2 to the quantity of NH_3 as specified by the balanced chemical equation. Note that you write the conversion factor with the quantity you are converting *from* on the bottom (3 mol H_2), and the quantity you are converting *to* on the top (2 mol NH_3).

To calculate the quantity of NH_3 produced from 4.8 mol H_2, you write 4.8 mol H_2 and multiply this by the preceding conversion factor:

$$4.8 \cancel{\text{mol } H_2} \times \frac{2 \text{ mol } NH_3}{3 \cancel{\text{mol } H_2}} = 3.2 \text{ mol } NH_3$$

Note how the unit mol H_2 cancels to give the answer in mol NH_3.

In this calculation, you converted moles of reactant to moles of product.

$$\text{Moles reactant} \longrightarrow \text{moles product}$$

It is just as easy to calculate the moles of reactant needed to obtain the specified moles of product. You mathematically convert moles of product to moles of reactant.

$$\text{Moles product} \longrightarrow \text{moles reactant}$$

To set up the conversion factor, you refer to the balanced chemical equation and place the quantity you are converting from on the bottom and the quantity you are converting to on the top.

$$\underbrace{\frac{3 \text{ mol } H_2}{2 \text{ mol } NH_3}}_{\substack{\text{Converts from} \\ \text{mol } NH_3 \text{ to mol } H_2}}$$

Now consider the problem asked in the previous section: How much hydrogen (in kg) is needed to yield 907 kg of ammonia by the Haber process? The balanced chemical equation directly relates moles of substances, not masses. Therefore, you must first convert the mass of ammonia to moles of ammonia, then convert moles of ammonia to moles of hydrogen. Finally, you convert moles of hydrogen to mass of hydrogen.

$$\text{Mass } NH_3 \longrightarrow \text{mol } NH_3 \longrightarrow \text{mol } H_2 \longrightarrow \text{mass } H_2$$

You learned how to convert mass to moles, and vice versa, in Section 3.2.

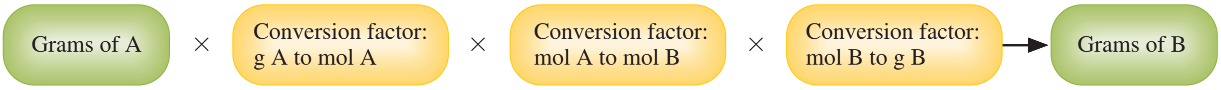


FIGURE 3.11

Steps in a stoichiometric calculation
You convert the mass of substance A in a reaction to moles of substance A, then to moles of another substance B, and finally to mass of substance B.

The calculation to convert 907 kg NH_3, or 9.07×10^5 g NH_3, to mol NH_3 is as follows:

$$9.07 \times 10^5\ \cancel{\text{g NH}_3} \times \underbrace{\frac{1\ \text{mol NH}_3}{17.0\ \cancel{\text{g NH}_3}}}_{\substack{\text{Converts from} \\ \text{g NH}_3 \text{ to mol NH}_3}} = 5.34 \times 10^4\ \text{mol NH}_3$$

Now you convert from moles NH_3 to moles H_2.

$$5.34 \times 10^4\ \cancel{\text{mol NH}_3} \times \underbrace{\frac{3\ \text{mol H}_2}{2\ \cancel{\text{mol NH}_3}}}_{\substack{\text{Converts from} \\ \text{mol NH}_3 \text{ to mol H}_2}} = 8.01 \times 10^4\ \text{mol H}_2$$

Finally, you convert moles H_2 to grams H_2.

$$8.01 \times 10^4\ \cancel{\text{mol H}_2} \times \underbrace{\frac{2.02\ \text{g H}_2}{1\ \cancel{\text{mol H}_2}}}_{\substack{\text{Converts from} \\ \text{mol H}_2 \text{ to g H}_2}} = 1.62 \times 10^5\ \text{g H}_2$$

The result says that to produce 907 kg NH_3, you need 1.62×10^5 g H_2, or 162 kg H_2.

Once you feel comfortable with the individual conversions, you can do this type of calculation in a single step by multiplying successively by conversion factors, as follows:

$$9.07 \times 10^5\ \cancel{\text{g NH}_3} \times \frac{1\ \cancel{\text{mol NH}_3}}{17.0\ \cancel{\text{g NH}_3}} \times \frac{3\ \cancel{\text{mol H}_2}}{2\ \cancel{\text{mol NH}_3}} \times \frac{2.02\ \text{g H}_2}{1\ \cancel{\text{mol H}_2}} =$$
$$1.62 \times 10^5\ \text{g H}_2\ (\text{or } 162\ \text{kg H}_2)$$

Note that the unit in the denominator of each conversion factor cancels the unit in the numerator of the preceding factor. Figure 3.11 illustrates this calculation diagrammatically.

The following two examples illustrate additional variations of this type of calculation.

Example 3.13 Relating the Quantity of Reactant to Quantity of Product

Hematite, Fe_2O_3, is an important ore of iron; see Figure 3.12. (An ore is a natural substance from which the metal can be profitably obtained.) The free metal is obtained by reacting hematite with carbon monoxide, CO, in a blast furnace. Carbon monoxide is formed in the furnace by partial combustion of carbon. The reaction is

$$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$$

How many grams of iron can be produced from 1.00 kg Fe_2O_3?

FIGURE 3.12

Hematite
The name of this iron mineral stems from the Greek word for blood, which alludes to the color of certain forms of the mineral.

Problem Strategy This calculation involves the conversion of a quantity of Fe_2O_3 to a quantity of Fe. In performing this calculation, we assume that there is enough CO for the complete reaction of the Fe_2O_3. An essential feature of this type of calculation is that you must use the information from the balanced

(*continued*)

(continued)

chemical equation to convert from the moles of a given substance to the moles of another substance. Therefore, you first convert the mass of Fe_2O_3 (1.00 kg Fe_2O_3 = 1.0×10^3 g Fe_2O_3) to moles of Fe_2O_3. Then, using the relationship from the balanced chemical equation, you convert moles of Fe_2O_3 to moles of Fe. Finally, you convert the moles of Fe to grams of Fe.

Solution The calculation is as follows:

$$1.00 \times 10^3\ \cancel{\text{g Fe}_2\text{O}_3} \times \frac{1\ \cancel{\text{mol Fe}_2\text{O}_3}}{160\ \cancel{\text{g Fe}_2\text{O}_3}} \times \frac{2\ \cancel{\text{mol Fe}}}{1\ \cancel{\text{mol Fe}_2\text{O}_3}} \times \frac{55.8\ \text{g Fe}}{1\ \cancel{\text{mol Fe}}} = \mathbf{698\ g\ Fe}$$

Answer Check When calculating the mass of product produced in a chemical reaction such as this, keep in mind that the total mass of reactants must equal the total mass of products. Because of this, you should be suspicious of any calculation where you find a few grams of reactant produces a large mass of product.

Exercise 3.14 Sodium is a soft, reactive metal that instantly reacts with water to give hydrogen gas and a solution of sodium hydroxide, NaOH. How many grams of sodium metal are needed to give 7.81 g of hydrogen by this reaction? (Remember to write the balanced equation first.)

■ See Problems 3.83, 3.84, 3.85, and 3.86.

Example 3.14 Relating the Quantities of Two Reactants (or Two Products)

Today chlorine is prepared from sodium chloride by electrochemical decomposition. Formerly chlorine was produced by heating hydrochloric acid with pyrolusite (manganese dioxide, MnO_2), a common manganese ore. Small amounts of chlorine may be prepared in the laboratory by the same reaction (see Figure 3.13):

$$4HCl(aq) + MnO_2(s) \longrightarrow 2H_2O(l) + MnCl_2(aq) + Cl_2(g)$$

How many grams of HCl react with 5.00 g of manganese dioxide, according to this equation?

Problem Strategy When starting a problem like this, determine and note which quantities in the balanced chemical equation are being related. Here you are looking at the two reactants, and the relationship is that 4 mol HCl reacts with 1 mol MnO_2. Answer this problem following the same strategy as outlined in Example 3.13, only this time use the relationship between the HCl and MnO_2.

Solution You write what is given (5.00 g MnO_2) and convert this to moles, then to moles of what is desired (mol HCl). Finally you convert this to mass (g HCl). The calculation is:

$$5.00\ \cancel{\text{g MnO}_2} \times \frac{1\ \cancel{\text{mol MnO}_2}}{86.9\ \cancel{\text{g MnO}_2}} \times \frac{4\ \cancel{\text{mol HCl}}}{1\ \cancel{\text{mol MnO}_2}} \times \frac{36.5\ \text{g HCl}}{1\ \cancel{\text{mol HCl}}} = \mathbf{8.40\ g\ HCl}$$

Answer Check To avoid incorrect answers, before starting any stoichiometry problem, make sure that the chemical equation is complete and balanced and that the chemical formulas are correct.

FIGURE 3.13 ▲
Preparation of chlorine
Concentrated hydrochloric acid was added to manganese dioxide in the beaker. Note the formation of yellowish green gas (chlorine), which is depicted by molecular models.

(continued)

(continued)

Exercise 3.15 Sphalerite is a zinc sulfide (ZnS) mineral and an important commercial source of zinc metal. The first step in the processing of the ore consists of heating the sulfide with oxygen to give zinc oxide, ZnO, and sulfur dioxide, SO_2. How many kilograms of oxygen gas combine with 5.00×10^3 g of zinc sulfide in this reaction? (You must first write the balanced chemical equation.)

■ See Problems 3.87 and 3.88.

Exercise 3.16 The British chemist Joseph Priestley prepared oxygen in 1774 by heating mercury(II) oxide, HgO. Mercury metal is the other product. If 6.47 g of oxygen is collected, how many grams of mercury metal are also produced?

■ See Problems 3.89 and 3.90.

Concept Check 3.4

The main reaction of a charcoal grill is $C(s) + O_2(g) \longrightarrow CO_2(g)$. Which of the statements below are incorrect? Why?

a. 1 atom of carbon reacts with 1 molecule of oxygen to produce 1 molecule of CO_2.

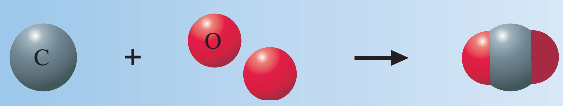
b. 1 g of C reacts with 1 g of O_2 to produce 2 grams of CO_2.

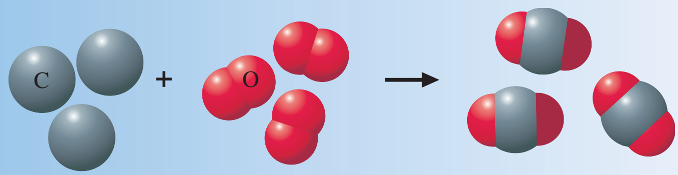
c. 1 g of C reacts with 0.5 g of O_2 to produce 1 g of CO_2.

d. 12 g of C reacts with 32 g of O_2 to produce 44 g of CO_2.

e. 1 mol of C reacts with 1 mol of O_2 to produce 1 mol of CO_2.

f. 1 mol of C reacts with 0.5 mol of O_2 to produce 1 mol of CO_2.

g. 

h. 

3.8 Limiting Reactant; Theoretical and Percentage Yields

Often reactants are added to a reaction vessel in amounts different from the molar proportions given by the chemical equation. In such cases, only one of the reactants may be completely consumed at the end of the reaction, whereas some amounts of other reactants will remain unreacted. The **limiting reactant** (or **limiting reagent**) is *the reactant that is entirely consumed when a reaction goes to completion.* A reactant that is not completely consumed is often referred to as an *excess reactant.* Once one of the reactants is used up, the reaction stops. This means that:

> The moles of product are always determined by the starting moles of limiting reactant.

A couple of analogies may help you understand the limiting reactant problem. Suppose you want to make some cheese sandwiches. Each is made from two slices of bread and a slice of cheese. Let's write that in the form of a chemical equation:

$$2 \text{ slices bread} + 1 \text{ slice cheese} \longrightarrow 1 \text{ sandwich}$$

You look in the kitchen and see that you have six slices of bread and two slices of cheese. The six slices of bread would be enough to make three sandwiches if you had enough cheese. The two slices of cheese would be enough to make two sandwiches if you had enough bread. How many sandwiches can you make? What you will find is that once you have made two sandwiches, you will be out of cheese (Figure 3.14). Cheese is the "limiting reactant" in the language of chemistry. If you look at each "reactant," and ask how much "product" you can make from it, the reactant that limits your amount of product is called the limiting reactant.

Here is another analogy. Suppose you are supervising the assembly of automobiles. Your plant has in stock 300 steering wheels and 900 tires, plus an excess of every other needed component. How many autos can you assemble from this stock? Here is the "balanced equation" for the auto assembly:

$$1 \text{ steering wheel} + 4 \text{ tires} + \text{other components} \longrightarrow 1 \text{ auto}$$

One way to solve this problem is to calculate the number of autos that you could assemble from each component. In this case, you only need to concentrate on the effects of the steering wheels and tires since production will not be limited by the other, excess components. Looking at the equation, you can determine that from 300 steering wheels, you could assemble 300 autos; from 900 tires you could assemble $900 \div 4 = 225$ autos.

How many autos can you produce, 225 or 300? Note that by the time you have assembled 225 autos, you will have exhausted your stock of tires, so no more autos can be assembled. Tires are the "limiting reactant," since they limit the number of automobiles that you can actually assemble (225).

You can set up these calculations in the same way for a chemical reaction. First, you calculate the numbers of autos you could assemble from the number of steering

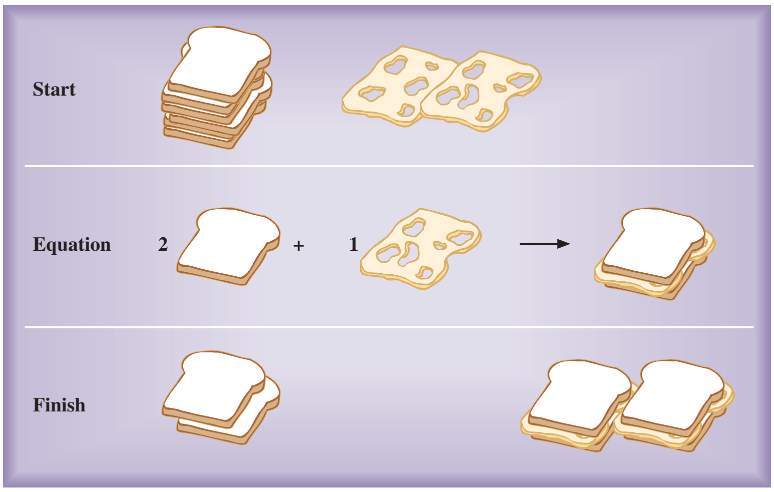


FIGURE 3.14

Limiting reactant analogy using cheese sandwiches
Start with six slices of bread, two slices of cheese, and the sandwich-making equation. Even though you have extra bread, you are limited to making two sandwiches by the amount of cheese you have on hand. Cheese is the limiting reactant.

wheels and from the number of tires available, and then you compare the results. From the balanced equation, you can see that one steering wheel is equivalent to one auto, and four tires are equivalent to one auto. Therefore:

$$300 \text{ ~~steering wheels~~} \times \frac{1 \text{ auto}}{1 \text{ ~~steering wheel~~}} = 300 \text{ autos}$$

$$900 \text{ ~~tires~~} \times \frac{1 \text{ auto}}{4 \text{ ~~tires~~}} = 225 \text{ autos}$$

Comparing the numbers of autos produced (225 autos versus 300 autos), you conclude that tires are the limiting component. (The component producing the fewer autos is the limiting component.) Note that apart from the units (or factor labels), the calculation is identical with what was done previously.

Now consider a chemical reaction, the burning of hydrogen in oxygen.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$

Suppose you put 1 mol H_2 and 1 mol O_2 into a reaction vessel. How many moles of H_2O will be produced? First, you note that 2 mol H_2 produces 2 mol H_2O and that 1 mol O_2 produces 2 mol H_2O. Now you calculate the moles of H_2O that you could produce from each quantity of reactant, assuming that there is sufficient other reactant.

$$1 \cancel{\text{mol } H_2} \times \frac{2 \text{ mol } H_2O}{2 \cancel{\text{mol } H_2}} = 1 \text{ mol } H_2O$$

$$1 \cancel{\text{mol } O_2} \times \frac{2 \text{ mol } H_2O}{1 \cancel{\text{mol } O_2}} = 2 \text{ mol } H_2O$$

Comparing these results, you see that hydrogen, H_2, yields the least amount of product, so it must be the limiting reactant. By the time 1 mol H_2O is produced, all of the hydrogen is used up; the reaction stops. Oxygen, O_2, is the excess reactant. Figure 3.15 depicts this reaction from a molecular viewpoint.

We can summarize the limiting-reactant problem as follows. Suppose you are given the amounts of reactants added to a vessel, and you wish to calculate the amount of product obtained when the reaction is complete. Unless you know that the reactants have been added in the molar proportions given by the chemical equation, the problem is twofold: (1) you must first identify the limiting reactant; (2) you then calculate the amount of product from the amount of limiting reactant. The next examples illustrate the steps.

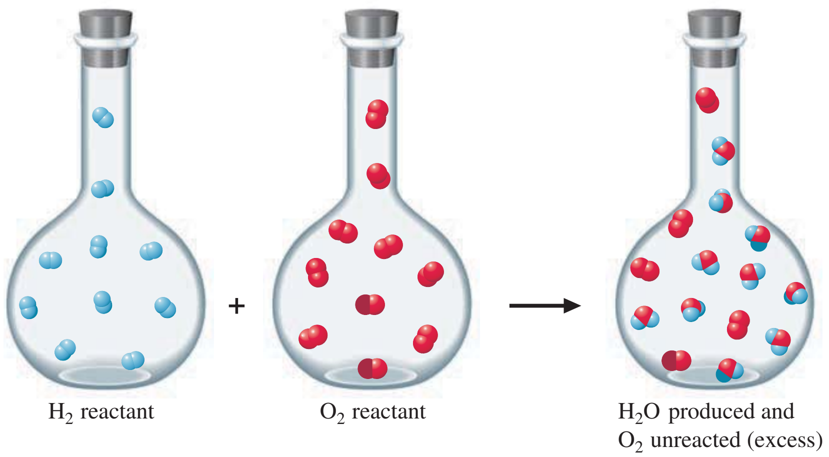


FIGURE 3.15
Molecular view of $2H_2 + O_2 \longrightarrow 2H_2O$ reaction with H_2 as the limiting reactant
When an equal number of moles of H_2 and O_2 are reacted according to the equation $2H_2 + O_2 \longrightarrow 2H_2O$, all of the H_2 completely reacts, whereas only half of the O_2 is consumed. In this case, the H_2 is the limiting reactant and the O_2 is the excess reactant.

Example 3.15 Calculating with a Limiting Reactant (Involving Moles)

Zinc metal reacts with hydrochloric acid by the following reaction:

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

If 0.30 mol Zn is added to hydrochloric acid containing 0.52 mol HCl, how many moles of H_2 are produced?

Problem Strategy

Step 1: Which is the limiting reactant? To answer this, using the relationship from the balanced chemical equation, you take each reactant in turn and ask how much product (H_2) would be obtained if each were totally consumed. The reactant that gives the smaller amount of product is the limiting reactant. (Remember how you obtained the limiting component in the auto-assembly analogy.)

Step 2: You obtain the amount of product actually obtained from the amount of limiting reactant.

Solution

Step 1:

$$0.30\ \cancel{\text{mol Zn}} \times \frac{1\ \text{mol H}_2}{1\ \cancel{\text{mol Zn}}} = 0.30\ \text{mol H}_2$$

$$0.52\ \cancel{\text{mol HCl}} \times \frac{1\ \text{mol H}_2}{2\ \cancel{\text{mol HCl}}} = 0.26\ \text{mol H}_2$$

You see that hydrochloric acid must be the limiting reactant and that some zinc must be left unconsumed. (Zinc is the excess reactant.)

Step 2: Since HCl is the limiting reactant, the amount of H_2 produced must be **0.26 mol.**

Answer Check A common assumption that often leads to errors in solving a problem of this type is to assume that whichever reactant is present in the least quantity (in mass or moles of material) is automatically the limiting reactant. Note how that assumption would have led to an incorrect answer in this problem. Always be sure to account for the stoichiometry of the balanced chemical equation.

Exercise 3.17 Aluminum chloride, $AlCl_3$, is used as a catalyst in various industrial reactions. It is prepared from hydrogen chloride gas and aluminum metal shavings.

$$2Al(s) + 6HCl(g) \longrightarrow 2AlCl_3(s) + 3H_2(g)$$

Suppose a reaction vessel contains 0.15 mol Al and 0.35 mol HCl. How many moles of $AlCl_3$ can be prepared from this mixture?

■ See Problems 3.91 and 3.92.

Example 3.16 Calculating with a Limiting Reactant (Involving Masses)

In a process for producing acetic acid, oxygen gas is bubbled into acetaldehyde, CH_3CHO, containing manganese(II) acetate (catalyst) under pressure at 60°C.

$$2CH_3CHO(l) + O_2(g) \longrightarrow 2HC_2H_3O_2(l)$$

In a laboratory test of this reaction, 20.0 g CH_3CHO and 10.0 g O_2 were put into a reaction vessel. a. How many grams of acetic acid can be produced by this reaction from these amounts of reactants? b. How many grams of the excess reactant remain after the reaction is complete?

Problem Strategy

a. This part is similar to the preceding example, but now you must convert grams of each reactant (acetaldehyde and oxygen) to moles of product (acetic acid). From these results, you decide which is the limiting reactant and the moles of product obtained, which you convert to grams of product.

b. In order to calculate the amount of excess reactant remaining after the reaction is complete, you need to know the identity of the excess reactant and how much of this excess reactant was needed for the reaction. The result from Step 1 provides the identity of the limiting reactant,

(continued)

(continued)

so you will know which reactant was in excess. From the moles of product produced by the limiting reactant, you calculate the grams of the excess reactant needed in the reaction. You now know how much of this excess reactant was consumed, so subtracting the amount consumed from the starting amount will yield the amount of excess reactant that remains.

Solution

a. How much acetic acid is produced?

Step 1: To determine which reactant is limiting, you convert grams of each reactant (20.0 g CH_3CHO and 10.0 g O_2) to moles of product, $HC_2H_3O_2$. Acetaldehyde has a molar mass of 44.1 g/mol, and oxygen has a molar mass of 32.0 g/mol.

$$20.0\ \cancel{\text{g } CH_3CHO} \times \frac{1\ \cancel{\text{mol } CH_3CHO}}{44.1\ \cancel{\text{g } CH_3CHO}} \times \frac{2\ \text{mol } HC_2H_3O_2}{2\ \cancel{\text{mol } CH_3CHO}} = 0.454\ \text{mol } HC_2H_3O_2$$

$$10.0\ \cancel{\text{g } O_2} \times \frac{1\ \cancel{\text{mol } O_2}}{32.0\ \cancel{\text{g } O_2}} \times \frac{2\ \text{mol } HC_2H_3O_2}{1\ \cancel{\text{mol } O_2}} = 0.625\ \text{mol } HC_2H_3O_2$$

Thus, acetaldehyde, CH_3CHO, is the limiting reactant, so 0.454 mol $HC_2H_3O_2$ was produced.

Step 2: You convert 0.454 mol $HC_2H_3O_2$ to grams of $HC_2H_3O_2$.

$$0.454\ \cancel{\text{mol } HC_2H_3O_2} \times \frac{60.1\ \text{g } HC_2H_3O_2}{1\ \cancel{\text{mol } HC_2H_3O_2}} = \mathbf{27.3\ g\ HC_2H_3O_2}$$

b. How much of the excess reactant (oxygen) was left over? You convert the moles of acetic acid to grams of oxygen (the quantity of oxygen needed to produce this amount of acetic acid).

$$0.454\ \cancel{\text{mol } HC_2H_3O_2} \times \frac{1\ \cancel{\text{mol } O_2}}{2\ \cancel{\text{mol } HC_2H_3O_2}} \times \frac{32.0\ \text{g } O_2}{1\ \cancel{\text{mol } O_2}} = 7.26\ \text{g } O_2$$

You started with 10.0 g O_2, so the quantity remaining is

$$(10.0 - 7.26)\ \text{g } O_2 = \mathbf{2.7\ g\ O_2} \qquad \text{(mass remaining)}$$

Answer Check Whenever you are confronted with a stoichiometry problem you should always determine if you are going to have to solve a limiting reactant problem like this one, or a problem like Example 3.13 that involves a single reactant and one reactant in excess. A good rule of thumb is that when two or more reactant quantities are specified, you should approach the problem as was done here.

FIGURE 3.16

Reaction of zinc and sulfur
When a hot nail is stuck into a pile of zinc and sulfur, a fiery reaction occurs and zinc sulfide forms.

Exercise 3.18 In an experiment, 7.36 g of zinc was heated with 6.45 g of sulfur (Figure 3.16). Assume that these substances react according to the equation

$$8Zn + S_8 \longrightarrow 8ZnS$$

What amount of zinc sulfide was produced?

■ See Problems 3.93 and 3.94.

The **theoretical yield** of product is *the maximum amount of product that can be obtained by a reaction from given amounts of reactants.* It is the amount that you calculate from the stoichiometry based on the limiting reactant. In Example 3.16, the theoretical yield of acetic acid is 27.3 g. In practice, the *actual yield* of a product may be much less for several possible reasons. First, some product may be lost during the process of separating it from the final reaction mixture. Second, there may be other, competing reactions that occur simultaneously with the reactant on which the theoretical yield is based. Finally, many reactions appear to stop before they reach completion; they give mixtures of reactants and products. <

Such reactions reach chemical equilibrium. We will discuss equilibrium quantitatively in Chapter 14.

It is important to know the actual yield from a reaction in order to make economic decisions about a preparation method. The reactants for a given method may not be too costly per kilogram, but if the actual yield is very low, the final cost can be very high. The **percentage yield** of product is *the actual yield (experimentally determined) expressed as a percentage of the theoretical yield (calculated).*

$$\text{Percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

To illustrate the calculation of percentage yield, recall that the theoretical yield of acetic acid calculated in Example 3.16 was 27.3 g. If the actual yield of acetic acid obtained in an experiment, using the amounts of reactants given in Example 3.16, is 23.8 g, then

$$\text{Percentage yield of } HC_2H_3O_2 = \frac{23.8\ \cancel{g}}{27.3\ \cancel{g}} \times 100\% = 87.2\%$$

Exercise 3.19 New industrial plants for acetic acid react liquid methanol with carbon monoxide in the presence of a catalyst.

$$CH_3OH(l) + CO(g) \longrightarrow HC_2H_3O_2(l)$$

In an experiment, 15.0 g of methanol and 10.0 g of carbon monoxide were placed in a reaction vessel. What is the theoretical yield of acetic acid? If the actual yield is 19.1 g, what is the percentage yield?

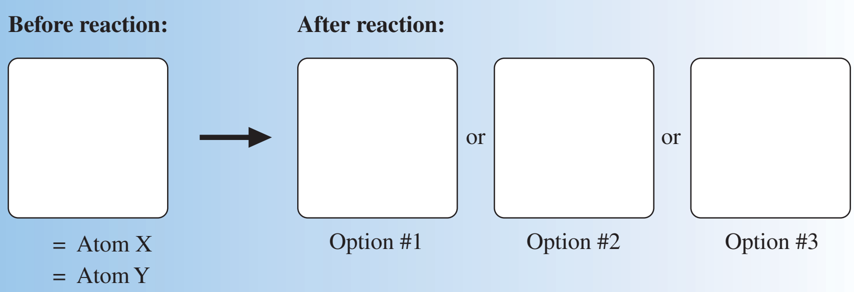
■ See Problems 3.97 and 3.98.

Concept Check 3.5

You perform the hypothetical reaction of an element, $X_2(g)$, with another element, $Y(g)$, to produce $XY(g)$.

a. Write the balanced chemical equation for the reaction.

b. If X_2 and Y were mixed in the quantities shown in the container on the left below and allowed to react, which of the three options is the correct representation of the contents of the container after the reaction has occurred?



c. Using the information presented in part b, identify the limiting reactant.

A Checklist for Review

Important Terms

molecular mass (3.1)
formula mass (3.1)
mole (mol) (3.2)
Avogadro's number (N_A) (3.2)
molar mass (3.2)
percentage composition (3.3)
mass percentage (3.3)
empirical (simplest) formula (3.5)
stoichiometry (3.6)
limiting reactant (reagent) (3.8)
theoretical yield (3.8)
percentage yield (3.8)

Key Equations

$$\text{Mass \% } A = \frac{\text{mass of } A \text{ in the whole}}{\text{mass of the whole}} \times 100\%$$

$$\text{Percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

$$n = \frac{\text{molecular mass}}{\text{empirical formula mass}}$$

Summary of Facts and Concepts

A *formula mass* equals the sum of the atomic masses of the atoms in the formula of a compound. If the formula corresponds to that of a molecule, this sum of atomic masses equals the *molecular mass* of the compound. The mass of *Avogadro's number* (6.02×10^{23}) of formula units—that is, the mass of one *mole* of substance—equals the mass in grams that corresponds to the numerical value of the formula mass in amu. This mass is called the *molar mass.*

The *empirical formula (simplest formula)* of a compound is obtained from the *percentage composition* of the substance, which is expressed as *mass percentages* of the elements. To calculate the empirical formula, you convert mass percentages to ratios of moles, which, when expressed in smallest whole numbers, give the subscripts in the formula. A molecular formula is a multiple of the empirical formula; this multiple is determined from the experimental value of the molecular mass.

A chemical equation may be interpreted in terms of moles of reactants and products, as well as in terms of molecules. Using this *molar interpretation,* you can convert from the mass of one substance in a chemical equation to the mass of another. The maximum amount of product from a reaction is determined by the *limiting reactant,* the reactant that is completely used up; the other reactants are in excess.

Media Summary

Visit the **student website at college.hmco.com/pic/ebbing9e** to help prepare for class, study for quizzes and exams, understand core concepts, and visualize molecular-level interactions. The following media activities are available for this chapter:

Prepare for Class

- **Video Lessons** *Mini lectures from chemistry experts*
  The Mole and Avogadro's Number
  Introducing Conversion of Masses, Moles, and Number of Particles
  Finding Empirical and Molecular Formulas
  Stoichiometry and Chemical Equations
  Finding Limiting Reagents
  CIA Demonstration: Self-Inflating Hydrogen Balloons
  Theoretical Yield and Percent Yield
  A Problem Involving the Combined Concepts of Stoichiometry

Improve Your Grade

- **Visualizations** *Molecular-level animations and lab demonstration videos*
  Oxidation of Zinc with Iodine
  Limiting Reactant
  Oxygen, Hydrogen, Soap Bubbles, and Balloons
- **Tutorials** *Animated examples and interactive activities*
  Formula Mass
  Limiting Reactants: Part One
  Limiting Reactants: Part Two
- **Flashcards** *Key terms and definitions*
  Online Flashcards
- **Self-Assessment Questions** *Additional questions with full worked-out solutions*
  6 Self-Assessment Questions

ACE the Test

Multiple-choice quizzes
3 ACE Practice Tests

Access these resources using the passkey available free with new texts or for purchase separately.

Learning Objectives

3.1 Molecular Mass and Formula Mass

- Define the terms *molecular mass* and *formula mass* of a substance.
- Calculate the formula mass from a formula. Example 3.1
- Calculate the formula mass from molecular models. Example 3.2

3.2 The Mole Concept

- Define the quantity called the *mole.*
- Learn *Avogadro's number.*
- Understand how the *molar mass* is related to the formula mass of a substance.
- Calculate the mass of atoms and molecules. Example 3.3
- Perform calculations using the mole.
- Convert from moles of substance to grams of substance. Example 3.4
- Convert from grams of substance to moles of substance. Example 3.5
- Calculate the number of molecules in a given mass of substance. Example 3.6

3.3 Mass Percentages from the Formula

- Define *mass percentage.*
- Calculate the percentage composition of the elements in a compound. Example 3.7
- Calculate the mass of an element in a given mass of compound. Example 3.8

3.4 Elemental Analysis: Percentage of Carbon, Hydrogen, and Oxygen

- Describe how C, H, and O combustion analysis is performed.
- Calculate the percentage of C, H, and O from combustion data. Example 3.9

3.5 Determining Formulas

- Define *empirical formula.*
- Determine the empirical formula of a binary compound from the masses of its elements. Example 3.10
- Determine the empirical formula from the percentage composition. Example 3.11
- Understand the relationship between the molecular mass of a substance and its *empirical formula mass.*
- Determine the molecular formula from the percentage composition and molecular mass. Example 3.12

3.6 Molar Interpretation of a Chemical Equation

- Relate the coefficients in a balanced chemical equation to the number of molecules or moles (*molar interpretation*).

3.7 Amounts of Substances in a Chemical Reaction

- Use the coefficients in a chemical reaction to perform calculations.
- Relate the quantities of reactant to the quantity of product. Example 3.13
- Relate the quantities of two reactants or two products. Example 3.14

3.8 Limiting Reactant; Theoretical and Percentage Yields

- Understand how a *limiting reactant* or *limiting reagent* determines the moles of product formed during a chemical reaction and how much *excess reactant* remains.
- Calculate with a limiting reactant involving moles. Example 3.15
- Calculate with a limiting reactant involving masses. Example 3.16
- Define and calculate the *theoretical yield* of chemical reactions.
- Determine the *percentage yield* of a chemical reaction.

Self-Assessment and Review Questions

3.1 What is the difference between a formula mass and a molecular mass? Could a given substance have both a formula mass and a molecular mass?

3.2 Describe in words how to obtain the formula mass of a compound from the formula.

3.3 One mole of N_2 contains how many N_2 molecules? How many N atoms are there in one mole of N_2? One mole of iron(III) sulfate, $Fe_2(SO_4)_3$, contains how many moles of SO_4^{2-} ions? How many moles of O atoms?

3.4 Explain what is involved in determining the composition of a compound of C, H, and O by combustion.

3.5 Explain what is involved in obtaining the empirical formula from the percentage composition.

3.6 A substance has the molecular formula $C_6H_{12}O_2$. What is its empirical formula?

3.7 Hydrogen peroxide has the empirical formula HO and an empirical formula weight of 17.0 amu. If the molecular mass is 34.0 amu, what is the molecular formula?

3.8 Describe in words the meaning of the equation

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

using a molecular, a molar, and then a mass interpretation.

3.9 Explain how a chemical equation can be used to relate the masses of different substances involved in a reaction.

3.10 What is a limiting reactant in a reaction mixture? Explain how it determines the amount of product.

3.11 Come up with some examples of limiting reactants that use the concept but don't involve chemical reactions.

3.12 Explain why it is impossible to have a theoretical yield of more than 100%.

3.13 How many grams of NH_3 will have the same number of molecules as 15.0 g of C_6H_6?

a. 3.27
b. 1.92
c. 15.0
d. 17.0
e. 14.2

3.14 Which of the following has the largest number of molecules?

a. 1 g of benzene, C_6H_6
b. 1 g of formaldehyde, CH_2O
c. 1 g of TNT, $C_7H_5N_3O_6$
d. 1 g of naphthalene, $C_{10}H_8$
e. 1 g of glucose, $C_6H_{12}O_6$

3.15 How many atoms are present in 123 g of magnesium cyanide?

a. 9.7×10^{23}
b. 2.91×10^{24}
c. 2.83×10^{28}
d. 4.85×10^{24}
e. 5.65×10^{27}

3.16 When 2.56 g of a compound containing only carbon, hydrogen, and oxygen is burned completely, 3.84 g of CO_2 and 1.05 g of H_2O are produced. What is the empirical formula of the compound?

a. $C_3H_4O_3$
b. $C_5H_6O_4$
c. $C_5H_6O_5$
d. $C_4H_4O_3$
e. $C_4H_6O_3$

Concept Explorations

3.17 Moles and Molar Mass

Part 1: The mole provides a convenient package where we can make a connection between the mass of a substance and the number (count) of that substance. This is a familiar concept if you have ever bought nails at a hardware store, where you purchase nails by mass rather than count. Typically, there is a scale provided for weighing the nails. For example, a notice placed above the nail bin might read, "For the nails in the bin below, there are 500 nails per kg." Using this conversion factor, perform the following calculations.

a. How many nails would you have if you had 0.2 kg?
b. If you had 10 dozen nails, what would be their mass?
c. What is the mass of one nail?
d. What is the mass of 2.0 moles of nails?

Part 2: The periodic table provides information about each element that serves somewhat the same purpose as the label on the nail bin described in Part 1, only in this case, the mass (molar mass) of each element is the number of grams of the element that contain 6.02×10^{23} atoms or molecules of the element. As you are aware, the quantity 6.02×10^{23} is called the mole.

a. If you had 0.2 kg of helium, how many helium atoms would you have?
b. If you had 10 dozen helium atoms, what would be their mass?
c. What is the mass of one helium atom?
d. What is the mass of 2.0 moles of helium atoms?

Part 3: Say there is a newly defined "package" called the binkle. One binkle is defined as being exactly 3×10^{12}.

a. If you had 1.0 kg of nails and 1.0 kg of helium atoms, would you expect them to have the same number of binkles? Using complete sentences, explain your answer.
b. If you had 3.5 binkles of nails and 3.5 binkles of helium atoms, which quantity would have more (count) and which would have more mass? Using complete sentences, explain your answers.
c. Which would contain more atoms, 3.5 g of helium or 3.5 g of lithium? Using complete sentences, explain your answer.

3.18 Moles Within Moles and Molar Mass

Part 1

a. How many hydrogen and oxygen atoms are present in 1 molecule of H_2O?
b. How many moles of hydrogen and oxygen atoms are present in 1 mol H_2O?
c. What are the masses of hydrogen and oxygen in 1.0 mol H_2O?
d. What is the mass of 1.0 mol H_2O?

Part 2: Two hypothetical ionic compounds are discovered with the chemical formulas XCl_2 and YCl_2, where X and Y represent symbols of the imaginary elements. Chemical analysis of the two compounds reveals that 0.25 mol XCl_2 has a mass of 100.0 g and 0.50 mol YCl_2 has a mass of 125.0 g.

a. What are the molar masses of XCl_2 and YCl_2?
b. If you had 1.0-mol samples of XCl_2 and YCl_2, how would the number of chloride ions compare?
c. If you had 1.0-mol samples of XCl_2 and YCl_2, how would the masses of elements X and Y compare?

d. What is the mass of chloride ions present in 1.0 mol XCl_2 and 1.0 mol YCl_2?

e. What are the molar masses of elements X and Y?

f. How many moles of X ions and chloride ions would be present in a 200.0-g sample of XCl_2?

g. How many grams of Y ions would be present in a 250.0-g sample of YCl_2?

h. What would be the molar mass of the compound YBr_3?

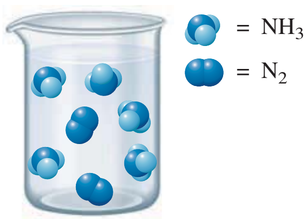
Part 3: A minute sample of $AlCl_3$ is analyzed for chlorine. The analysis reveals that there are 12 chloride ions present in the sample. How many aluminum ions must be present in the sample?

a. What is the total mass of $AlCl_3$ in this sample?

b. How many moles of $AlCl_3$ are in this sample?

Conceptual Problems

3.19 You react nitrogen and hydrogen in a container to produce ammonia, $NH_3(g)$. The following figure depicts the contents of the container after the reaction is complete.



a. Write a balanced chemical equation for the reaction.

b. What is the limiting reactant?

c. How many molecules of the limiting reactant would you need to add to the container in order to have a complete reaction (convert all reactants to products)?

3.20 Propane, C_3H_8, is the fuel of choice in a gas barbecue. When burning, the balanced equation is

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$$

a. What is the limiting reactant in cooking with a gas grill?

b. If the grill will not light and you know that you have an ample flow of propane to the burner, what is the limiting reactant?

c. When using a gas grill you can sometimes turn the gas up to the point at which the flame becomes yellow and smokey. In terms of the chemical reaction, what is happening?

3.21 A critical point to master in becoming proficient at solving problems is evaluating whether or not your answer is reasonable. A friend asks you to look over her homework to see if she has done the calculations correctly. Shown below are descriptions of some of her answers. Without using your calculator or doing calculations on paper, see if you can judge the answers below as being reasonable or ones that will require her to go back and work the problems again.

a. 0.33 mol of an element has a mass of 1.0×10^{-3} g.

b. The mass of one molecule of water is 1.80×10^{-10} g.

c. There are 3.01×10^{23} atoms of Na in 0.500 mol of Na.

d. The molar mass of CO_2 is 44.0 kg/mol.

3.22 An exciting, and often loud, chemical demonstration involves the simple reaction of hydrogen gas and oxygen gas to produce water vapor:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$

The reaction is carried out in soap bubbles or balloons that are filled with the reactant gases. We get the reaction to proceed by igniting the bubbles or balloons. The more H_2O that is formed during the reaction, the bigger the bang. Explain the following observations.

a. A bubble containing just H_2 makes a quiet "fffft" sound when ignited.

b. When a bubble containing equal amounts of H_2 and O_2 is ignited, a sizable bang results.

c. When a bubble containing a ratio of 2 to 1 in the amounts of H_2 and O_2 is ignited, the loudest bang results.

d. When a bubble containing just O_2 is ignited, virtually no sound is made.

3.23 High cost and limited availability of a reactant often dictate which reactant is limiting in a particular process. Identify the limiting reactant when the reactions below are run, and come up with a reason to support your decision.

a. Burning charcoal on a grill:

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

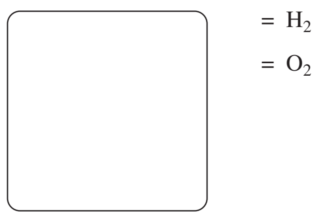
b. Burning a chunk of Mg in water:

$$Mg(s) + 2H_2O(l) \longrightarrow Mg(OH)_2(aq) + H_2(g)$$

c. The Haber process of ammonia production:

$$3H_2(g) + N_2(g) \longrightarrow 2NH_3(g)$$

3.24 A few hydrogen and oxygen molecules are introduced into a container in the quantities depicted in the following drawing. The gases are then ignited by a spark, causing them to react and form H_2O.



a. What is the maximum number of water molecules that can be formed in the chemical reaction?

b. Draw a molecular level representation of the container's contents after the chemical reaction.

3.25 A friend asks if you would be willing to check several homework problems to see if she is on the right track. Following are the problems and her proposed solutions. When you identify the problem with her work, make the appropriate correction.

a. Calculate the number of moles of calcium in 27.0 g of Ca.

$$27.0 \text{ g Ca} \times \frac{1 \text{ mol Ca}}{6.022 \times 10^{23} \text{ g Ca}} = ?$$

b. Calculate the number of potassium ions in 2.5 mol of K_2SO_4.

$$2.5 \text{ mol } K_2SO_4 \times \frac{1 \text{ mol } K^+ \text{ ions}}{1 \text{ mol } K_2SO_4} \times \frac{6.022 \times 10^{23}\ K^+ \text{ ions}}{1 \text{ mol } K^+ \text{ ions}} = ?$$

c. Sodium reacts with water according to the following chemical equation.

$$2Na + 2H_2O \longrightarrow H_2 + 2NaOH$$

Assuming complete reaction, calculate the number of moles of water required to react with 0.50 mol of Na.

$$0.50 \text{ mol Na} \times \frac{1 \text{ mol } H_2O}{2 \text{ mol Na}} = ?$$

3.26 A friend is doing his chemistry homework and is working with the following chemical reaction.

$$2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(g)$$

He tells you that if he reacts 2 moles of C_2H_2 with 4 moles of O_2, then the C_2H_2 is the limiting reactant since there are fewer moles of C_2H_2 than O_2.

a. How would you explain to him where he went wrong with his reasoning (what concept is he missing)?

b. After providing your friend with the explanation from part a, he still doesn't believe you because he *had* a homework problem where 2 moles of calcium were reacted with 4 moles of sulfur and he needed to determine the limiting reactant. The reaction is

$$Ca(s) + S(s) \longrightarrow CaS(s)$$

He obtained the correct answer, Ca, by reasoning that since there were fewer moles of calcium reacting, calcium *had* to be the limiting reactant. How would you explain his reasoning flaw and why he got "lucky" in choosing the answer that he did?

Practice Problems

Formula Masses and Mole Calculations

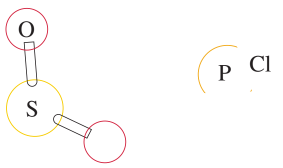
3.27 Find the formula masses of the following substances to three significant figures.

a. methanol, CH_3OH
b. nitrogen trioxide, NO_3
c. potassium carbonate, K_2CO_3
d. nickel phosphate, $Ni_3(PO_4)_2$

3.28 Find the formula masses of the following substances to three significant figures.

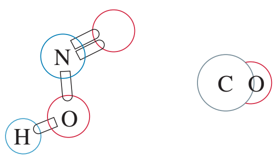
a. sulfuric acid, K_2SO_4
b. phosphorus pentachloride, PCl_5
c. potassium sulfite, K_2SO_3
d. calcium hydroxide, $Ca(OH)_2$

3.29 Calculate the formula mass of the following molecules to three significant figures.



(a) (b)

3.30 Calculate the formula mass of the following molecules to three significant figures.



(a) (b)

3.31 Ammonium nitrate, NH_4NO_3, is used as a nitrogen fertilizer and in explosives. What is the molar mass of NH_4NO_3?

3.32 Phosphoric acid, H_3PO_4, is used to make phosphate fertilizers and detergents and is also used in carbonated beverages. What is the molar mass of H_3PO_4?

3.33 Calculate the mass (in grams) of each of the following species.

a. Na atom **b.** N atom
c. CH_3Cl molecule **d.** $Hg(NO_3)_2$ formula unit

3.34 Calculate the mass (in grams) of each of the following species.

a. Ar atom **b.** Te atom
c. PBr_3 molecule **d.** $Fe(OH)_3$ formula unit

3.35 Diethyl ether, $(C_2H_5)_2O$, commonly known as ether, is used as an anesthetic. What is the mass in grams of a molecule of diethyl ether?

3.36 Glycerol, $C_3H_8O_3$, is used as a moistening agent for candy and is the starting material for nitroglycerin. Calculate the mass of a glycerol molecule in grams.

3.37 Calculate the mass in grams of the following.

a. 0.15 mol Na **b.** 0.594 mol S
c. 2.78 mol CH_2Cl_2 **d.** 38 mol $(NH_4)_2S$

3.38 Calculate the mass in grams of the following.

a. 0.205 mol Fe **b.** 0.79 mol F
c. 5.8 mol CO_2 **d.** 48.1 mol K_2CrO_4

3.39 Boric acid, H_3BO_3, is a mild antiseptic and is often used as an eyewash. A sample contains 0.543 mol H_3BO_3. What is the mass of boric acid in the sample?

3.40 Carbon disulfide, CS_2, is a colorless, highly flammable liquid used in the manufacture of rayon and cellophane. A sample contains 0.0205 mol CS_2. Calculate the mass of carbon disulfide in the sample.

3.41 Obtain the moles of substance in the following.
a. 2.86 g C b. 7.05 g Cl_2
c. 76 g C_4H_{10} d. 26.2 g $Al_2(CO_3)_3$

3.42 Obtain the moles of substance in the following.
a. 2.57 g As
b. 7.83 g S_8
c. 36.5 g N_2H_4
d. 227 g $Al_2(SO_4)_3$

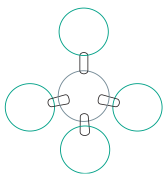
3.43 Calcium sulfate, $CaSO_4$, is a white, crystalline powder. Gypsum is a mineral, or natural substance, that is a hydrate of calcium sulfate. A 1.000-g sample of gypsum contains 0.791 g $CaSO_4$. How many moles of $CaSO_4$ are there in this sample? Assuming that the rest of the sample is water, how many moles of H_2O are there in the sample? Show that the result is consistent with the formula $CaSO_4{\cdot}2H_2O$.

3.44 A 1.547-g sample of blue copper(II) sulfate pentahydrate, $CuSO_4{\cdot}5H_2O$, is heated carefully to drive off the water. The white crystals of $CuSO_4$ that are left behind have a mass of 0.989 g. How many moles of H_2O were in the original sample? Show that the relative molar amounts of $CuSO_4$ and H_2O agree with the formula of the hydrate.

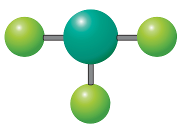
3.45 Calculate the following.
a. number of atoms in 8.21 g Li
b. number of atoms in 32.0 g Br_2
c. number of molecules in 45 g NH_3
d. number of formula units in 201 g $PbCrO_4$
e. number of SO_4^{2-} ions in 14.3 g $Cr_2(SO_4)_3$

3.46 Calculate the following.
a. number of atoms in 25.7 g Al
b. number of atoms in 8.71 g I_2
c. number of molecules in 14.9 g N_2O_5
d. number of formula units in 3.31 g $NaClO_4$
e. number of Ca^{2+} ions in 4.71 g $Ca_3(PO_4)_2$

3.47 Carbon tetrachloride is a colorless liquid used in the manufacture of fluorocarbons and as an industrial solvent. How many molecules are there in 7.58 mg of carbon tetrachloride?



3.48 Chlorine trifluoride is a colorless, reactive gas used in nuclear fuel reprocessing. How many molecules are there in a 5.88-mg sample of chlorine trifluoride?



Mass Percentage

3.49 A 1.836-g sample of coal contains 1.584 g C. Calculate the mass percentage of C in the coal.

3.50 A 6.01-g aqueous solution of isopropyl alcohol contains 4.01 g of isopropyl alcohol. What is the mass percentage of isopropyl alcohol in the solution?

3.51 Phosphorus oxychloride is the starting compound for preparing substances used as flame retardants for plastics. An 8.53-mg sample of phosphorus oxychloride contains 1.72 mg of phosphorus. What is the mass percentage of phosphorus in the compound?

3.52 Ethyl mercaptan is an odorous substance added to natural gas to make leaks easily detectable. A sample of ethyl mercaptan weighing 3.17 mg contains 1.64 mg of sulfur. What is the mass percentage of sulfur in the substance?

3.53 A fertilizer is advertised as containing 14.0% nitrogen (by mass). How much nitrogen is there in 4.15 kg of fertilizer?

3.54 Seawater contains 0.0065% (by mass) of bromine. How many grams of bromine are there in 2.50 L of seawater? The density of seawater is 1.025 g/cm^3.

3.55 A sample of an alloy of aluminum contains 0.0898 mol Al and 0.0381 mol Mg. What are the mass percentages of Al and Mg in the alloy?

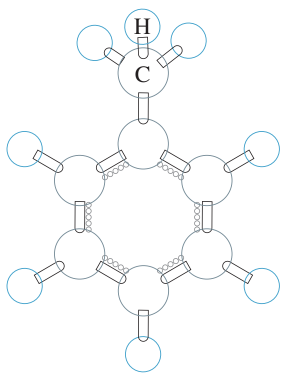
3.56 A sample of gas mixture from a neon sign contains 0.0856 mol Ne and 0.0254 mol Kr. What are the mass percentages of Ne and Kr in the gas mixture?

Chemical Formulas

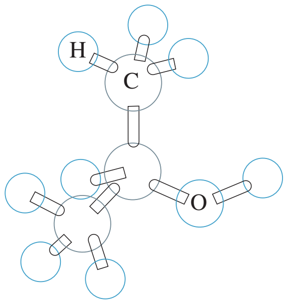
3.57 Calculate the percentage composition for each of the following compounds (three significant figures).
a. CO b. CO_2
c. NaH_2PO_4 d. $Co(NO_3)_2$

3.58 Calculate the percentage composition for each of the following compounds (three significant figures).
a. NO_2
b. H_2O_2
c. $KClO_4$
d. $Mg(NO_2)_2$

3.59 Calculate the mass percentage of each element in toluene, represented by the following molecular model.



3.60 Calculate the mass percentage of each element in 2-propanol, represented by the following molecular model.



3.61 Which contains more carbon, 6.01 g of glucose, $C_6H_{12}O_6$, or 5.85 g of ethanol, C_2H_6O?

3.62 Which contains more sulfur, 40.8 g of calcium sulfate, $CaSO_4$, or 35.2 g of sodium sulfite, Na_2SO_3?

3.63 Ethylene glycol is used as an automobile antifreeze and in the manufacture of polyester fibers. The name glycol stems from the sweet taste of this poisonous compound. Combustion of 6.38 mg of ethylene glycol gives 9.06 mg CO_2 and 5.58 mg H_2O. The compound contains only C, H, and O. What are the mass percentages of the elements in ethylene glycol?

3.64 Phenol, commonly known as carbolic acid, was used by Joseph Lister as an antiseptic for surgery in 1865. Its principal use today is in the manufacture of phenolic resins and plastics. Combustion of 5.23 mg of phenol yields 14.67 mg CO_2 and 3.01 mg H_2O. Phenol contains only C, H, and O. What is the percentage of each element in this substance?

3.65 An oxide of osmium (symbol Os) is a pale yellow solid. If 2.89 g of the compound contains 2.16 g of osmium, what is its empirical formula?

3.66 An oxide of tungsten (symbol W) is a bright yellow solid. If 5.34 g of the compound contains 4.23 g of tungsten, what is its empirical formula?

3.67 Potassium manganate is a dark green, crystalline substance whose composition is 39.6% K, 27.9% Mn, and 32.5% O, by mass. What is its empirical formula?

3.68 Hydroquinone, used as a photographic developer, is 65.4% C, 5.5% H, and 29.1% O, by mass. What is the empirical formula of hydroquinone?

3.69 Acrylic acid, used in the manufacture of acrylic plastics, has the composition 50.0% C, 5.6% H, and 44.4% O. What is its empirical formula?

3.70 Malonic acid is used in the manufacture of barbiturates (sleeping pills). The composition of the acid is 34.6% C, 3.9% H, and 61.5% O. What is malonic acid's empirical formula?

3.71 Two compounds have the same composition: 92.25% C and 7.75% H.

a. Obtain the empirical formula corresponding to this composition.

b. One of the compounds has a molecular mass of 52.03 amu; the other, of 78.05 amu. Obtain the molecular formulas of both compounds.

3.72 Two compounds have the same composition: 85.62% C and 14.38% H.

a. Obtain the empirical formula corresponding to this composition.

b. One of the compounds has a molecular mass of 28.03 amu; the other, of 56.06 amu. Obtain the molecular formulas of both compounds.

3.73 Putrescine, a substance produced by decaying animals, has the empirical formula C_2H_6N. Several determinations of molecular mass give values in the range of 87 to 90 amu. Find the molecular formula of putrescine.

3.74 Compounds of boron with hydrogen are called boranes. One of these boranes has the empirical formula BH_3 and a molecular mass of 28 amu. What is its molecular formula?

3.75 Oxalic acid is a toxic substance used by laundries to remove rust stains. Its composition is 26.7% C, 2.2% H, and 71.1% O (by mass), and its molecular mass is 90 amu. What is its molecular formula?

3.76 Adipic acid is used in the manufacture of nylon. The composition of the acid is 49.3% C, 6.9% H, and 43.8% O (by mass), and the molecular mass is 146 amu. What is the molecular formula?

Stoichiometry: Quantitative Relations in Reactions

3.77 Ethylene, C_2H_4, burns in oxygen to give carbon dioxide, CO_2, and water. Write the equation for the reaction, giving molecular, molar, and mass interpretations below the equation.

3.78 Hydrogen sulfide gas, H_2S, burns in oxygen to give sulfur dioxide, SO_2, and water. Write the equation for the reaction, giving molecular, molar, and mass interpretations below the equation.

3.79 Butane, C_4H_{10}, burns with the oxygen in air to give carbon dioxide and water.

$$2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(g)$$

What is the amount (in moles) of carbon dioxide produced from 0.30 mol C_4H_{10}?

3.80 Ethanol, C_2H_5OH, burns with the oxygen in air to give carbon dioxide and water.

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$$

What is the amount (in moles) of water produced from 0.69 mol C_2H_5OH?

3.81 Iron in the form of fine wire burns in oxygen to form iron(III) oxide.

$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$$

How many moles of O_2 are needed to produce 3.91 mol Fe_2O_3?

3.82 Nickel(II) chloride reacts with sodium phosphate to precipitate nickel(II) phosphate.

$$3NiCl_2(aq) + 2Na_3PO_4(aq) \longrightarrow Ni_3(PO_4)_2(s) + 6NaCl(aq)$$

How many moles of nickel(II) chloride are needed to produce 0.517 mol nickel(II) phosphate?

3.83 Nitric acid, HNO_3, is manufactured by the Ostwald process, in which nitrogen dioxide, NO_2, reacts with water.

$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$$

How many grams of nitrogen dioxide are required in this reaction to produce 7.50 g HNO_3?

3.84 White phosphorus, P_4, is prepared by fusing calcium phosphate, $Ca_3(PO_4)_2$, with carbon, C, and sand, SiO_2, in an electric furnace.

$$2Ca_3(PO_4)_2(s) + 6SiO_2(s) + 10C(s) \longrightarrow P_4(g) + 6CaSiO_3(l) + 10CO(g)$$

How many grams of calcium phosphate are required to give 15.0 g of phosphorus?

3.85 Tungsten metal, W, is used to make incandescent bulb filaments. The metal is produced from the yellow tungsten(VI) oxide, WO_3, by reaction with hydrogen.

$$WO_3(s) + 3H_2(g) \longrightarrow W(s) + 3H_2O(g)$$

How many grams of tungsten can be obtained from 4.81 kg of hydrogen with excess tungsten(VI) oxide?

3.86 Acrylonitrile, C_3H_3N, is the starting material for the production of a kind of synthetic fiber (acrylics). It can be made from propylene, C_3H_6, by reaction with nitric oxide, NO.

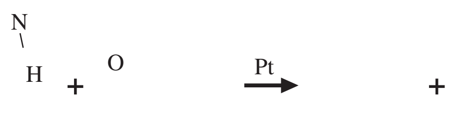
$$4C_3H_6(g) + 6NO(g) \longrightarrow 4C_3H_3N(g) + 6H_2O(g) + N_2(g)$$

How many grams of acrylonitrile are obtained from 452 kg of propylene and excess NO?

3.87 The following reaction, depicted using molecular models, is used to make carbon tetrachloride, CCl_4, a solvent and starting material for the manufacture of fluorocarbon refrigerants and aerosol propellants.

Calculate the number of grams of carbon disulfide, CS_2, needed for a laboratory-scale reaction with 62.7 g of chlorine, Cl_2.

3.88 Using the following reaction (depicted using molecular models), large quantities of ammonia are burned in the presence of a platinum catalyst to give nitric oxide, as the first step in the preparation of nitric acid.



Suppose a vessel contains 6.1 g of NH_3, how many grams of O_2 are needed for a complete reaction?

3.89 When dinitrogen pentoxide, N_2O_5, a white solid, is heated, it decomposes to nitrogen dioxide and oxygen.

$$2N_2O_5(s) \xrightarrow{\Delta} 4NO_2(g) + O_2(g)$$

If a sample of N_2O_5 produces 1.315 g O_2, how many grams of NO_2 are formed?

3.90 Copper metal reacts with nitric acid. Assume that the reaction is

$$3Cu(s) + 8HNO_3(aq) \longrightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$$

If 6.01 g $Cu(NO_3)_2$ is eventually obtained, how many grams of nitrogen monoxide, NO, would have formed?

Limiting Reactant; Theoretical and Percentage Yields

3.91 Potassium superoxide, KO_2, is used in rebreathing gas masks to generate oxygen.

$$4KO_2(s) + 2H_2O(l) \longrightarrow 4KOH(s) + 3O_2(g)$$

If a reaction vessel contains 0.25 mol KO_2 and 0.15 mol H_2O, what is the limiting reactant? How many moles of oxygen can be produced?

3.92 Solutions of sodium hypochlorite, NaClO, are sold as a bleach (such as Clorox). They are prepared by the reaction of chlorine with sodium hydroxide.

$$2NaOH(aq) + Cl_2(g) \longrightarrow NaCl(aq) + NaClO(aq) + H_2O(l)$$

If you have 1.23 mol of NaOH in solution and 1.47 mol of Cl_2 gas available to react, which is the limiting reactant? How many moles of NaClO(*aq*) could be obtained?

3.93 Methanol, CH_3OH, is prepared industrially from the gas-phase catalytic balanced reaction that has been depicted here using molecular models.

In a laboratory test, a reaction vessel was filled with 35.4 g CO and 10.2 g H_2. How many grams of methanol would be produced in a complete reaction? Which reactant remains unconsumed at the end of the reaction? How many grams of it remain?

3.94 Carbon disulfide, CS_2, burns in oxygen. Complete combustion gives the balanced reaction that has been depicted here using molecular models.

Calculate the grams of sulfur dioxide, SO_2, produced when a mixture of 35.0 g of carbon disulfide and 30.0 g of oxygen reacts. Which reactant remains unconsumed at the end of the combustion? How many grams remain?

3.95 Titanium, which is used to make airplane engines and frames, can be obtained from titanium(IV) tetrachloride, which in turn is obtained from titanium(IV) dioxide by the following process:

$$3TiO_2(s) + 4C(s) + 6Cl_2(g) \longrightarrow 3TiCl_4(g) + 2CO_2(g) + 2CO(g)$$

A vessel contains 4.15 g TiO_2, 5.67 g C, and 6.78 g Cl_2. Suppose the reaction goes to completion as written. How many grams of titanium(IV) tetrachloride can be produced?

3.96 Hydrogen cyanide, HCN, is prepared from ammonia, air, and natural gas (CH_4) by the following process:

$$2NH_3(g) + 3O_2(g) + 2CH_4(g) \xrightarrow{Pt} 2HCN(g) + 6H_2O(g)$$

Hydrogen cyanide is used to prepare sodium cyanide, which is used in part to obtain gold from gold-containing rock. If a reaction vessel contains 11.5 g NH_3, 12.0 g O_2, and 10.5 g CH_4, what is the maximum mass in grams of hydrogen cyanide that could be made, assuming the reaction goes to completion as written?

3.97 Aspirin (acetylsalicylic acid) is prepared by heating salicylic acid, $C_7H_6O_3$, with acetic anhydride, $C_4H_6O_3$. The other product is acetic acid, $C_2H_4O_2$.

$$C_7H_6O_3 + C_4H_6O_3 \longrightarrow C_9H_8O_4 + C_2H_4O_2$$

What is the theoretical yield (in grams) of aspirin, $C_9H_8O_4$, when 2.00 g of salicylic acid is heated with 4.00 g of acetic anhydride? If the actual yield of aspirin is 1.86 g, what is the percentage yield?

3.98 Methyl salicylate (oil of wintergreen) is prepared by heating salicylic acid, $C_7H_6O_3$, with methanol, CH_3OH.

$$C_7H_6O_3 + CH_3OH \longrightarrow C_8H_8O_3 + H_2O$$

In an experiment, 1.50 g of salicylic acid is reacted with 11.20 g of methanol. The yield of methyl salicylate, $C_8H_8O_3$, is 1.27 g. What is the percentage yield?

General Problems

3.99 Caffeine, the stimulant in coffee and tea, has the molecular formula $C_8H_{10}N_4O_2$. Calculate the mass percentage of each element in the substance. Give the answers to three significant figures.

3.100 Morphine, a narcotic substance obtained from opium, has the molecular formula $C_{17}H_{19}NO_3$. What is the mass percentage of each element in morphine (to three significant figures)?

3.101 A moth repellent, *para*-dichlorobenzene, has the composition 49.1% C, 2.7% H, and 48.2% Cl. Its molecular mass is 147 amu. What is its molecular formula?

3.102 Sorbic acid is added to food as a mold inhibitor. Its composition is 64.3% C, 7.2% H, and 28.5% O, and its molecular mass is 112 amu. What is its molecular formula?

3.103 Thiophene is a liquid compound of the elements C, H, and S. A sample of thiophene weighing 7.96 mg was burned in oxygen, giving 16.65 mg CO_2. Another sample was subjected to a series of reactions that transformed all of the sulfur in the compound to barium sulfate. If 4.31 mg of thiophene gave 11.96 mg of barium sulfate, what is the empirical formula of thiophene? Its molecular mass is 84 amu. What is its molecular formula?

3.104 Aniline, a starting compound for urethane plastic foams, consists of C, H, and N. Combustion of such compounds yields CO_2, H_2O, and N_2 as products. If the combustion of 9.71 mg of aniline yields 6.63 mg H_2O and 1.46 mg N_2, what is its empirical formula? The molecular mass of aniline is 93 amu. What is its molecular formula?

3.105 A sample of limestone (containing calcium carbonate, $CaCO_3$) weighing 438 mg is treated with oxalic acid, $H_2C_2O_4$, to give calcium oxalate, CaC_2O_4.

$$CaCO_3(s) + H_2C_2O_4(aq) \longrightarrow CaC_2O_4(s) + H_2O(l) + CO_2(g)$$

The mass of the calcium oxalate produced is 472 mg. What is the mass percentage of calcium carbonate in this limestone?

3.106 A titanium ore contains rutile (TiO_2) plus some iron oxide and silica. When it is heated with carbon in the presence of chlorine, titanium tetrachloride, $TiCl_4$, is formed.

$$TiO_2(s) + C(s) + 2Cl_2(g) \longrightarrow TiCl_4(g) + CO_2(g)$$

Titanium tetrachloride, a liquid, can be distilled from the mixture. If 35.4 g of titanium tetrachloride is recovered from 17.4 g of crude ore, what is the mass percentage of TiO_2 in the ore (assuming all TiO_2 reacts)?

3.107 Ethylene oxide, C_2H_4O, is made by the oxidation of ethylene, C_2H_4.

$$2C_2H_4(g) + O_2(g) \longrightarrow 2C_2H_4O(g)$$

Ethylene oxide is used to make ethylene glycol for automobile antifreeze. In a pilot study, 10.6 g of ethylene gave 9.91 g of ethylene oxide. What is the percentage yield of ethylene oxide?

3.108 Nitrobenzene, $C_6H_5NO_2$, an important raw material for the dye industry, is prepared from benzene, C_6H_6, and nitric acid, HNO_3.

$$C_6H_6(l) + HNO_3(l) \longrightarrow C_6H_5NO_2(l) + H_2O(l)$$

When 22.4 g of benzene and an excess of HNO_3 are used, what is the theoretical yield of nitrobenzene? If 31.6 g of nitrobenzene is recovered, what is the percentage yield?

3.109 Zinc metal can be obtained from zinc oxide, ZnO, by reaction at high temperature with carbon monoxide, CO.

$$ZnO(s) + CO(g) \longrightarrow Zn(s) + CO_2(g)$$

The carbon monoxide is obtained from carbon.

$$2C(s) + O_2(g) \longrightarrow 2CO(g)$$

What is the maximum amount of zinc that can be obtained from 75.0 g of zinc oxide and 50.0 g of carbon?

3.110 Hydrogen cyanide, HCN, can be made by a two-step process. First, ammonia is reacted with O_2 to give nitric oxide, NO.

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$$

Then nitric oxide is reacted with methane, CH_4.

$$2NO(g) + 2CH_4(g) \longrightarrow 2HCN(g) + 2H_2O(g) + H_2(g)$$

When 24.2 g of ammonia and 25.1 g of methane are used, how many grams of hydrogen cyanide can be produced?

3.111 Calcium carbide, CaC_2, used to produce acetylene, C_2H_2, is prepared by heating calcium oxide, CaO, and carbon, C, to high temperature.

$$CaO(s) + 3C(s) \longrightarrow CaC_2(s) + CO(g)$$

If a mixture contains 2.60 kg of each reactant, how many grams of calcium carbide can be prepared?

3.112 A mixture consisting of 11.9 g of calcium fluoride, CaF_2, and 10.3 g of sulfuric acid, H_2SO_4, is heated to drive off hydrogen fluoride, HF.

$$CaF_2(s) + H_2SO_4(l) \longrightarrow 2HF(g) + CaSO_4(s)$$

What is the maximum number of grams of hydrogen fluoride that can be obtained?

3.113 Alloys, or metallic mixtures, of mercury with another metal are called amalgams. Sodium in sodium amalgam reacts with water. (Mercury does not.)

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$$

If a 15.23-g sample of sodium amalgam evolves 0.108 g of hydrogen, what is the percentage of sodium in the amalgam?

3.114 A sample of sandstone consists of silica, SiO_2, and calcite, $CaCO_3$. When the sandstone is heated, calcium carbonate, $CaCO_3$, decomposes into calcium oxide, CaO, and carbon dioxide.

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

What is the percentage of silica in the sandstone if 18.7 mg of the rock yields 3.95 mg of carbon dioxide?

3.115 What type of information can you obtain from a compound using a mass spectrometer?

3.116 Why is the mass spectrum of a molecule much more complicated than that of an atom?

Strategy Problems

3.117 Exactly 4.0 g of hydrogen gas combines with 32 g of oxygen gas according to the following reaction.

$$2H_2 + O_2 \longrightarrow 2H_2O$$

- **a.** How many hydrogen molecules are required to completely react with 48 oxygen molecules?
- **b.** If you ran the reaction and it produced 5.0 mol H_2O, how many moles of both O_2 and H_2 did you start with?
- **c.** If you started with 37.5 g O_2, how many grams of H_2 did you start with to have a complete reaction?
- **d.** How many grams of O_2 and H_2 were reacted to produce 30.0 g H_2O?

3.118 Aluminum metal reacts with iron(III) oxide to produce aluminum oxide and iron metal.

- **a.** How many moles of Fe_2O_3 are required to completely react with 41 g Al?
- **b.** How many moles of Fe are produced by the reaction of 3.14 mol Fe_2O_3 and 99.1 g Al?
- **c.** How many atoms of Al are required to produce 7.0 g Fe?

3.119 Consider the equation

$$2KOH + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O$$

- **a.** If 25 g H_2SO_4 is reacted with 7.7 g KOH, how many grams of K_2SO_4 are produced?
- **b.** For part a of this problem, identify the limiting reactant and calculate the mass of excess reactant that remains after the reaction is completed.
- **c.** Calculate the theoretical yield of the reaction. How many grams of material would you expect to obtain if the reaction has a 47.2% yield?

3.120 You perform combustion analysis on 255 mg of a molecule that contains only C, H, and O, and you find that 561 mg CO_2 is produced, along with 306 mg H_2O.

- **a.** If the molecule contains only C, H, and O, what is the empirical formula?
- **b.** If the molar mass of the compound is 180 g/mol, what is the molecular formula of the compound?

3.121 When ammonia and oxygen are reacted, they produce nitric oxide and water. When 8.5 g of ammonia is allowed to react with an excess of O_2, the reaction produces 12.0 g of nitrogen monoxide. What is the percentage yield of the reaction?

3.122 A 3.0-L sample of paint that has a density of 4.65 g/mL is found to contain 27.5 g $Pb_3N_2(s)$. How many grams of lead were in the paint sample?

3.123 A 12.1-g sample of Na_2SO_3 is mixed with a 15.5-g sample of $MgSO_4$. What is the total mass of oxygen present in the mixture?

3.124 Potassium superoxide, KO_2, is employed in a self-contained breathing apparatus used by emergency personnel as a source of oxygen. The reaction is

$$4KO_2(s) + 2H_2O(l) \longrightarrow 4KOH(s) + 3O_2(g)$$

Say a self-contained breathing apparatus is charged with 750 g KO_2 and then is used to produce 195 g of oxygen. Was all of the KO_2 consumed in this reaction? If the KO_2 wasn't all consumed, how much is left over and what mass of additional O_2 could be produced?

3.125 Calcium carbonate is a common ingredient in stomach antacids. If an antacid tablet has 68.4 mg of calcium carbonate, how many moles of calcium carbonate are there in 175 tablets?

3.126 While cleaning out your closet, you find a jar labeled "2.21 moles lead nitrite." Since Stock convention was not used, you do not know the oxidation number of the lead. You weigh the contents, and find a mass of 6.61×10^5 mg. What is the percentage composition of nitrite?

Cumulative-Skills Problems

3.127 A 0.500-g mixture of Cu_2O and CuO contains 0.425 g Cu. What is the mass of CuO in the mixture?

3.128 A mixture of Fe_2O_3 and FeO was found to contain 72.00% Fe by mass. What is the mass of Fe_2O_3 in 0.500 g of this mixture?

3.129 Hemoglobin is the oxygen-carrying molecule of red blood cells, consisting of a protein and a nonprotein substance. The nonprotein substance is called heme. A sample of heme weighing 35.2 mg contains 3.19 mg of iron. If a heme molecule contains one atom of iron, what is the molecular mass of heme?

3.130 Penicillin V was treated chemically to convert sulfur to barium sulfate, $BaSO_4$. An 8.19-mg sample of penicillin V gave 5.46 mg $BaSO_4$. What is the percentage of sulfur in penicillin V? If there is one sulfur atom in the molecule, what is the molecular mass?

3.131 A 3.41-g sample of a metallic element, M, reacts completely with 0.0158 mol of a gas, X_2, to form 4.52 g MX. What are the identities of M and X?

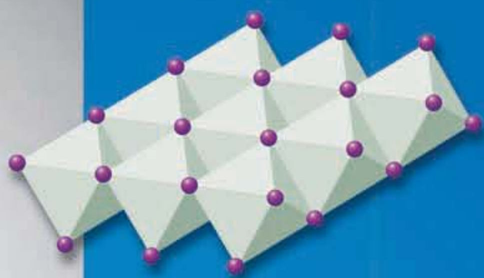
3.132 1.92 g M^+ ion reacts with 0.158 mol X^- ion to produce a compound, MX_2, which is 86.8% X by mass. What are the identities of M^+ and X^-?

3.133 An alloy of iron (54.7%), nickel (45.0%), and manganese (0.3%) has a density of 8.17 g/cm^3. How many iron atoms are there in a block of alloy measuring 10.0 cm $\times$ 20.0 cm $\times$ 15.0 cm?

3.134 An alloy of iron (71.0%), cobalt (12.0%), and molybdenum (17.0%) has a density of 8.20 g/cm^3. How many cobalt atoms are there in a cylinder with a radius of 2.50 cm and a length of 10.0 cm?

4

Chemical Reactions



Adding lead(II) nitrate to potassium iodide gives a yellow precipitate of lead(II) iodide. Precipitation reactions are important in biological organisms–for example, in the production of bone (calcium phosphate) and seashell (calcium carbonate).

Contents and Concepts

Ions in Aqueous Solution

4.1 Ionic Theory of Solutions and Solubility Rules

4.2 Molecular and Ionic Equations

Explore how molecular and ionic substances behave when they dissolve in water to form solutions.

Types of Chemical Reactions

4.3 Precipitation Reactions

4.4 Acid–Base Reactions

4.5 Oxidation–Reduction Reactions

4.6 Balancing Simple Oxidation–Reduction Equations

Investigate several important types of reactions that typically occur in aqueous solution: precipitation reactions, acid–base reactions, and oxidation–reduction reactions.

Working with Solutions

4.7 Molar Concentration

4.8 Diluting Solutions

Now that we have looked at how substances behave in solution, it is time to quantitatively describe these solutions using concentration.

Quantitative Analysis

4.9 Gravimetric Analysis

4.10 Volumetric Analysis

Using chemical reactions in aqueous solution, determine the amount of substance or species present in materials

Chemical reactions are the heart of chemistry. Some reactions, such as those accompanying a forest fire or the explosion of dynamite, are quite dramatic. Others are much less obvious, although all chemical reactions must involve detectable change. A chemical reaction involves a change from reactant substances to product substances, and the product substances will have physical and chemical properties different from those of the reactants.

Figure 4.1 shows an experimenter adding a colorless solution of potassium iodide, KI, to a colorless solution of lead(II) nitrate, $Pb(NO_3)_2$. What you see is the formation of a cloud of bright yellow crystals where the two solutions have come into contact, clear evidence of a chemical reaction. The bright yellow crystals are lead(II) iodide, PbI_2, one of the reaction products. We call a solid that forms during a chemical reaction in solution a *precipitate;* the reaction is a precipitation reaction.

FIGURE 4.1

Reaction of potassium iodide solution and lead(II) nitrate solution

The reactant solutions are colorless, but one of the products, lead(II) iodide, forms as a yellow precipitate.

In this chapter, we will discuss the major types of chemical reactions, including precipitation reactions. Some of the most important reactions we will describe involve ions in aqueous (water) solution. Therefore, we will first look at these ions and see how we represent by chemical equations the reactions involving ions in aqueous solution.

Some questions we will answer are: What is the evidence for ions in solution? How do we write chemical equations for reactions involving ions? How can we classify and describe the many reactions we observe so that we can begin to understand them? What is the quantitative description of solutions and reactions in solution?

■ **See pages 163–164 for the Media Summary.**

Ions in Aqueous Solution

You probably have heard that you should not operate electrical equipment while standing in water. And you may have read a murder mystery in which the victim was electrocuted when an electrical appliance "accidentally" fell into his or her bath water. Actually, if the water were truly pure, the person would be safe from electrocution, because pure water is a nonconductor of electricity. Bath water, or water as it flows from the faucet, however, is a *solution* of water with small amounts of dissolved substances in it, and these dissolved substances make the solution an electrical conductor. This allows an electric current to flow from an electrical appliance to the human body. Let us look at the nature of such solutions.

4.1 Ionic Theory of Solutions and Solubility Rules

Arrhenius submitted his ionic theory as part of his doctoral dissertation to the faculty at Uppsala, Sweden, in 1884. It was not well received and he barely passed. In 1903, however, he was awarded the Nobel Prize in chemistry for this theory.

Chemists began studying the electrical behavior of substances in the early nineteenth century, and they knew that you could make pure water electrically conducting by dissolving certain substances in it. In 1884, the young Swedish chemist Svante Arrhenius proposed the *ionic theory of solutions* to account for this conductivity. He said that certain substances produce freely moving ions when they dissolve in water, and these ions conduct an electric current in an aqueous solution. <

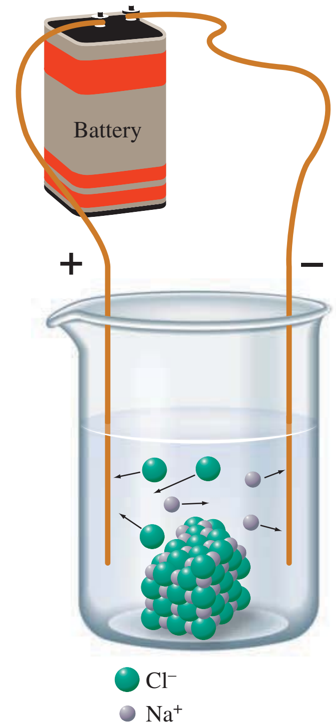


FIGURE 4.2

Motion of ions in solution
Ions are in fixed positions in a crystal. During the solution process, however, ions leave the crystal and become freely moving. Note that Na^+ ions (small gray spheres) are attracted to the negative wire, whereas Cl^- ions (large green spheres) are attracted to the positive wire.

Suppose you dissolve sodium chloride, NaCl, in water. From our discussion in Section 2.6, you may remember that sodium chloride is an ionic solid consisting of sodium ions, Na^+, and chloride ions, Cl^-, held in a regular, fixed array. When you dissolve solid sodium chloride in water, the Na^+ and Cl^- ions go into solution as freely moving ions. Now suppose you dip electric wires that are connected to the poles of a battery into a solution of sodium chloride. The wire that connects to the positive pole of the battery attracts the negatively charged chloride ions in solution, because of their opposite charges. Similarly, the wire connected to the negative pole of the battery attracts the positively charged sodium ions in solution (Figure 4.2). Thus, the ions in the solution begin to move, and these moving charges form the electric current in the solution. (In a wire, it is moving electrons that constitute the electric current.)

Now consider pure water. Water consists of molecules, each of which is electrically neutral. Since each molecule carries no net electric charge, it carries no overall electric charge when it moves. Thus, pure water is a nonconductor of electricity.

In summary, although water is itself nonconducting, it has the ability to dissolve various substances, some of which go into solution as freely moving ions. An aqueous solution of ions is electrically conducting.

Electrolytes and Nonelectrolytes

We can divide the substances that dissolve in water into two broad classes, electrolytes and nonelectrolytes. An **electrolyte** is *a substance that dissolves in water to give an electrically conducting solution.* Sodium chloride, table salt, is an example of an electrolyte. When most ionic substances dissolve in water, ions that were in fixed sites in the crystalline solid go into the surrounding aqueous solution, where they are free to move about. The resulting solution is conducting because the moving ions form an electric current. Thus, in general, *ionic solids that dissolve in water are electrolytes.*

Not all electrolytes are ionic substances. Certain molecular substances dissolve in water to form ions. The resulting solution is electrically conducting, and so we say that the molecular substance is an electrolyte. An example is hydrogen chloride gas, HCl(g), which is a molecular substance. Hydrogen chloride gas dissolves in water, giving HCl(aq), which in turn produces hydrogen ions, H^+, and chloride ions, Cl^-, in aqueous solution. (The solution of H^+ and Cl^- ions is called hydrochloric acid.)

$$\mathrm{HCl}(q\ ) \xrightarrow{H_2O} \mathrm{H}^+(q\ ) + \mathrm{Cl}^-(q\ )$$

We will look more closely at molecular electrolytes, such as HCl, at the end of this section.

A **nonelectrolyte** is *a substance that dissolves in water to give a nonconducting or very poorly conducting solution.* A common example is sucrose, $C_{12}H_{22}O_{11}$, which is ordinary table sugar. Another example is methanol, CH_3OH, a compound used in car window washer solution. Both of these are molecular substances. The solution process occurs because molecules of the substance mix with molecules of water. Molecules are electrically neutral and cannot carry an electric current, so the solution is electrically nonconducting.

Observing the Electrical Conductivity of a Solution

Figure 4.3 shows a simple apparatus that allows you to observe the ability of a solution to conduct an electric current. The apparatus has two electrodes; here they are flat metal plates, dipping into the solution in a beaker. One electrode connects directly to a battery through a wire. The other electrode connects by a wire to a light bulb

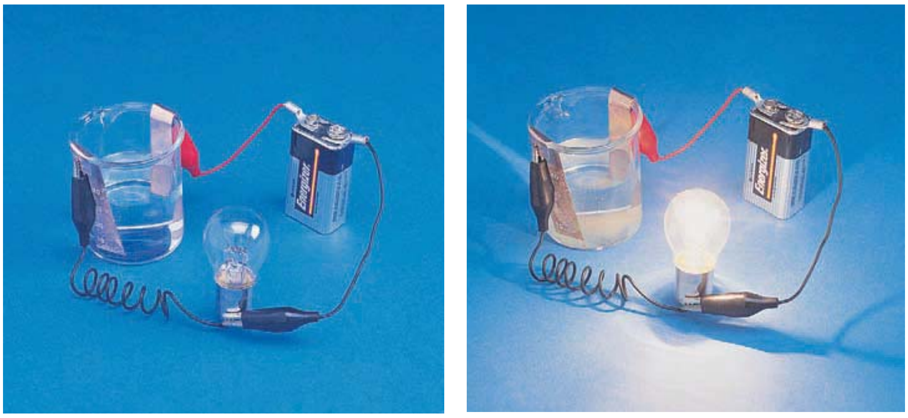


FIGURE 4.3

Testing the electrical conductivity of a solution

Left: Pure water does not conduct; therefore, the bulb does not light. *Right:* A solution of sodium chloride allows the current to pass through it, and the bulb lights.

that connects with another wire to the other side of the battery. For an electric current to flow from the battery, there must be a complete circuit, which allows the current to flow from the positive pole of the battery through the circuit to the negative pole of the battery. To have a complete circuit, the solution in the beaker must conduct electricity, as the wires do. If the solution is conducting, the circuit is complete and the bulb lights. If the solution is nonconducting, the circuit is incomplete and the bulb does not light.

The beaker shown on the left side of Figure 4.3 contains pure water. Because the bulb is not lit, we conclude that pure water is a nonconductor (or very poor conductor) of electricity, which is what we expect from our earlier discussion. The beaker shown on the right side of Figure 4.3 contains a solution of sodium chloride in water. In this case, the bulb burns brightly, showing that the solution is a very good conductor of electricity, due to the movement of ions in the solution.

How brightly the bulb lights tells you whether the solution is a very good conductor (contains a "strong" electrolyte) or only a moderately good conductor (contains a "weak" electrolyte). The solution of sodium chloride burns brightly, so we conclude that sodium chloride is a strong electrolyte. Let us look more closely at such strong and weak electrolytes.

Strong and Weak Electrolytes

When electrolytes dissolve in water they produce ions, but to varying extents. A **strong electrolyte** is *an electrolyte that exists in solution almost entirely as ions.* Most ionic solids that dissolve in water do so by going into the solution almost completely as ions, so they are strong electrolytes. An example is sodium chloride. We can represent the dissolution of sodium chloride in water by the following equation:

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

A **weak electrolyte** is *an electrolyte that dissolves in water to give a relatively small percentage of ions.* These are generally molecular substances. Ammonia, NH_3, is an example. Pure ammonia is a gas that readily dissolves in water and goes into solution as ammonia molecules, $NH_3(aq)$. When you buy "ammonia" in the grocery store, you are buying an aqueous solution of ammonia. Ammonia molecules react with water to form ammonium ions, NH_4^+, and hydroxide ions, OH^-.

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

However, these ions, $NH_4^+ + OH^-$, react with each other to give back ammonia molecules and water molecules.

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

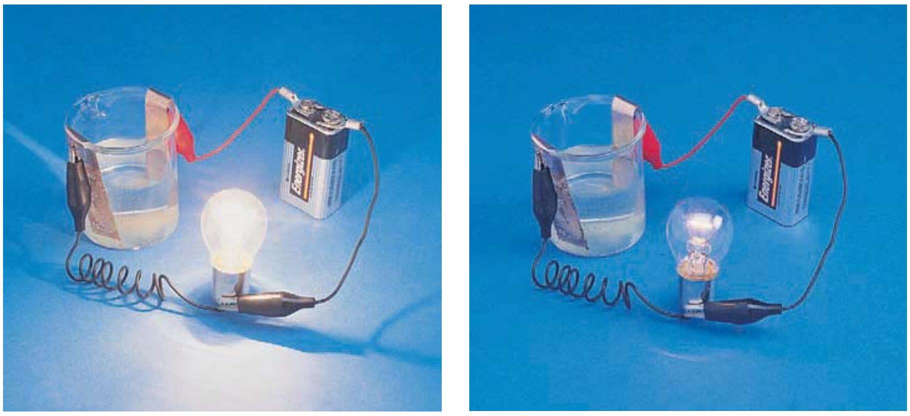


FIGURE 4.4

Comparing strong and weak electrolytes The apparatus is similar to that in Figure 4.3, but this time strong and weak electrolytes are compared. The solution on the left is of HCl (a strong electrolyte) and that on the right is of NH_3 (a weak electrolyte). Note how much more brightly the bulb on the left burns compared with that on the right.

Both reactions, the original one and its reverse, occur constantly and simultaneously. We denote this situation by writing a single equation with a double arrow:

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

As a result of this forward and reverse reaction, just a small percentage of the NH_3 molecules (about 3%) have reacted at any given moment to form ions. Thus, ammonia is a weak electrolyte. The electrical conductivities of a strong and a weak electrolyte are contrasted in Figure 4.4.

Most soluble molecular substances are either nonelectrolytes or weak electrolytes. An exception is hydrogen chloride gas, HCl(*g*), which dissolves in water to produce hydrogen ions and chloride ions. We represent its reaction with water by an equation with a single arrow:

$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

Since hydrogen chloride dissolves to give almost entirely ions, hydrogen chloride (or hydrochloric acid) is a strong electrolyte.

Solubility Rules

It is clear from the preceding discussion that substances vary widely in their *solubility,* or ability to dissolve, in water. Some compounds, such as sodium chloride and ethyl alcohol (CH_3CH_2OH), dissolve readily and are said to be *soluble.* Others, such as calcium carbonate (which occurs naturally as limestone and marble) and benzene (C_6H_6), have quite limited solubilities and are thus said to be *insoluble.*

Soluble ionic compounds form solutions that contain many ions and therefore are strong electrolytes. To predict the solubility of ionic compounds, chemists have developed solubility rules. Table 4.1 lists eight solubility rules for ionic compounds. These rules apply to most of the common ionic compounds that we will discuss in this course. Example 4.1 illustrates how to use the rules.

Example 4.1 Using the Solubility Rules

Determine whether the following compounds are soluble or insoluble in water.

a. Hg_2Cl_2 b. KI c. lead(II) nitrate

Problem Strategy You should refer to Table 4.1 for the solubility rules of ionic compounds to see which compounds are soluble in water. The soluble ionic

(*continued*)

(continued)

compounds are those that readily dissolve in water. The insoluble compounds hardly dissolve at all.

Solution a. According to Rule 3 in Table 4.1, most compounds that contain chloride, Cl^-, are soluble. However, Hg_2Cl_2 is listed as one of the exceptions to this rule, so it does not dissolve in water. Therefore, **Hg_2Cl_2 is not soluble in water.**

b. According to both Rule 1, Group IA compounds are soluble, and Rule 3, most iodides are soluble, KI is expected to be soluble. Therefore, **KI is soluble in water.**

c. According to Rule 2, compounds containing nitrates, NO_3^-, are soluble. Since there are no exceptions to this rule, **lead(II) nitrate, $Pb(NO_3)_2$, is soluble in water.**

Answer Check Most incorrect determinations of solubility occur when the exceptions are overlooked, so always be sure to check the exceptions column of Table 4.1.

Exercise 4.1 Determine whether the following compounds are soluble or insoluble in water.

a. NaBr b. $Ba(OH)_2$ c. calcium carbonate

■ See Problems 4.29 and 4.30.

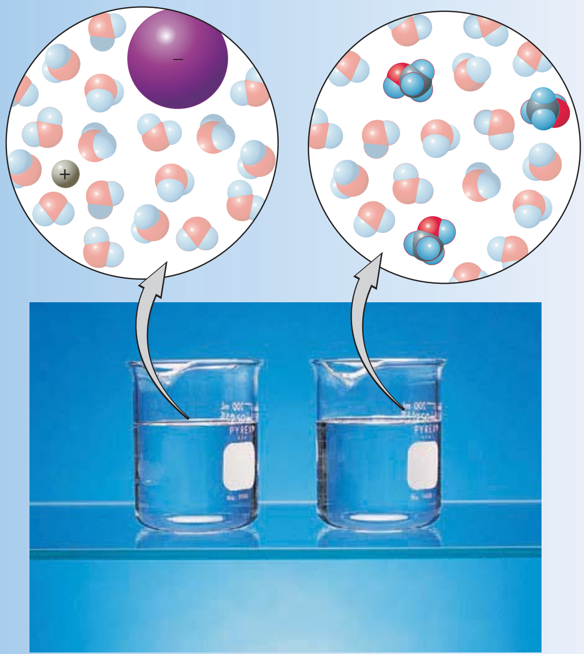
Let us summarize the main points in this section. Compounds that dissolve in water are soluble; those that dissolve little, or not at all, are insoluble. Soluble substances are either electrolytes or nonelectrolytes. Nonelectrolytes form nonconducting aqueous solutions because they dissolve completely as molecules. Electrolytes form electrically conducting solutions in water because they dissolve to give ions in solution. Electrolytes can be strong or weak. Almost all soluble ionic substances are strong electrolytes. Soluble molecular substances usually are nonelectrolytes or weak electrolytes; the latter solution consists primarily of molecules, but has a small percentage of ions. Ammonia, NH_3, is an example of a molecular substance that is a weak electrolyte. A few molecular substances (such as HCl) dissolve almost entirely as ions in the solution and are therefore strong electrolytes. The solubility rules can be used to predict the solubility of ionic compounds in water.

TABLE 4.1 Solubility Rules for Ionic Compounds

Rule	Applies to	Statement	Exceptions
1	Li^+, Na^+, K^+, NH_4^+	Group IA and ammonium compounds are soluble.	—
2	$C_2H_3O_2^-$, NO_3^-	Acetates and nitrates are soluble.	—
3	Cl^-, Br^-, I^-	Most chlorides, bromides, and iodides are soluble.	AgCl, Hg_2Cl_2, $PbCl_2$, AgBr, $HgBr_2$, Hg_2Br_2, $PbBr_2$, AgI, HgI_2, Hg_2I_2, PbI_2
4	SO_4^{2-}	Most sulfates are soluble.	$CaSO_4$, $SrSO_4$, $BaSO_4$, Ag_2SO_4, Hg_2SO_4, $PbSO_4$
5	CO_3^{2-}	Most carbonates are insoluble.	Group IA carbonates, $(NH_4)_2CO_3$
6	PO_4^{3-}	Most phosphates are insoluble.	Group IA phosphates, $(NH_4)_3PO_4$
7	S^{2-}	Most sulfides are insoluble.	Group IA sulfides, $(NH_4)_2S$
8	OH^-	Most hydroxides are insoluble.	Group IA hydroxides, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$

Concept Check 4.1

$LiI(s)$ and $CH_3OH(l)$ are introduced into separate beakers containing water. Using the drawings shown here, label each beaker with the appropriate compound and indicate whether you would expect each substance to be a strong electrolyte, a weak electrolyte, or a nonelectrolyte.



4.2 Molecular and Ionic Equations

We use chemical equations to help us describe chemical reactions. For a reaction involving ions, we have a choice of chemical equations, depending on the kind of information we want to convey. We can represent such a reaction by a *molecular equation,* a *complete ionic equation,* or a *net ionic equation.*

To illustrate these different kinds of equations, consider the preparation of precipitated calcium carbonate, $CaCO_3$. This white, fine, powdery compound is used as a paper filler to brighten and retain ink, as an antacid (as in the trade-named Tums), and as a mild abrasive in toothpastes. One way to prepare this compound is to react calcium hydroxide, $Ca(OH)_2$, with sodium carbonate, Na_2CO_3. Let us look at the different ways to write the equation for this reaction.

Molecular Equations

You could write the equation for this reaction as follows:

$$Ca(OH)_2(aq) + Na_2CO_3(aq) \longrightarrow CaCO_3(s) + 2NaOH(aq)$$

We call this a **molecular equation,** which is *a chemical equation in which the reactants and products are written as if they were molecular substances, even though they may actually exist in solution as ions.* The molecular equation is useful because it is explicit about what the reactant solutions are and what products you obtain. The equation says that you add aqueous solutions of calcium hydroxide and sodium carbonate to the reaction vessel. As a result of the reaction, the insoluble, white calcium carbonate solid forms in the solution; that is, calcium carbonate precipitates. After you remove the precipitate, you are left with a solution of sodium hydroxide. The molecular equation closely describes what you actually do in the laboratory or in an industrial process.

Complete Ionic Equations

Although a molecular equation is useful in describing the actual reactant and product substances, it does not tell you what is happening at the level of ions. That is, it does not give you an ionic-theory interpretation of the reaction. Because this kind of information is useful, you often need to rewrite the molecular equation as an ionic equation.

Again, consider the reaction of calcium hydroxide, $Ca(OH)_2$, and sodium carbonate, Na_2CO_3. Both are soluble ionic substances and therefore strong electrolytes; when they dissolve in water, they go into solution as ions. Each formula unit of $Ca(OH)_2$ forms one Ca^{2+} ion and two OH^- ions in solution. If you want to emphasize that the solution contains freely moving ions, it would be better to write $Ca^{2+}(aq) + 2OH^-(aq)$ in place of $Ca(OH)_2(aq)$. Similarly, each formula unit of Na_2CO_3 forms two Na^+ ions and one CO_3^{2-} ion in solution, and you would emphasize this by writing $2Na^+(aq) +$ $CO_3^{2-}(aq)$ in place of $Na_2CO_3(aq)$. The reactant side of the equation becomes

$$Ca^{2+}(aq) + 2OH^-(aq) + 2Na^+(aq) + CO_3^{2-}(aq) \longrightarrow$$

Thus, the reaction mixture begins as a solution of four different kinds of ions.

Now let us look at the product side of the equation. One product is the precipitate $CaCO_3(s)$. According to the solubility rules, this is an insoluble ionic compound, so it will exist in water as a solid. We leave the formula as $CaCO_3(s)$ to convey this information in the equation. On the other hand, NaOH is a soluble ionic substance and therefore a strong electrolyte; it dissolves in aqueous solution to give the freely moving ions, which we denote by writing $Na^+(aq) + OH^-(aq)$. The complete equation is

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

The purpose of such a *complete ionic equation* is to represent each substance by its predominant form in the reaction mixture. For example, if the substance is a soluble ionic compound, it probably dissolves as individual ions (so it is a strong electrolyte). In a complete ionic equation, you represent the compound as separate ions. If the substance is a weak electrolyte, it is present in solution primarily as molecules, so you represent it by its molecular formula. If the substance is an insoluble ionic compound, you represent it by the formula of the compound, not by the formulas of the separate ions in solution.

Thus, a **complete ionic equation** is *a chemical equation in which strong electrolytes (such as soluble ionic compounds) are written as separate ions in the solution.* You represent other reactants and products by the formulas of the compounds, indicating any soluble substance by (*aq*) after its formula and any insoluble solid substance by (*s*) after its formula.

Net Ionic Equations

In the complete ionic equation representing the reaction of calcium hydroxide and sodium carbonate, some ions (OH^- and Na^+) appear on both sides of the equation. This means that nothing happens to these ions as the reaction occurs. They are called spectator ions. A **spectator ion** is *an ion in an ionic equation that does not take part in the reaction.* You can cancel such ions from both sides to express the essential reaction that occurs.

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

The resulting equation is

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

This is the **net ionic equation,** *an ionic equation from which spectator ions have been canceled.* It shows that the reaction that actually occurs at the ionic level is between calcium ions and carbonate ions to form solid calcium carbonate.

From the net ionic equation, you can see that mixing any solution of calcium ion with any solution of carbonate ion will give you this same reaction. For example, the strong electrolyte calcium nitrate, $Ca(NO_3)$, dissolves readily in water to provide a source of calcium ions. (According to the solubility rules, calcium nitrate is soluble, so it goes into solution as Ca^{2+} and NO_3^- ions.) Similarly, the strong electrolyte potassium carbonate, K_2CO_3, dissolves readily in water to provide a source of carbonate ions. (According to the solubility rules, potassium carbonate is soluble, so it goes into solution as K^+ and CO_3^{2-} ions.) When you mix solutions of these two compounds, you obtain a solution of calcium ions and carbonate ions, which react to form the insoluble calcium carbonate. The other product is potassium nitrate, a soluble ionic compound, and therefore a strong electrolyte. The molecular equation representing the reaction is

$$Ca(NO_3)_2(aq) + K_2CO_3(aq) \longrightarrow CaCO_3(s) + 2KNO_3(aq)$$

You obtain the complete ionic equation from this molecular equation by rewriting each of the soluble ionic compounds as ions, but retaining the formula for the precipitate $CaCO_3(s)$:

$$Ca^{2+}(aq) + \cancel{2NO_3^-(aq)} + \cancel{2K^+(aq)} + CO_3^{2-}(aq) \longrightarrow CaCO_3(s) + \cancel{2K^+(aq)} + \cancel{2NO_3^-(aq)}$$

The net ionic equation is

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

Note that the net ionic equation is identical to the one obtained from the reaction of $Ca(OH)_2$ and Na_2CO_3. The essential reaction is the same whether you mix solutions of calcium hydroxide and sodium carbonate or solutions of calcium nitrate and potassium carbonate.

The value of the net ionic equation is its generality. For example, seawater contains Ca^{2+} and CO_3^{2-} ions from various sources. Whatever the sources of these ions, you expect them to react to form a precipitate of calcium carbonate. In seawater, this precipitate results in sediments of calcium carbonate, which eventually form limestone (Figure 4.5).

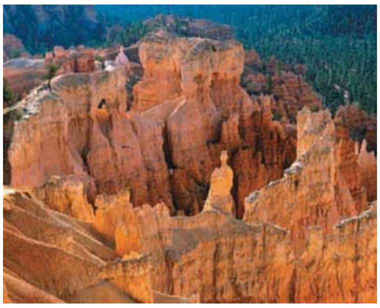


FIGURE 4.5 ▲

Limestone formations

It is believed that most limestone formed as a precipitate of calcium carbonate (and other carbonates) from seawater. The photograph shows limestone formations at Bryce Point, Bryce Canyon National Park, Utah. More than 60 million years ago, this area was covered by seawater.

Example 4.2 Writing Net Ionic Equations

Write a net ionic equation for each of the following molecular equations.

a. $2HClO_4(aq) + Ca(OH)_2(aq) \longrightarrow Ca(ClO_4)_2(aq) + 2H_2O(l)$
Perchloric acid, $HClO_4$, is a strong electrolyte, forming H^+ and ClO_4^- ions in solution. $Ca(ClO_4)_2$ is a soluble ionic compound.

b. $HC_2H_3O_2(aq) + NaOH(aq) \longrightarrow NaC_2H_3O_2(aq) + H_2O(l)$
Acetic acid, $HC_2H_3O_2$, is a molecular substance and a weak electrolyte.

Problem Strategy You will need to convert the molecular equation to the complete ionic equation, then cancel spectator ions to obtain the net ionic equation. For each ionic compound in the reaction, use the solubility rules to determine if the compound will be soluble (in the solution as ions) or insoluble (present as an undissolved solid). For the complete ionic equation, represent all of the strong electrolytes by their separate ions in solution, adding (*aq*) after the formula of each. Retain the formulas of the other compounds. An ionic compound should have (*aq*) after its formula if it is soluble or (*s*) if it is insoluble.

Solution a. According to the solubility rules presented in Table 4.1 and the problem statement, $Ca(OH)_2$ and $Ca(ClO_4)_2$ are soluble ionic compounds, so they are strong

(*continued*)

(*continued*)

electrolytes. The problem statement notes that $HClO_4$ is also a strong electrolyte. You write each strong electrolyte in the form of separate ions. Water, H_2O, is a nonelectrolyte (or very weak electrolyte), so you retain its molecular formula. The complete ionic equation is

$$2H^+(aq) + \cancel{2ClO_4^-(aq)} + \cancel{Ca^{2+}(aq)} + 2OH^-(aq) \longrightarrow \cancel{Ca^{2+}(aq)} + \cancel{2ClO_4^-(aq)} + 2H_2O(l)$$

After canceling spectator ions and dividing by 2, you get the following net ionic equation:

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

b. According to the solubility rules, NaOH and $NaC_2H_3O_2$ are soluble ionic compounds, so they are strong electrolytes. The problem statement notes that $HC_2H_3O_2$ is a weak electrolyte, which you write by its molecular formula. Water, H_2O, is a nonelectrolyte, so you retain its molecular formula also. The complete ionic equation is

$$HC_2H_3O_2(aq) + \cancel{Na^+(aq)} + OH^-(aq) \longrightarrow \cancel{Na^+(aq)} + C_2H_3O_2^-(aq) + H_2O(l)$$

and the net ionic equation is

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

Answer Check If both of the reactants are strong electrolytes and a reaction occurs, your correct net ionic equation should not have any ions as products of the reaction. In this case, because the reaction is with a weak electrolyte, ions in the net ionic equation are possible.

Exercise 4.2 Write complete ionic and net ionic equations for each of the following molecular equations.

a. $2HNO_3(aq) + Mg(OH)_2(s) \longrightarrow 2H_2O(l) + Mg(NO_3)_2(aq)$
 Nitric acid, HNO_3, is a strong electrolyte.

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

■ See Problems 4.33 and 4.34.

Types of Chemical Reactions

Among the several million known substances, many millions of chemical reactions are possible. Beginning students are often bewildered by the possibilities. How can I know whether two substances will react whether they are mixed? How can I predict the products? Although it is not possible to give completely general answers to these questions, it is possible to make sense of chemical reactions. Most of the reactions we will study belong to one of three types:

1. Precipitation reactions. In these reactions, you mix solutions of two ionic substances, and a solid ionic substance (a precipitate) forms.
2. Acid–base reactions. An acid substance reacts with a substance called a base. Such reactions involve the transfer of a proton between reactants.
3. Oxidation–reduction reactions. These involve the transfer of electrons between reactants.

We will look at each of these types of reactions. By the time you finish this chapter, you should feel much more comfortable with the descriptions of chemical reactions that you will encounter in this course.

4.3 Precipitation Reactions

In the previous section, we used a precipitation reaction to illustrate how to convert a molecular equation to an ionic equation. A precipitation reaction occurs in aqueous solution because one product is insoluble. A **precipitate** is *an insoluble solid compound formed during a chemical reaction in solution.* To predict whether a precipitate will form when you mix two solutions of ionic compounds, you need to know whether any of the potential products that might form are insoluble. This is another application of the solubility rules (Section 4.1).

Predicting Precipitation Reactions

Now let us see how you would go about predicting whether a precipitation reaction will occur. Suppose you mix together solutions of magnesium chloride, $MgCl_2$, and silver nitrate, $AgNO_3$. You can write the potential reactants as follows:

$$MgCl_2 + AgNO_3 \longrightarrow$$

How can you tell if a reaction will occur, and if it does, what products to expect?

When you write a precipitation reaction as a molecular equation, the reaction has the form of an exchange reaction. An **exchange** (or **metathesis**) **reaction** is *a reaction between compounds that, when written as a molecular equation, appears to involve the exchange of parts between the two reactants.* In a precipitation reaction, the anions exchange between the two cations (or vice versa).

Let us momentarily assume that a reaction does occur between magnesium chloride and silver nitrate. If you exchange the anions, you get silver chloride and magnesium nitrate. Once you figure out the formulas of these potential products, you can write the molecular equation. The formulas are AgCl and $Mg(NO_3)_2$. (If you do not recall how to write the formula of an ionic compound, given the ions, turn back to Example 2.3.) The balanced equation, assuming there *is* a reaction, is

$$MgCl_2 + 2AgNO_3 \longrightarrow 2AgCl + Mg(NO_3)_2$$

Let us verify that $MgCl_2$ and $AgNO_3$ are soluble and then check the solubilities of the products. Rule 3 in Table 4.1 says that chlorides are soluble, with certain exceptions, which do not include magnesium chloride. Thus, we predict that magnesium chloride is soluble. Rule 2 indicates that nitrates are soluble, so $AgNO_3$ is soluble as well. The potential products are silver chloride and magnesium nitrate. According to Rule 3, silver chloride is one of the exceptions to the general solubility of chlorides. Therefore, we predict that the silver chloride is insoluble. Magnesium nitrate is soluble according to Rule 2.

Now we can append the appropriate phase labels to the compounds in the preceding equation.

$$MgCl_2(aq) + 2AgNO_3(aq) \longrightarrow 2AgCl(s) + Mg(NO_3)_2(aq)$$

We predict that reaction occurs because silver chloride is insoluble, and precipitates from the reaction mixture. Figure 4.6 shows the formation of the white silver chloride from this reaction. If you separate the precipitate from the solution by pouring it through filter paper, the solution that passes through (the filtrate) contains magnesium nitrate, which you could obtain by evaporating the water. The molecular equation is a summary of the actual reactants and products in the reaction. <

To see the reaction that occurs on an ionic level, you need to rewrite the molecular equation as a net ionic equation. You first write the strong electrolytes (here

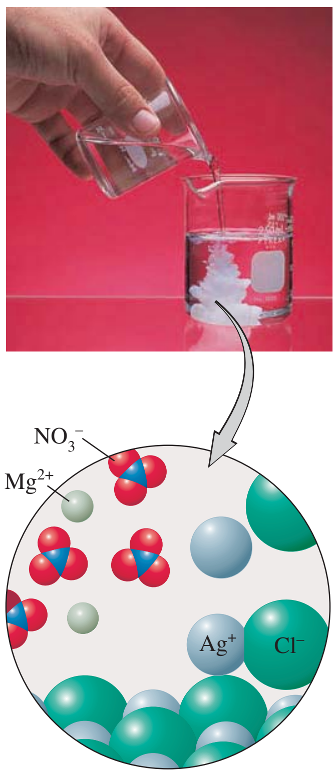


FIGURE 4.6

Reaction of magnesium chloride and silver nitrate
Magnesium chloride solution is added to a beaker of silver nitrate solution. A white precipitate of silver chloride forms.

The reactants $MgCl_2$ and $AgNO_3$ must be added in correct amounts; otherwise, the excess reactant will remain along with the product $Mg(NO_3)_2$.

soluble ionic compounds) in the form of ions, leaving the formula of the precipitate unchanged.

$$\cancel{Mg^{2+}(aq)} + 2Cl^-(aq) + 2Ag^+(aq) + \cancel{2NO_3^-(aq)} \longrightarrow$$
$$2AgCl(s) + \cancel{Mg^{2+}(aq)} + \cancel{2NO_3^-(aq)}$$

After canceling spectator ions and reducing the coefficients to the smallest whole numbers, you obtain the net ionic equation:

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

This equation represents the essential reaction that occurs: Ag^+ ions and Cl^- ions in aqueous solution react to form solid silver chloride.

If silver chloride were soluble, a reaction would not have occurred. When you first mix solutions of $MgCl_2(aq)$ and $AgNO_3(aq)$, you obtain a solution of four ions: $Mg^{2+}(aq)$, $Cl^-(aq)$, $Ag^+(aq)$, and $NO_3^-(aq)$. If no precipitate formed, you would end up simply with a solution of these four ions. However, because Ag^+ and Cl^- react to give the precipitate AgCl, the effect is to remove these ions from the reaction mixture as an insoluble compound and leave behind a solution of $Mg(NO_3)_2(aq)$.

Example 4.3 Deciding Whether Precipitation Occurs

For each of the following, decide whether a precipitation reaction occurs. If it does, write the balanced molecular equation and then the net ionic equation. If no reaction occurs, write the compounds followed by an arrow and then *NR* (no reaction).

a. Aqueous solutions of sodium chloride and iron(II) nitrate are mixed.

b. Aqueous solutions of aluminum sulfate and sodium hydroxide are mixed.

Problem Strategy When aqueous solutions containing soluble salts are mixed, a precipitation reaction occurs if an insoluble compound (precipitate) forms. Start by writing the formulas of the compounds that are mixed. (If you have trouble with this, see Examples 2.3 and 2.4.) Then, assuming momentarily that the compounds do react, write the exchange reaction. Make sure that you write the correct formulas of the products. Using the solubility rules, append phase labels to each formula in the equation consulting the solubility rules. If one of the products forms an insoluble compound (precipitate), reaction occurs; otherwise, no reaction occurs.

Solution a. The formulas of the compounds are NaCl and $Fe(NO_3)_2$. Exchanging anions, you get sodium nitrate, $NaNO_3$, and iron(II) chloride, $FeCl_2$. The equation for the exchange reaction is

$$NaCl + Fe(NO_3)_2 \longrightarrow NaNO_3 + FeCl_2 \qquad \text{(not balanced)}$$

Referring to Table 4.1, note that NaCl and $NaNO_3$ are soluble (Rule 1). Also, iron(II) nitrate is soluble (Rule 2), and iron(II) chloride is soluble. (Rule 3 says that chlorides are soluble with some exceptions, none of which include $FeCl_2$.) Since there is no precipitate, no reaction occurs. You obtain simply an aqueous solution of the four different ions (Na^+, Cl^-, Fe^{2+}, and NO_3^-). For the answer, we write

$$\mathbf{NaCl(\mathit{aq}) + Fe(NO_3)_2(\mathit{aq}) \longrightarrow NR}$$

b. The formulas of the compounds are $Al_2(SO_4)_3$ and NaOH. Exchanging anions, you get aluminum hydroxide, $Al(OH)_3$, and sodium sulfate, Na_2SO_4. The equation for the exchange reaction is

$$Al_2(SO_4)_3 + NaOH \longrightarrow Al(OH)_3 + Na_2SO_4 \qquad \text{(not balanced)}$$

(*continued*)

(continued)

From Table 4.1, you see that $Al_2(SO_4)_3$ is soluble (Rule 4), NaOH and Na_2SO_4 are soluble (Rule 1), and $Al(OH)_3$ is insoluble (Rule 8). Thus, aluminum hydroxide precipitates. The balanced molecular equation with phase labels is

$$\mathbf{Al_2(SO_4)_3(\mathit{aq}) + 6NaOH(\mathit{aq}) \longrightarrow 2Al(OH)_3(\mathit{s}) + 3Na_2SO_4(\mathit{aq})}$$

To get the net ionic equation, you write the strong electrolytes (here, soluble ionic compounds) as ions in aqueous solution and cancel spectator ions.

$$2Al^{3+}(aq) + \cancel{3SO_4^{2-}(aq)} + \cancel{6Na^+(aq)} + 6OH^-(aq) \longrightarrow$$
$$2Al(OH)_3(s) + \cancel{6Na^+(aq)} + \cancel{3SO_4^{2-}(aq)}$$

The net ionic equation is

$$\mathbf{Al^{3+}(\mathit{aq}) + 3OH^-(\mathit{aq}) \longrightarrow Al(OH)_3(\mathit{s})}$$

Thus, aluminum ion reacts with hydroxide ion to precipitate aluminum hydroxide.

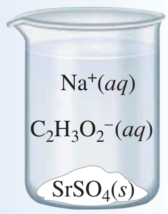
Answer Check One of the most critical aspects of getting this type of problem right is making certain that you are using the correct chemical formulas for the reactants and products.

Exercise 4.3 You mix aqueous solutions of sodium iodide and lead(II) acetate. If a reaction occurs, write the balanced molecular equation and the net ionic equation. If no reaction occurs, indicate this by writing the formulas of the compounds and an arrow followed by *NR*.

■ See Problems 4.37, 4.38, 4.39, and 4.40.

Concept Check 4.2

Your lab partner tells you that she mixed two solutions that contain ions. You analyze the solution and find that it contains the ions and precipitate shown in the beaker.



a. Write the molecular equation for the reaction.

b. Write the complete ionic equation for the reaction.

c. Write the net ionic equation for the reaction.

4.4 Acid–Base Reactions

Acids and bases are some of the most important electrolytes. You can recognize acids and bases by some simple properties. Acids have a sour taste. Solutions of bases, on the other hand, have a bitter taste and a soapy feel. (Of course, you should *never* taste laboratory chemicals.) Some examples of acids are acetic acid, present in vinegar; citric acid, a constituent of lemon juice; and hydrochloric acid, found in the digestive fluid of the stomach. An example of a base is aqueous ammonia, often used as a household cleaner. Table 4.2 lists further examples; see also Figure 4.7.

Another simple property of acids and bases is their ability to cause color changes in certain dyes. An **acid–base indicator** is *a dye used to distinguish between acidic and basic solutions by means of the color changes it undergoes in these solutions.* Such dyes are common in natural materials. The amber color of tea, for example, is lightened by the addition of lemon juice (citric acid). Red cabbage juice changes to

TABLE 4.2 Common Acids and Bases

Name	Formula	Remarks
Acids		
Acetic acid	$HC_2H_3O_2$	Found in vinegar
Acetylsalicylic acid	$HC_9H_7O_4$	Aspirin
Ascorbic acid	$H_2C_6H_6O_6$	Vitamin C
Citric acid	$H_3C_6H_5O_7$	Found in lemon juice
Hydrochloric acid	HCl	Found in gastric juice (digestive fluid in stomach)
Sulfuric acid	H_2SO_4	Battery acid
Bases		
Ammonia	NH_3	Aqueous solution used as a household cleaner
Calcium hydroxide	$Ca(OH)_2$	Slaked lime (used in mortar for building construction)
Magnesium hydroxide	$Mg(OH)_2$	Milk of magnesia (antacid and laxative)
Sodium hydroxide	$NaOH$	Drain cleaners, oven cleaners

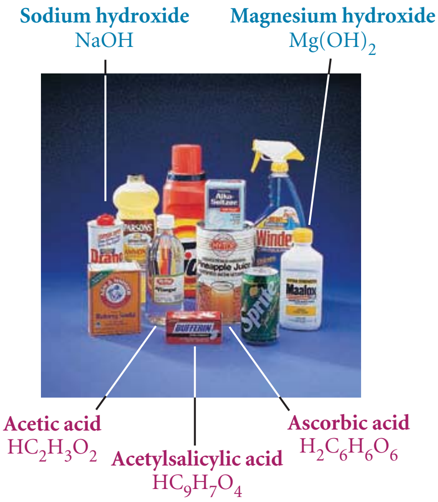


FIGURE 4.7
Household acids and bases
Shown are a variety of household products that are either acids or bases.

green and then yellow when a base is added (Figure 4.8). The green and yellow colors change back to red when an acid is added. Litmus is a common laboratory acid–base indicator. This dye, produced from certain species of lichens, turns red in acidic solution and blue in basic solution. Phenolphthalein (fee′ nol thay′ leen), another laboratory acid–base indicator, is colorless in acidic solution and pink in basic solution.

An important chemical characteristic of acids and bases is the way they react with one another. To understand these acid–base reactions, we need to have precise definitions of the terms *acid* and *base*.

Definitions of Acid and Base

When Arrhenius developed his ionic theory of solutions, he also gave the classic definitions of acids and bases. According to Arrhenius, an **acid** is *a substance that produces hydrogen ions, H^+, when it dissolves in water.* An example is nitric acid, HNO_3, a molecular substance that dissolves in water to give H^+ and NO_3^-.

$$HNO_3(aq) \xrightarrow{H_2O} H^+(aq) + NO_3^-(aq)$$

FIGURE 4.8
Red cabbage juice as an acid–base indicator
Left: Preparation of red cabbage juice. The beaker (green solution) contains red cabbage juice and sodium bicarbonate (baking soda). *Right:* Red cabbage juice has been added from a pipet to solutions in the beakers. These solutions vary in acidity from highly acidic on the left to highly basic on the right.

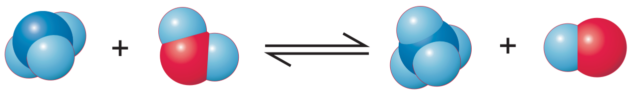
An Arrhenius **base** is *a substance that produces hydroxide ions, OH^-, when it dissolves in water.* For example, sodium hydroxide is a base.

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

The molecular substance ammonia, NH_3, is also a base because it yields hydroxide ions when it reacts with water. <

Solutions of ammonia are sometimes called ammonium hydroxide and given the formula $NH_4OH(aq)$, based on analogy with NaOH. No NH_4OH molecule or compound has ever been found, however.

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



Although the Arrhenius concept of acids and bases is useful, it is somewhat limited. For example, it tends to single out the OH^- ion as the source of base character, when other ions or molecules can play a similar role. In 1923, Johannes N. Brønsted and Thomas M. Lowry independently noted that many reactions involve nothing more than the transfer of a proton (H^+) between reactants, and they realized that they could use this idea to expand the definitions of acids and bases to describe a large class of chemical reactions. In this view, acid–base reactions are *proton-transfer reactions.*

Consider the preceding reaction. It involves the transfer of a proton from the water molecule, H_2O, to the ammonia molecule, NH_3.

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

Once the proton, H^+, has left the H_2O molecule, it leaves behind an OH^- ion. When the H^+ adds to NH_3, an NH_4^+ ion results. H_2O is said to *donate* a proton to NH_3, and NH_3 is said to *accept* a proton from H_2O.

Brønsted and Lowry defined an **acid** as *the species (molecule or ion) that donates a proton to another species in a proton-transfer reaction.* They defined a **base** as *the species (molecule or ion) that accepts a proton in a proton-transfer reaction.* In the reaction of ammonia with water, the H_2O molecule is the acid, because it donates a proton. The NH_3 molecule is a base, because it accepts a proton.

$$\underset{\text{base}}{NH_3(aq)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The dissolution of nitric acid, HNO_3, in water is actually a proton-transfer reaction, although the following equation, which we used as an illustration of an Arrhenius acid, does not spell that out.

$$HNO_3(aq) \xrightarrow{H_2O} H^+(aq) + NO_3^-(aq)$$

To see that this is a proton-transfer reaction, we need to clarify the structure of the hydrogen ion, $H^+(aq)$. This ion consists of a proton (H^+) in association with water molecules, which is what (aq) means. This is not a weak association, however, because the proton (or hydrogen nucleus) would be expected to attract electrons strongly to itself. In fact, the $H^+(aq)$ ion might be better thought of as a proton chemically bonded to a water molecule to give the H_3O^+ ion, with other water molecules less strongly associated with this ion, which we represent by the phase-labeled formula $H_3O^+(aq)$. Written in this form, we usually call this the *hydronium ion.* It is important to understand that the hydrogen ion, $H^+(aq)$, and the hydronium ion, $H_3O^+(aq)$, represent precisely the same physical ion. For simplicity, we often write the formula for this ion as $H^+(aq)$, but when we want to be explicit about the proton-transfer aspect of a reaction, we write the formula as $H_3O^+(aq)$. <

The $H^+(aq)$ ion has variable structure in solution. In solids, there is evidence for $[H(H_2O)_n]^+$, where n is 1, 2, 3, 4, or 6.

TABLE 4.3

Common Strong Acids and Bases

Strong Acids	Strong Bases
$HClO_4$	LiOH
H_2SO_4	NaOH
HI	KOH
HBr	$Ca(OH)_2$
HCl	$Sr(OH)_2$
HNO_3	$Ba(OH)_2$

We will discuss the Brønsted–Lowry concept of acids and bases more thoroughly in Chapter 15.

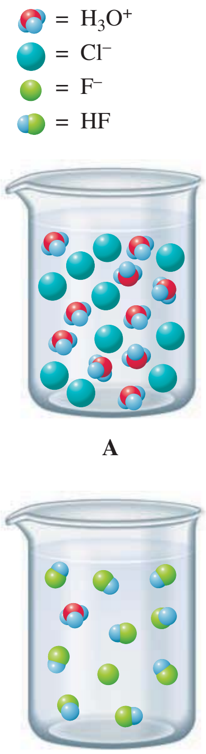
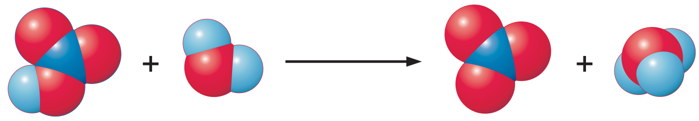


FIGURE 4.9

Molecular views comparing the strong acid HCl and the weak acid HF in water (H_2O molecules are omitted for clarity) *Top:* Due to its complete reaction with water, the strong acid HCl exists as the hydronium ion, $H_3O^+(aq)$, and $Cl^-(aq)$ in aqueous solution. Because of this complete reaction, there are essentially no HCl(*aq*) molecules in the solution. *Bottom:* Due to the reaction with only very few of the water molecules, the weak acid HF(*aq*) exists in aqueous solution largely as HF(*aq*) molecules, with very little $H_3O^+(aq)$ and $F^-(aq)$ being produced.

Now let us rewrite the preceding equation by replacing $H^+(aq)$ by $H_3O^+(aq)$. To maintain a balanced equation, we will also need to add $H_2O(l)$ to the left side.

$$HNO_3(aq) + H_2O(l) \longrightarrow NO_3^-(aq) + H_3O^+(aq)$$



Note that the reaction involves simply a transfer of a proton (H^+) from HNO_3 to H_2O:

$$\underset{\text{acid}}{HNO_3(aq)} + \overset{H^+}{\underset{\text{base}}{H_2O(l)}} \longrightarrow NO_3^-(aq) + H_3O^+(aq)$$

The HNO_3 molecule is an acid (proton donor) and H_2O is a base (proton acceptor). Note that H_2O may function as an acid or a base, depending on the other reactant.

The Arrhenius definitions and those of Brønsted and Lowry are essentially equivalent for aqueous solutions, although their points of view are different. For instance, sodium hydroxide and ammonia are bases in the Arrhenius view because they increase the percentage of OH^- ion in the aqueous solution. They are bases in the Brønsted–Lowry view because they provide species (OH^- from the strong electrolyte sodium hydroxide and NH_3 from ammonia) that can accept protons. <

Strong and Weak Acids and Bases

Acids and bases are classified as strong or weak, depending on whether they are strong or weak electrolytes. A **strong acid** is *an acid that ionizes completely in water; it is a strong electrolyte.* Hydrochloric acid, HCl(*aq*), and nitric acid, $HNO_3(aq)$, are examples of strong acids. Using the hydronium ion notation, we write the respective equations as follows:

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

$$HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$$

Table 4.3 lists six common strong acids. Most of the other acids we will discuss are weak acids.

A **weak acid** is *an acid that only partly ionizes in water; it is a weak electrolyte.* Examples of weak acids are hydrocyanic acid, HCN(*aq*), and hydrofluoric acid, HF(*aq*). These molecules react with water to produce a small percentage of ions in solution.

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

Figure 4.9 presents molecular views of the strong acid HCl(*aq*) and the weak acid HF(*aq*). Note how both the strong and weak acid undergo the same reaction with water (proton donors); however, in the case of the weak acid such as HF, only a small portion of the acid molecules actually undergoes reaction leaving the majority of the acid molecules unreacted. On the other hand, strong acids like HCl and HNO_3 undergo complete reaction with water. The result is that weak acids can produce little H_3O^+ in aqueous solution, whereas strong acids can produce large amounts. Hence, when chemists refer to a weak acid, they are often thinking about a substance that produces a limited amount of $H_3O^+(aq)$, whereas when chemists refer to a strong acid, they are thinking about a substance that can produce large amounts of $H_3O^+(aq)$.

A **strong base** is *a base that is present in aqueous solution entirely as ions, one of which is OH^-; it is a strong electrolyte.* The ionic compound sodium hydroxide, NaOH, is an example of a strong base. It dissolves in water as Na^+ and OH^-.

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

The hydroxides of Groups IA and IIA elements, except for beryllium hydroxide, are strong bases (see Table 4.3).

A **weak base** is *a base that is only partly ionized in water; it is a weak electrolyte.* Ammonia, NH_3, is an example.

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

In many cases, when chemists are thinking about strong versus weak bases in aqueous solution, they consider a weak base to be a substance that can produce only limited amounts of $OH^-(aq)$ and a strong base to be a substance that can produce large amounts of $OH^-(aq)$.

You will find it important to be able to identify an acid or base as strong or weak. When you write an ionic equation, you represent strong acids and bases by the ions they form and weak acids and bases by the formulas of the compounds. < The next example will give you some practice identifying acids and bases as strong or weak.

Example 4.4 Classifying Acids and Bases as Strong or Weak

Identify each of the following compounds as a strong or weak acid or base:

a. LiOH b. $HC_2H_3O_2$ c. HBr d. HNO_2

Problem Strategy Refer to Table 4.3 for the common strong acids and bases. You can assume that other acids and bases are weak.

Solution

a. As noted in Table 4.3, **LiOH is a strong base.**

b. Acetic acid, $HC_2H_3O_2$, is not one of the strong acids listed in Table 4.3; therefore, we assume **$HC_2H_3O_2$ is a weak acid.**

c. As noted in Table 4.3, **HBr is a strong acid.**

d. Nitrous acid, HNO_2, is not one of the strong acids listed in Table 4.3; therefore, we assume **HNO_2 is a weak acid.**

Answer Check Do not fall into the trap of assuming that if a compound has OH in the formula, it must be a base. For example, methyl alcohol, CH_3OH, has OH in the formula, but it is not a strong base. Likewise, do not assume that a compound is an acid just because it has H.

Exercise 4.4 Label each of the following as a strong or weak acid or base:

a. H_3PO_4 b. HClO c. $HClO_4$ d. $Sr(OH)_2$

■ See Problems 4.41 and 4.42.

Neutralization Reactions

One of the chemical properties of acids and bases is that they neutralize one another. A **neutralization reaction** is *a reaction of an acid and a base that results in an ionic compound and possibly water.* When a base is added to an acid solution, the acid is said to be neutralized. *The ionic compound that is a product of a neutralization reaction* is called a **salt.** Most ionic compounds other than hydroxides and oxides are salts. Salts can be obtained from neutralization reactions such as

$$\underset{\text{acid}}{2HCl(aq)} + \underset{\text{base}}{Ca(OH)_2(aq)} \longrightarrow \underset{\text{salt}}{CaCl_2(aq)} + 2H_2O(l)$$

$$\underset{\text{acid}}{HCN(aq)} + \underset{\text{base}}{KOH(aq)} \longrightarrow \underset{\text{salt}}{KCN(aq)} + H_2O(l)$$

The salt formed in a neutralization reaction consists of cations obtained from the base and anions obtained from the acid. In the first example, the base is $Ca(OH)_2$, which supplies Ca^{2+} cations; the acid is HCl, which supplies Cl^- anions. The salt contains Ca^{2+} and Cl^- ions ($CaCl_2$).

We wrote these reactions as molecular equations. Written in this form, the equations make explicit the reactant compounds and the salts produced. However, to discuss the essential reactions that occur, you need to write the net ionic equations. You will see that the net ionic equation for each acid–base reaction involves the transfer of a proton.

The first reaction involves a strong acid, $HCl(aq)$, and a strong base, $Ca(OH)_2(aq)$. Both $Ca(OH)_2$ and the product $CaCl_2$, being soluble ionic compounds, are strong electrolytes. Writing these strong electrolytes in the form of ions gives the following complete ionic equation:

$$2H^+(aq) + \cancel{2Cl^-(aq)} + \cancel{Ca^{2+}(aq)} + 2OH^-(aq) \longrightarrow \cancel{Ca^{2+}(aq)} + \cancel{2Cl^-(aq)} + 2H_2O(l)$$

Canceling spectator ions and dividing by 2 give the net ionic equation:

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

Note the transfer of a proton from the hydrogen ion (or hydronium ion, H_3O^+) to the hydroxide ion.

The second reaction involves $HCN(aq)$, a weak acid, and $KOH(aq)$, a strong base; the product is KCN, a strong electrolyte. The net ionic equation is

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

Note the proton transfer, characteristic of an acid–base reaction.

In each of these examples, hydroxide ions latch strongly onto protons to form water. Because water is a very stable substance, it effectively provides the driving force of the reaction.

Although water is one of the products in most neutralization reactions, the reaction of an acid with the base ammonia provides a prominent exception. Consider the reaction of sulfuric acid with ammonia:

$$\underset{\text{acid}}{H_2SO_4(aq)} + \underset{\text{base}}{2NH_3(aq)} \longrightarrow \underset{\text{salt}}{(NH_4)_2SO_4(aq)}$$

The net ionic equation is

$$H^+(aq) + NH_3(aq) \longrightarrow NH_4^+(aq) \quad (H^+)$$

Note the proton transfer, a hallmark of an acid–base reaction. In this case, NH_3 molecules latch onto protons and form relatively stable NH_4^+ ions.

Example 4.5 Writing an Equation for a Neutralization

Write the molecular equation and then the net ionic equation for the neutralization of nitrous acid, HNO_2, by sodium hydroxide, NaOH, both in aqueous solution. Use an arrow with H^+ over it to show the proton transfer.

Problem Strategy Because this is a neutralization reaction, you know that the reactants are an acid and a base and that there will be a salt and possibly water as a product. Therefore, start by writing the acid and base reactants and the salt product. Recall that the salt consists of cations from the base and anions from the acid. Note also that water is frequently a product; if it is, you will not be able to balance the equation

(*continued*)

(continued)

without it. Once you have the balanced molecular equation, write the complete ionic equation. Do that by representing any strong electrolytes by the formulas of their ions. Finally, write the net ionic equation by canceling any spectator ions, and from it note the proton transfer.

Solution The salt consists of the cation from the base (Na^+) and the anion from the acid (NO_2^-); its formula is $NaNO_2$. You will need to add H_2O as a product to complete and balance the molecular equation:

$$\mathbf{HNO_2}(\boldsymbol{aq}) + \mathbf{NaOH}(\boldsymbol{aq}) \longrightarrow \mathbf{NaNO_2}(\boldsymbol{aq}) + \mathbf{H_2O}(\boldsymbol{l}) \qquad \textbf{(molecular equation)}$$

Note that NaOH (a strong base) and $NaNO_2$ (a soluble ionic substance) are strong electrolytes; HNO_2 is a weak electrolyte (it is not one of the strong acids in Table 4.3). You write both NaOH and $NaNO_2$ in the form of ions. The complete ionic equation is

$$HNO_2(aq) + \cancel{Na^+(aq)} + OH^-(aq) \longrightarrow \cancel{Na^+(aq)} + NO_2^-(aq) + H_2O(l)$$

The net ionic equation is

$$HNO_2(aq) + OH^-(aq) \longrightarrow NO_2^-(aq) + H_2O(l)$$

Note that a proton is transferred from HNO_2 to the OH^- ion to yield the products:

$$\overset{\mathbf{H^+}}{\mathbf{HNO_2}(\boldsymbol{aq}) + \mathbf{OH^-}(\boldsymbol{aq})} \longrightarrow \mathbf{NO_2^-}(\boldsymbol{aq}) + \mathbf{H_2O}(\boldsymbol{l}) \qquad \textbf{(net ionic equation)}$$

Answer Check Remember that correct answers include phase labels and that ions must have correct charges.

Exercise 4.5 Write the molecular equation and the net ionic equation for the neutralization of hydrocyanic acid, HCN, by lithium hydroxide, LiOH, both in aqueous solution.

■ See Problems 4.43, 4.44, 4.45, and 4.46.

Acids such as HCl and HNO_3 that have only one acidic hydrogen atom per acid molecule are called *monoprotic* acids. A **polyprotic acid** is *an acid that yields two or more acidic hydrogens per molecule.* Phosphoric acid is an example of a triprotic acid. By reacting this acid with different amounts of a base, you can obtain a series of salts:

$$H_3PO_4(aq) + NaOH(aq) \longrightarrow NaH_2PO_4(aq) + H_2O(l)$$

$$H_3PO_4(aq) + 2NaOH(aq) \longrightarrow Na_2HPO_4(aq) + 2H_2O(l)$$

$$H_3PO_4(aq) + 3NaOH(aq) \longrightarrow Na_3PO_4(aq) + 3H_2O(l)$$

Salts such as NaH_2PO_4 and Na_2HPO_4 that have acidic hydrogen atoms and can undergo neutralization with bases are called *acid salts.*

Exercise 4.6 Write molecular and net ionic equations for the successive neutralizations of each of the acidic hydrogens of sulfuric acid with potassium hydroxide. (That is, write equations for the reaction of sulfuric acid with KOH to give the acid salt and for the reaction of the acid salt with more KOH to give potassium sulfate.)

■ See Problems 4.47, 4.48, 4.49, and 4.50.

Acid–Base Reactions with Gas Formation

Certain salts, notably carbonates, sulfites, and sulfides, react with acids to form a gaseous product. Consider the reaction of sodium carbonate with hydrochloric acid. The molecular equation for the reaction is

$$\underset{\text{carbonate}}{Na_2CO_3(aq)} + \underset{\text{acid}}{2HCl(aq)} \longrightarrow \underset{\text{salt}}{2NaCl(aq)} + H_2O(l) + CO_2(g)$$

FIGURE 4.10

Reaction of a carbonate with an acid
Baking soda (sodium hydrogen carbonate) reacts with acetic acid in vinegar to evolve bubbles of carbon dioxide.

Here, a carbonate (sodium carbonate) reacts with an acid (hydrochloric acid) to produce a salt (sodium chloride), water, and carbon dioxide gas. A similar reaction is shown in Figure 4.10, in which baking soda (sodium hydrogen carbonate) reacts with the acetic acid in vinegar. Note the bubbles of carbon dioxide gas that evolve during the reaction. This reaction of a carbonate with an acid is the basis of a simple test for carbonate minerals. When you treat a carbonate mineral or rock, such as limestone, with hydrochloric acid, the material fizzes, as bubbles of odorless carbon dioxide form.

It is useful to consider the preceding reaction as an exchange, or metathesis, reaction. Recall that in an exchange reaction, you obtain the products from the reactants by exchanging the anions (or the cations) between the two reactants. In this case, we interchange the carbonate ion with the chloride ion and we obtain the following:

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

The last product shown in the equation is carbonic acid, H_2CO_3. (You obtain the formula of carbonic acid by noting that you need to associate two H^+ ions with the carbonate ion, CO_3^{2-}, to obtain a neutral compound.) Carbonic acid is unstable and decomposes to water and carbon dioxide gas. The overall result is the equation we wrote earlier:

$$Na_2CO_3(aq) + 2HCl(aq) \longrightarrow 2NaCl(aq) + \underbrace{H_2O(l) + CO_2(g)}_{H_2CO_3(aq)}$$

The net ionic equation for this reaction is

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

The carbonate ion reacts with hydrogen ion from the acid. If you write the hydrogen ion as H_3O^+ (hydronium ion), you can see also that the reaction involves a proton transfer:

$$\overset{2H^+}{}$$
$$CO_3^{2-}(aq) + 2H_3O^+(aq) \longrightarrow H_2CO_3(aq) + 2H_2O(l) \longrightarrow 3H_2O(l) + CO_2(g)$$

From the broader perspective of the Brønsted–Lowry view, this is an acid–base reaction.

Sulfites behave similarly to carbonates. When a sulfite, such as sodium sulfite (Na_2SO_3), reacts with an acid, sulfur dioxide (SO_2) is a product. Sulfides, such as sodium sulfide (Na_2S), react with acids to produce hydrogen sulfide gas. The reaction can be viewed as a simple exchange reaction. The reactions are summarized in Table 4.4. <

CO_3^{2-}, S^{2-}, and SO_3^{2-} are bases. Thus the net equations involve a basic anion with H^+, an acid.

TABLE 4.4 Some Ionic Compounds That Evolve Gases When Treated with Acids

Ionic Compound	Gas	Example
Carbonate (CO_3^{2-})	CO_2	$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$
Sulfite (SO_3^{2-})	SO_2	$Na_2SO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2$
Sulfide (S^{2-})	H_2S	$Na_2S + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S$

Example 4.6 Writing an Equation for a Reaction with Gas Formation

Write the molecular equation and the net ionic equation for the reaction of zinc sulfide with hydrochloric acid.

Problem Strategy Start by writing the reactants, using the solubility rules to determine the phase labels. Next think about the ways in which this reaction can occur; first try to write it as an exchange reaction. Examine the products to see whether an insoluble compound forms and/or there is gas formation; either indicates a reaction.

Solution First write the reactants, noting from Table 4.1 that most sulfides (except those of the group IA metals and $(NH_4)_2S$) are insoluble.

$$ZnS(s) + HCl(aq) \longrightarrow$$

If you look at this as an exchange reaction, the products are $ZnCl_2$ and H_2S. Since chlorides are soluble (with some exceptions, not including $ZnCl_2$), we write the following balanced equation.

$$\mathbf{ZnS(\mathit{s}) + 2HCl(\mathit{aq}) \longrightarrow ZnCl_2(\mathit{aq}) + H_2S(\mathit{g})}$$

The complete ionic equation is

$$ZnS(s) + 2H^+(aq) + \cancel{2Cl^-(aq)} \longrightarrow Zn^{2+}(aq) + \cancel{2Cl^-(aq)} + H_2S(g)$$

and the net ionic equation is

$$\mathbf{ZnS(\mathit{s}) + 2H^+(\mathit{aq}) \longrightarrow Zn^{2+}(\mathit{aq}) + H_2S(\mathit{g})}$$

Answer Check When you are trying to solve problems of this type, if starting with an exchange reaction doesn't yield the desired results, use the examples in Table 4.4 as a guide.

Exercise 4.7 Write the molecular equation and the net ionic equation for the reaction of calcium carbonate with nitric acid.

■ See Problems 4.51, 4.52, 4.53, and 4.54.

Concept Check 4.3

At times, we want to generalize the formula of certain important chemical substances; acids and bases fall into this category. Given the following reactions, try to identify the acids, bases, and some examples of what the general symbols (M and A^-) represent.

a. $MOH(s) \longrightarrow M^+(aq) + OH^-(aq)$
b. $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$
c. $H_2A(aq) + 2H_2O(l) \rightleftharpoons H_3O^+(aq) + HA^-(aq)$
d. For parts a through c, come up with real examples for M and A.

4.5 Oxidation–Reduction Reactions

In the two preceding sections, we described precipitation reactions (reactions producing a precipitate) and acid–base reactions (reactions involving proton transfer). Here we discuss the third major class of reactions, oxidation–reduction reactions, which are reactions involving a transfer of electrons from one species to another.

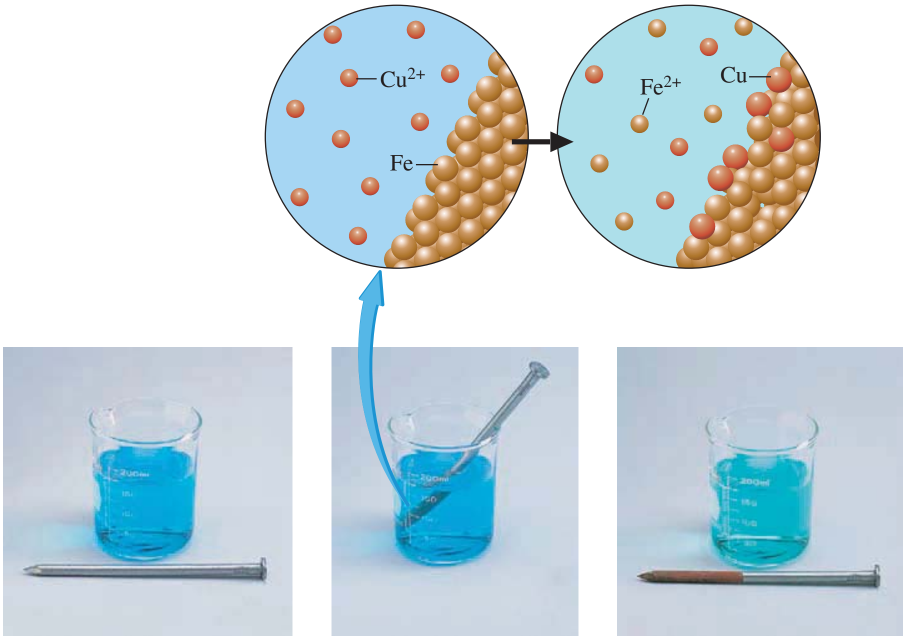


FIGURE 4.11

Reaction of iron with $Cu^{2+}(aq)$
Left: Iron nail and copper(II) sulfate solution, which has a blue color. *Center:* Fe reacts with $Cu^{2+}(aq)$ to yield $Fe^{2+}(aq)$ and Cu(*s*). In the molecular view, water and the sulfate anion have been omitted. *Right:* The copper metal plates out on the nail.

As a simple example of an oxidation–reduction reaction, let us look at what happens when you dip an iron nail into a blue solution of copper(II) sulfate (Figure 4.11). What you see is that the iron nail becomes coated with a reddish-brown tinge of metallic copper. The molecular equation for this reaction is

$$Fe(s) + CuSO_4(aq) \longrightarrow FeSO_4(aq) + Cu(s)$$

The net ionic equation is

$$Fe(s) + Cu^{2+}(aq) \longrightarrow Fe^{2+}(aq) + Cu(s)$$

The electron-transfer aspect of the reaction is apparent from this equation. Note that each iron atom in the metal loses two electrons to form an iron(II) ion, and each copper(II) ion gains two electrons to form a copper atom in the metal. The net effect is that two electrons are transferred from each iron atom in the metal to each copper(II) ion.

The concept of *oxidation numbers* was developed as a simple way of keeping track of electrons in a reaction. Using oxidation numbers, you can determine whether electrons have been transferred from one atom to another. If electrons have been transferred, an oxidation–reduction reaction has occurred.

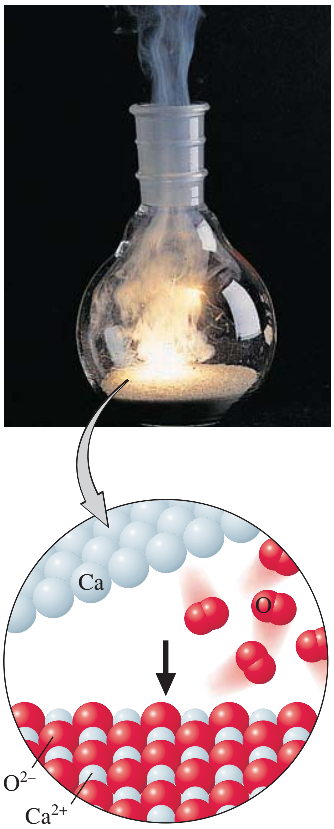


FIGURE 4.12

The burning of calcium metal in oxygen
The burning calcium emits a red-orange flame.

Oxidation Numbers

We define the **oxidation number** (or **oxidation state**) of an atom in a substance as *the actual charge of the atom if it exists as a monatomic ion, or a hypothetical charge assigned to the atom in the substance by simple rules.* An oxidation–reduction reaction is one in which one or more atoms change oxidation number, implying that there has been a transfer of electrons.

Consider the combustion of calcium metal in oxygen gas (Figure 4.12).

$$2Ca(s) + O_2(g) \longrightarrow 2CaO(s)$$

This is an oxidation–reduction reaction. To see this, you assign oxidation numbers to the atoms in the equation and then note that the atoms change oxidation number during the reaction.

Since the oxidation number of an atom in an element is always zero, Ca and O in O_2 have oxidation numbers of zero. Another rule follows from the definition of oxidation number: The oxidation number of an atom that exists in a substance as a monatomic ion equals the charge on that ion. So the oxidation number of Ca in CaO

FIGURE 4.13

The burning of calcium metal in chlorine The reaction appears similar to the burning of calcium in oxygen.

is +2 (the charge on Ca^{2+}), and the oxidation number of O in CaO is −2 (the charge on O^{2-}). To emphasize these oxidation numbers in an equation, we will write them above the atomic symbols in the formulas.

$$2\overset{0}{\mathrm{Ca}}(s) + \overset{0}{\mathrm{O}}_2(g) \longrightarrow 2\overset{+2}{\mathrm{Ca}}\overset{-2}{\mathrm{O}}(s)$$

From this, you see that the Ca and O atoms change in oxidation number during the reaction. In effect, each calcium atom in the metal loses two electrons to form Ca^{2+} ions, and each oxygen atom in O_2 gains two electrons to form O^{2-} ions. The net result is a transfer of electrons from calcium to oxygen, so this reaction is an oxidation–reduction reaction. In other words, an **oxidation–reduction reaction** (or **redox reaction**) is *a reaction in which electrons are transferred between species or in which atoms change oxidation number.*

Note that calcium has gained in oxidation number from 0 to +2. (Each calcium atom loses two electrons.) We say that calcium has been *oxidized.* Oxygen, on the other hand, has decreased in oxidation number from 0 to −2. (Each oxygen atom gains two electrons.) We say that oxygen has been *reduced.* An oxidation–reduction reaction always involves both oxidation (the loss of electrons) and reduction (the gain of electrons).

Formerly, the term *oxidation* meant "reaction with oxygen." The current definition greatly enlarges the meaning of this term. Consider the reaction of calcium metal with chlorine gas (Figure 4.13); the reaction looks similar to the burning of calcium in oxygen. The chemical equation is

$$\overset{0}{\mathrm{Ca}}(s) + \overset{0}{\mathrm{Cl}}_2(g) \longrightarrow \overset{+2}{\mathrm{Ca}}\overset{-1}{\mathrm{Cl}}_2(s)$$

In this reaction, the calcium atom is oxidized, because it increases in oxidation number (from 0 to +2, as in the previous equation). Chlorine is reduced; it decreases in oxidation number from 0 to −1. This is clearly an oxidation–reduction reaction that does not involve oxygen.

Oxidation-Number Rules

So far, we have used two rules for obtaining oxidation numbers: (1) the oxidation number of an atom in an element is zero, and (2) the oxidation number of an atom in a monatomic ion equals the charge on the ion. These and several other rules for assigning oxidation numbers are given in Table 4.5.

TABLE 4.5 Rules for Assigning Oxidation Numbers

Rule	Applies to	Statement
1	Elements	The oxidation number of an atom in an element is zero.
2	Monatomic ions	The oxidation number of an atom in a monatomic ion equals the charge on the ion.
3	Oxygen	The oxidation number of oxygen is −2 in most of its compounds. (An exception is O in H_2O_2 and other peroxides, where the oxidation number is −1.)
4	Hydrogen	The oxidation number of hydrogen is +1 in most of its compounds. (The oxidation number of hydrogen is −1 in binary compounds with a metal, such as CaH_2.)
5	Halogens	The oxidation number of fluorine is −1 in all of its compounds. Each of the other halogens (Cl, Br, I) has an oxidation number of −1 in binary compounds, except when the other element is another halogen above it in the periodic table or the other element is oxygen.
6	Compounds and ions	The sum of the oxidation numbers of the atoms in a compound is zero. The sum of the oxidation numbers of the atoms in a polyatomic ion equals the charge on the ion.

In molecular substances, we use these rules to give the *approximate* charges on the atoms. Consider the molecule SO_2. Oxygen atoms tend to attract electrons, pulling them from other atoms (sulfur in the case of SO_2). As a result, an oxygen atom in SO_2 takes on a negative charge relative to the sulfur atom. The magnitude of the charge on an oxygen atom in a molecule is not a full -2 charge as in the O^{2-} ion. However, it is convenient to assign an oxidation number of -2 to oxygen in SO_2 (and in most other compounds of oxygen) to help us express the approximate charge distribution in the molecule. Rule 3 in Table 4.5 says that an oxygen atom has an oxidation number of -2 in most of its compounds.

Rules 4 and 5 are similar in that they tell you what to expect for the oxidation number of certain elements in their compounds. Rule 4, for instance, says that hydrogen has an oxidation number of $+1$ in most of its compounds.

Rule 6 states that the sum of the oxidation numbers of the atoms in a compound is zero. This rule follows from the interpretation of oxidation numbers as (hypothetical) charges on the atoms. Because any compound is electrically neutral, the sum of the charges on its atoms must be zero. This rule is easily extended to ions: the sum of the oxidation numbers (hypothetical charges) of the atoms in a polyatomic ion equals the charge on the ion.

You can use Rule 6 to obtain the oxidation number of one atom in a compound or ion, if you know the oxidation numbers of the other atoms in the compound or ion. Consider the SO_2 molecule. According to Rule 6,

$$(\text{Oxidation number of S}) + 2 \times (\text{oxidation number of O}) = 0$$

or

$$(\text{Oxidation number of S}) + 2 \times (-2) = 0.$$

Therefore,

$$\text{Oxidation number of S (in } SO_2) = -2 \times (-2) = +4$$

The next example illustrates how to use the rules in Table 4.5 to assign oxidation numbers.

Example 4.7 Assigning Oxidation Numbers

Use the rules from Table 4.5 to obtain the oxidation number of the chlorine atom in each of the following: (a) $HClO_4$ (perchloric acid), (b) ClO_3^- (chlorate ion).

Problem Strategy We need to apply the rules in Table 4.5. Rule 6 is the best place to start. Therefore, in each case, write the expression for the sum of the oxidation numbers, equating this to zero for a compound or to the charge for an ion. Now, use Rules 2 to 5 to substitute oxidation numbers for particular atoms, such as -2 for oxygen and $+1$ for hydrogen, and solve for the unknown oxidation number (Cl in this example).

Solution a. For perchloric acid, Rule 6 gives the equation

$$(\text{Oxidation number of H}) + (\text{oxidation number of Cl}) + 4 \times (\text{oxidation number of O}) = 0$$

Using Rules 3 and 4, you obtain

$$(+1) + (\text{oxidation number of Cl}) + 4 \times (-2) = 0$$

(*continued*)

(continued)

Therefore,

$$\text{Oxidation number of Cl (in } HClO_4) = -(+1) - 4 \times (-2) = \mathbf{+7}$$

b. For the chlorate ion, Rule 6 gives the equation

$$(\text{Oxidation number of Cl}) + 3 \times (\text{oxidation number of O}) = -1$$

Using Rule 3, you obtain

$$(\text{Oxidation number of Cl}) + 3 \times (-2) = -1$$

Therefore,

$$\text{Oxidation number of Cl (in } ClO_3^{\,-}) = -1 - 3 \times (-2) = \mathbf{+5}$$

Answer Check Because most compounds do not have elements with very large positive or very large negative oxidation numbers, you should always be on the alert for a *possible* assignment mistake when you find oxidation states greater than +6 or less than −4. (From this example you see that a +7 oxidation state is possible; however, it occurs in only a limited number of cases.)

Exercise 4.8 Obtain the oxidation numbers of the atoms in each of the following: (a) potassium dichromate, $K_2Cr_2O_7$, (b) permanganate ion, $MnO_4^{\,-}$.

■ See Problems 4.55, 4.56, 4.57, and 4.58.

Describing Oxidation–Reduction Reactions

We use special terminology to describe oxidation–reduction reactions. To illustrate this, we will look again at the reaction of iron with copper(II) sulfate. The net ionic equation is

$$\overset{0}{Fe}(s) + \overset{+2}{Cu}{}^{2+}(aq) \longrightarrow \overset{+2}{Fe}{}^{2+}(aq) + \overset{0}{Cu}(s)$$

We can write this reaction in terms of two half-reactions. A **half-reaction** is *one of two parts of an oxidation–reduction reaction, one part of which involves a loss of electrons (or increase of oxidation number) and the other a gain of electrons (or decrease of oxidation number).* The half-reactions for the preceding equation are

$$\overset{0}{Fe}(s) \longrightarrow \overset{+2}{Fe}{}^{2+}(aq) + 2e^- \qquad \text{(electrons lost by Fe)}$$

$$\overset{+2}{Cu}{}^{2+}(aq) + 2e^- \longrightarrow \overset{0}{Cu}(s) \qquad \text{(electrons gained by } Cu^{2+})$$

Oxidation is *the half-reaction in which there is a loss of electrons by a species (or an increase of oxidation number of an atom).* **Reduction** is *the half-reaction in which there is a gain of electrons by a species (or a decrease in the oxidation number of an atom).* Thus, the equation $Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$ represents the oxidation half-reaction, and the equation $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ represents the reduction half-reaction.

Recall that a species that is *oxidized* loses electrons (or contains an atom that increases in oxidation number) and a species that is *reduced* gains electrons (or contains an atom that decreases in oxidation number). An **oxidizing agent** is *a species that oxidizes another species; it is itself reduced.* Similarly, a **reducing agent** is *a species that reduces another species; it is itself oxidized.* In our example reaction, the copper(II) ion is the oxidizing agent, whereas iron metal is the reducing agent.

The relationships among these terms are shown in the following diagram for the reaction of iron with copper(II) ion.

oxidation

$$\underset{\text{reducing agent}}{\overset{0}{\mathrm{Fe}(s)}} + \underset{\text{oxidizing agent}}{\overset{+2}{\mathrm{Cu}^{2+}(aq)}} \longrightarrow \overset{+2}{\mathrm{Fe}^{2+}(aq)} + \overset{0}{\mathrm{Cu}(s)}$$

reduction

Some Common Oxidation–Reduction Reactions

Many oxidation–reduction reactions can be described as one of the following:

1. Combination reaction
2. Decomposition reaction
3. Displacement reaction
4. Combustion reaction

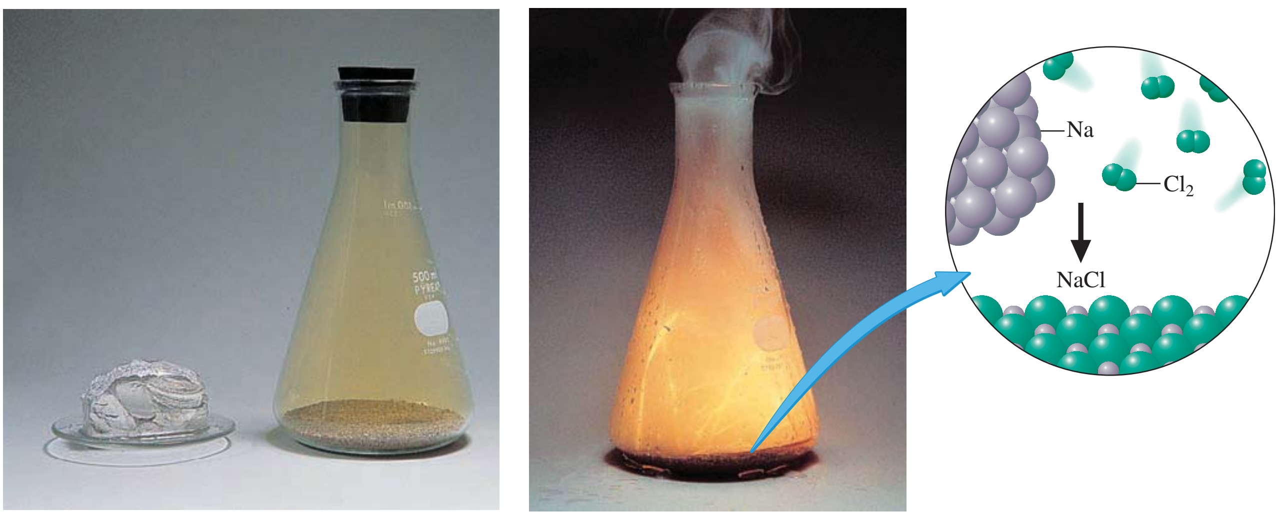
We will describe examples of each of these in this section.

Combination Reactions A **combination reaction** is *a reaction in which two substances combine to form a third substance.* Note that not all combination reactions are oxidation–reduction reactions. However, the simplest cases are those in which two elements react to form a compound; these are clearly oxidation–reduction reactions. In Chapter 2, we discussed the reaction of sodium metal and chlorine gas, which is a redox reaction (Figure 4.14).

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

FIGURE 4.14

Combination reaction
Left: Sodium metal and chlorine gas.
Right: The spectacular combination reaction of sodium and chlorine.



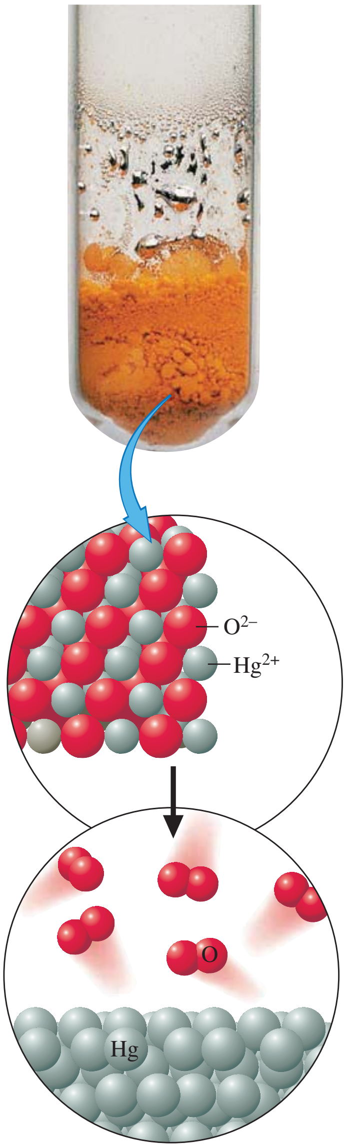


FIGURE 4.15

Decomposition reaction
The decomposition reaction of mercury(II) oxide into its elements, mercury and oxygen.

Antimony and chlorine also combine in a fiery reaction.

$$2Sb + 3Cl_2 \longrightarrow 2SbCl_3$$

Some combination reactions involve compounds as reactants and are not oxidation–reduction reactions. For example,

$$CaO(s) + SO_2(g) \longrightarrow CaSO_3(s)$$

(If you check the oxidation numbers, you will see that this is not an oxidation–reduction reaction.)

Decomposition Reactions A **decomposition reaction** is *a reaction in which a single compound reacts to give two or more substances.* Often these reactions occur when the temperature is raised. In Chapter 1, we described the decomposition of mercury(II) oxide into its elements when the compound is heated (Figure 4.15). This is an oxidation–reduction reaction.

$$2HgO(s) \xrightarrow{\Delta} 2Hg(l) + O_2(g)$$

Another example is the preparation of oxygen by heating potassium chlorate with manganese(IV) oxide as a catalyst.

$$2KClO_3(s) \xrightarrow[MnO_2]{\Delta} 2KCl(s) + 3O_2(g)$$

In this reaction, a compound decomposes into another compound and an element; it also is an oxidation–reduction reaction.

Not all decomposition reactions are of the oxidation–reduction type. For example, calcium carbonate at high temperatures decomposes into calcium oxide and carbon dioxide.

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$$

Is there a change in oxidation numbers? If not, this confirms that this is not an oxidation–reduction reaction.

Displacement Reactions A **displacement reaction** (also called a **single-replacement reaction**) is *a reaction in which an element reacts with a compound, displacing another element from it.* Since these reactions involve an element and one of its compounds, these must be oxidation–reduction reactions. An example is the reaction that occurs when you dip a copper metal strip into a solution of silver nitrate.

$$Cu(s) + 2AgNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2Ag(s)$$

From the molecular equation, it appears that copper displaces silver in silver nitrate, producing crystals of silver metal and a greenish-blue solution of copper(II) nitrate. The net ionic equation, however, shows that the reaction involves the transfer of electrons from copper metal to silver ion:

$$Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$$

When you dip a zinc metal strip into an acid solution, bubbles of hydrogen form on the metal and escape from the solution (Figure 4.16).

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

Zinc displaces hydrogen in the acid, producing zinc chloride solution and hydrogen gas. The net ionic equation is

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

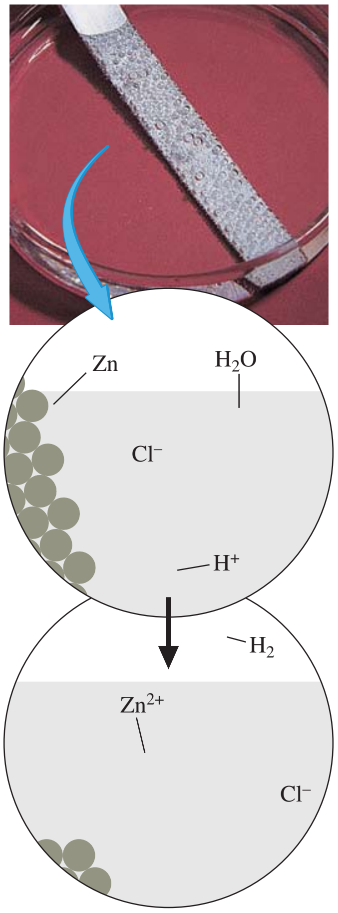


FIGURE 4.16

Displacement reaction

Displacement reaction of zinc metal and hydrochloric acid. Hydrogen gas formed in the reaction bubbles from the metal surface that dips into the acid.

Whether a reaction occurs between a given element and a monatomic ion depends on the relative ease with which the two species gain or lose electrons. Table 4.6 shows the activity series of the elements, a listing of the elements in decreasing order of their ease of losing electrons during reactions in aqueous solution. The metals listed at the top are the strongest reducing agents (they lose electrons easily); those at the bottom, the weakest. A free element reacts with the monatomic ion of another element if the free element is above the other element in the activity series. The highlighted elements react slowly with liquid water, but readily with steam, to give H_2.

Consider this reaction:

$$2K(s) + 2H^+(aq) \longrightarrow 2K^+(aq) + H_2(g)$$

You would expect this reaction to proceed as written, because potassium metal (K) is well above hydrogen in the activity series. In fact, potassium metal reacts violently with water, which contains only a very small percentage of H^+ ions. Imagine the reaction of potassium metal with a strong acid like HCl!

TABLE 4.6 Activity Series of the Elements

React vigorously with acidic solutions and water to give H_2	Li
	K
	Ba
	Ca
	Na
React with acids to give H_2	Mg
	Al
	Zn
	Cr
	Fe
	Cd
	Co
	Ni
	Sn
	Pb
	H_2
Do not react with acids to give H_2*	Cu
	Hg
	Ag
	Au

*Cu, Hg, and Ag react with HNO_3 but do not produce H_2. In these reactions, the metal is oxidized to the metal ion, and NO_3^- ion is reduced to NO_2 or other nitrogen species.

Combustion Reactions A **combustion reaction** is *a reaction in which a substance reacts with oxygen, usually with the rapid release of heat to produce a flame.* The products include one or more oxides. Oxygen changes oxidation number from 0 to −2, so combustions are oxidation–reduction reactions.

Organic compounds usually burn in oxygen or air to yield carbon dioxide. If the compound contains hydrogen (as most do), water is also a product. For instance, butane (C_4H_{10}) burns in air as follows:

$$2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(g)$$

Many metals burn in air as well. Although chunks of iron do not burn readily in air, iron wool, which consists of fine strands of iron, does (Figure 4.17 on page 152). The increased surface area of the metal in iron wool allows oxygen from air to react quickly with it.

$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$$

4.6 Balancing Simple Oxidation–Reduction Equations

Balancing equations was discussed in Section 2.10.

Oxidation–reduction reactions can often be quite difficult to balance. < Some are so complex in fact that chemists have written computer programs to accomplish the task. In this section, we will develop a method for balancing simple oxidation–reduction

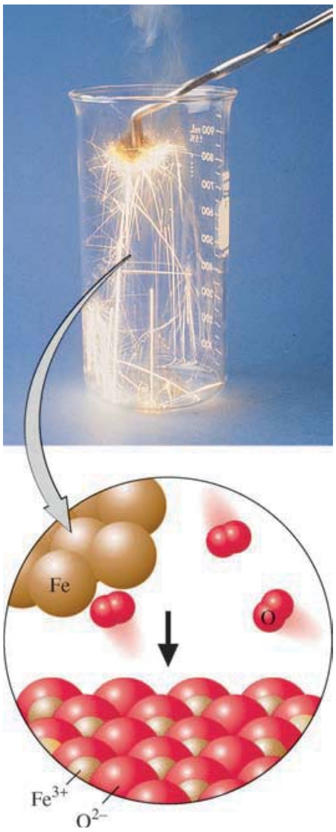


FIGURE 4.17

The combustion of iron wool
Iron reacts with oxygen in the air to produce iron(III) oxide, Fe_2O_3. The reaction is similar to the rusting of iron but is much faster.

reactions that can later be generalized for far more complex reactions. One of the advantages of using this technique for even simple reactions is that you focus on what makes oxidation–reduction reactions different from other reaction types. See Chapter 19 for a comprehensive treatment of this topic.

At first glance, the equation representing the reaction of zinc metal with silver(I) ions in solution might appear to be balanced.

$$Zn(s) + Ag^+(aq) \longrightarrow Zn^{2+}(aq) + Ag(s)$$

However, because a balanced chemical equation must have a charge balance as well as a mass balance, this equation is not balanced: it has a total charge of +1 for the reactants and +2 for the products. Let us apply the half-reaction method for balancing this equation.

Half-Reaction Method Applied to Simple Oxidation–Reduction Equations

The *half-reaction method* consists of first separating the equation into two half-reactions, one for oxidation, the other for reduction. You balance each half-reaction, then combine them to obtain a balanced oxidation–reduction reaction. Here is an illustration of the process. First we identify the species being oxidized and reduced and assign the appropriate oxidation states.

$$\overset{0}{Zn}(s) + \overset{+1}{Ag^+}(aq) \longrightarrow \overset{+2}{Zn^{2+}}(aq) + \overset{0}{Ag}(s)$$

Next, write the half-reactions in an unbalanced form.

$$Zn \longrightarrow Zn^{2+} \qquad \text{(oxidation)}$$

$$Ag^+ \longrightarrow Ag \qquad \text{(reduction)}$$

Next, balance the charge in each equation by adding electrons to the more positive side to create balanced half-reactions. Following this procedure, the balanced half-reactions are:

$$Zn \longrightarrow Zn^{2+} + 2e^- \qquad \text{(oxidation half-reaction)}$$

$$Ag^+ + e^- \longrightarrow Ag \qquad \text{(reduction half-reaction)}$$

Note that the number of electrons that Zn loses during the oxidation process (two) exceeds the number of electrons gained by Ag^+ during the reduction (one). Since, according to the reduction half-reaction, each Ag^+ is capable of gaining only one electron, we need to double the amount of Ag^+ in order for it to accept all of the electrons produced by Zn during oxidation. To meet this goal and obtain the balanced oxidation–reduction reaction, we multiply each half-reaction by a factor (integer) so that when we add them together, the electrons cancel. We multiply the first equation by 1 (the number of electrons in the second half-reaction) and multiply the second equation by 2 (the number of electrons in the first half-reaction).

$$\begin{array}{r} 1 \times (Zn \longrightarrow Zn^{2+} + 2e^-) \\ 2 \times (Ag^+ + e^- \longrightarrow Ag) \\ \hline Zn + 2Ag^+ + \cancel{2e^-} \longrightarrow Zn^{2+} + 2Ag + \cancel{2e^-} \end{array}$$

The electrons cancel, which finally yields the balanced oxidation–reduction equation:

$$Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$$

Example 4.8 further illustrates this technique.

Example 4.8 Balancing Simple Oxidation–Reduction Reactions by the Half-Reaction Method

Consider a more difficult problem, the combination (oxidation–reduction) reaction of magnesium metal and nitrogen gas:

$$Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)$$

Apply the half-reaction method to balance this equation.

Problem Strategy Start by identifying the species undergoing oxidation and reduction and assigning oxidation numbers. Then write the two balanced half-reactions, keeping in mind that you add the electrons to the more positive side of the reaction. Next, multiply each of the half-reactions by a whole number that will cancel the electrons on each side of the equation. Finally, add the half-reactions together to yield the balanced equation.

Solution Identify the oxidation states of the elements:

$$\overset{0}{Mg}(s) + \overset{0}{N_2}(g) \longrightarrow \overset{+2}{Mg_3}\overset{-3}{N_2}(s)$$

In this problem, a molecular compound, nitrogen (N_2), is undergoing reduction. When a species undergoing reduction or oxidation is a molecule, write the formula of the molecule (do not split it up) in the half-reaction. Also, make sure that both the mass and the charge are balanced. (Note the $6e^-$ required to balance the charge due to the $2N^{3-}$.)

$$Mg \longrightarrow Mg^{2+} + 2e^- \qquad \text{(balanced oxidation half-reaction)}$$

$$N_2 + 6e^- \longrightarrow 2N^{3-} \qquad \text{(balanced reduction half-reaction)}$$

We now need to multiply each half-reaction by a factor that will cancel the electrons.

$$\begin{array}{r} 3 \times (Mg \longrightarrow Mg^{2+} + 2e^-) \\ 1 \times (N_2 + 6e^- \longrightarrow 2N^{3-}) \\ \hline 3Mg + N_2 + \cancel{6e^-} \longrightarrow 3Mg^{2+} + 2N^{3-} + \cancel{6e^-} \end{array}$$

Therefore, the balanced combination (oxidation–reduction) reaction is

$$\mathbf{3Mg + N_2 \longrightarrow 3Mg^{2+} + 2N^{3-}}$$

From inspecting the coefficients in this reaction, looking at the original equation, and knowing that Mg^{2+} and N^{3-} will combine to form an ionic compound (Mg_3N_2), we can rewrite the equation in the following form:

$$3Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)$$

Answer Check Do a final check for balance by counting the number of atoms of each element on both sides of the equation.

Exercise 4.9 Use the half-reaction method to balance the equation $Ca(s) + Cl_2(g) \longrightarrow CaCl_2(s)$.

■ See Problems 4.65 and 4.66.

Working with Solutions

The majority of the chemical reactions discussed in this chapter take place in solution. This is because the reaction between two solid reactants often proceeds very slowly or not at all. In a solid, the molecules or ions in a crystal tend to occupy approximately fixed positions, so the chance of two molecules or ions coming together to react is small. In liquid solutions, reactant molecules are free to move throughout the liquid; therefore, reaction is much faster. When you run reactions in liquid solutions, it is convenient to dispense the amounts of reactants by measuring out volumes of reactant solutions. In the next two sections, we will discuss calculations involved in making up solutions, and in Section 4.10 we will describe stoichiometric calculations involving such solutions.

4.7 Molar Concentration

When we dissolve a substance in a liquid, we call the substance the *solute* and the liquid the *solvent.* Consider ammonia solutions. Ammonia gas dissolves readily in water, and aqueous ammonia solutions are often used in the laboratory. In such solutions, ammonia gas is the solute and water is the solvent.

The general term *concentration* refers to the quantity of solute in a standard quantity of solution. Qualitatively, we say that a solution is *dilute* when the solute concentration is low and *concentrated* when the solute concentration is high. Usually these terms are used in a comparative sense and do not refer to a specific concentration. We say that one solution is more dilute, or less concentrated, than another. However, for commercially available solutions, the term *concentrated* refers to the maximum, or near maximum, concentration available. For example, concentrated aqueous ammonia contains about 28% NH_3 by mass.

In this example, we expressed the concentration quantitatively by giving the mass percentage of solute—that is, the mass of solute in 100 g of solution. However, we need a unit of concentration that is convenient for dispensing reactants in solution, such as one that specifies moles of solute per solution volume.

Molar concentration, or **molarity (*M*),** is defined as *the moles of solute dissolved in one liter (cubic decimeter) of solution.*

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

An aqueous solution that is 0.15 *M* NH_3 (read this as "0.15 molar NH_3") contains 0.15 mol NH_3 per liter of solution. If you want to prepare a solution that is, for example, 0.200 *M* $CuSO_4$, you place 0.200 mol $CuSO_4$ in a 1.000-L volumetric flask, or a proportional amount in a flask of a different size (Figure 4.18). You add a small quantity of water to dissolve the $CuSO_4$. Then you fill the flask with additional water to the mark on the neck and mix the solution. The following example shows how to calculate the molarity of a solution given the mass of solute and the volume of solution.

Example 4.9 Calculating Molarity from Mass and Volume

A sample of $NaNO_3$ weighing 0.38 g is placed in a 50.0 mL volumetric flask. The flask is then filled with water to the mark on the neck, dissolving the solid. What is the molarity of the resulting solution?

Problem Strategy To calculate the molarity, you need the moles of solute. Therefore, you first convert grams $NaNO_3$ to moles. The molarity equals the moles of solute divided by the liters of solution.

(*continued*)

FIGURE 4.18

Preparing a 0.200 *M* $CuSO_4$ solution
Left: 0.0500 mol $CuSO_4 \cdot 5H_2O$ (12.48 g) is weighed on a platform balance. *Center:* The copper(II) sulfate pentahydrate is transferred carefully to the volumetric flask. *Right:* Water is added to bring the solution level to the mark on the neck of the 250-mL volumetric flask. The molarity is 0.0500 mol/0.250 L = 0.200 *M*.

(*continued*)

Solution You find that 0.38 g $NaNO_3$ is $4.\underline{4}7 \times 10^{-3}$ mol $NaNO_3$; the last significant figure is underlined. The volume of solution is 50.0 mL, or 50.0×10^{-3} L, so the molarity is

$$\text{Molarity} = \frac{4.\underline{4}7 \times 10^{-3}\ \text{mol NaNO}_3}{50.0 \times 10^{-3}\ \text{L soln}} = \mathbf{0.089\ \mathit{M}\ NaNO_3}$$

Answer Check Although very dilute solutions are possible, there is a limit as to how concentrated solutions can be. Therefore, any answer that leads to solution concentrations that are in excess of 20 *M* should be suspect.

Exercise 4.10 A sample of sodium chloride, NaCl, weighing 0.0678 g is placed in a 25.0-mL volumetric flask. Enough water is added to dissolve the NaCl, and then the flask is filled to the mark with water and carefully shaken to mix the contents. What is the molarity of the resulting solution?

■ See Problems 4.67, 4.68, 4.69, and 4.70.

The advantage of molarity as a concentration unit is that the amount of solute is related to the volume of solution. Rather than having to weigh out a specified mass of substance, you can instead measure out a definite volume of solution of the substance, which is usually easier. As the following example illustrates, molarity can be used as a factor for converting from moles of solute to liters of solution, and vice versa.

Example 4.10 Using Molarity as a Conversion Factor

An experiment calls for the addition to a reaction vessel of 0.184 g of sodium hydroxide, NaOH, in aqueous solution. How many milliliters of 0.150 *M* NaOH should be added?

Problem Strategy Because molarity relates moles of solute to volume of solution, you first need to convert grams of NaOH to moles of NaOH. Then, you can convert moles NaOH

(*continued*)

(continued)

to liters of solution, using the molarity as a conversion factor. Here, 0.150 *M* means that 1 L of solution contains 0.150 moles of solute, so the conversion factor is

$$\underbrace{\frac{1 \text{ L soln}}{0.150 \text{ mol NaOH}}}_{\substack{\text{Converts} \\ \text{mol NaOH to L soln}}}$$

Solution Here is the calculation. (The molar mass of NaOH is 40.0 g/mol.)

$$0.184 \cancel{\text{g NaOH}} \times \frac{1 \cancel{\text{mol NaOH}}}{40.0 \cancel{\text{g NaOH}}} \times \frac{1 \text{ L soln}}{0.150 \cancel{\text{mol NaOH}}} = 3.07 \times 10^{-2} \text{ L soln (or 30.7 mL)}$$

You need to add **30.7 mL** of 0.150 *M* NaOH solution to the reaction vessel.

Answer Check Note that the mass of NaOH required for the experiment is relatively small. Because of this, you should not expect that a large volume of the 0.150 *M* NaOH solution will be required.

Exercise 4.11 How many milliliters of 0.163 *M* NaCl are required to give 0.0958 g of sodium chloride?

■ See Problems 4.71, 4.72, 4.73, and 4.74.

Exercise 4.12 How many moles of sodium chloride should be put in a 50.0-mL volumetric flask to give a 0.15 *M* NaCl solution when the flask is filled to the mark with water? How many grams of NaCl is this?

■ See Problems 4.75, 4.76, 4.77, and 4.78.

4.8 Diluting Solutions

Commercially available aqueous ammonia (28.0% NH_3) is 14.8 *M* NH_3. Suppose, however, that you want a solution that is 1.00 *M* NH_3. You need to dilute the concentrated solution with a definite quantity of water. For this purpose, you must know the relationship between the molarity of the solution before dilution (the *initial molarity*) and that after dilution (the *final molarity*).

To obtain this relationship, first recall the equation defining molarity:

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

You can rearrange this to give

$$\text{Moles of solute} = \text{molarity} \times \text{liters of solution}$$

The product of molarity and the volume (in liters) gives the moles of solute in the solution. Writing M_i for the initial molar concentration and V_i for the initial volume of solution, you get

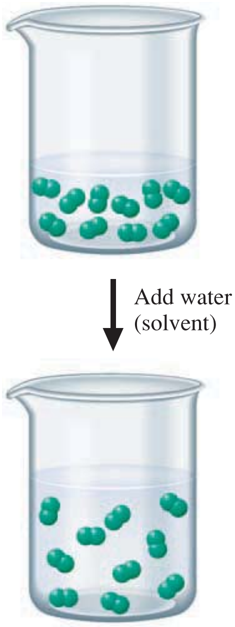
$$\text{Moles of solute} = M_i \times V_i$$

When the solution is diluted by adding more water, the concentration and volume change to M_f (the final molar concentration) and V_f (the final volume), and the moles of solute equals

$$\text{Moles of solute} = M_f \times V_f$$

FIGURE 4.19

Molecular view of the dilution process
Top: A molecular view of a solution of Cl_2 dissolved in water. *Bottom:* The solution after performing a dilution by adding water. Note how the number of moles of Cl_2 in the container does not change when performing the dilution; only the concentration changes. In this particular case, the concentration of Cl_2 drops to half of the starting concentration because the volume was doubled.



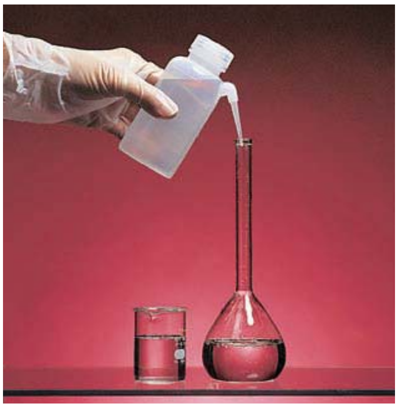


FIGURE 4.20

Preparing a solution by diluting a concentrated one
A volume of concentrated ammonia, similar to the one in the beaker, has been added to the volumetric flask. Here water is being added from the plastic squeeze bottle to bring the volume up to the mark on the flask.

Because the moles of solute has not changed during the dilution (Figure 4.19),

$$M_i \times V_i = M_f \times V_f$$

(Note: You can use any volume units, but both V_i and V_f must be in the same units.)

The next example illustrates how you can use this formula to find the volume of a concentrated solution needed to prepare a given volume of dilute solution.

Example 4.11 Diluting a Solution

You are given a solution of 14.8 M NH_3. How many milliliters of this solution do you require to give 100.0 mL of 1.00 M NH_3 when diluted (Figure 4.20)?

Problem Strategy Because this problem is a dilution, you can use the dilution formula. In this case you want to know the initial volume (V_i) of the solution that you are going to dilute; all of the other quantities needed for the formula are given in the problem.

Solution You know the final volume (100.0 mL), final concentration (1.00 M), and initial concentration (14.8 M). You write the dilution formula and rearrange it to give the initial volume.

$$M_iV_i = M_fV_f$$

$$V_i = \frac{M_fV_f}{M_i}$$

Now you substitute the known values into the right side of the equation.

$$V_i = \frac{1.00\ \cancel{M} \times 100.0\ \text{mL}}{14.8\ \cancel{M}} = \mathbf{6.76\ mL}$$

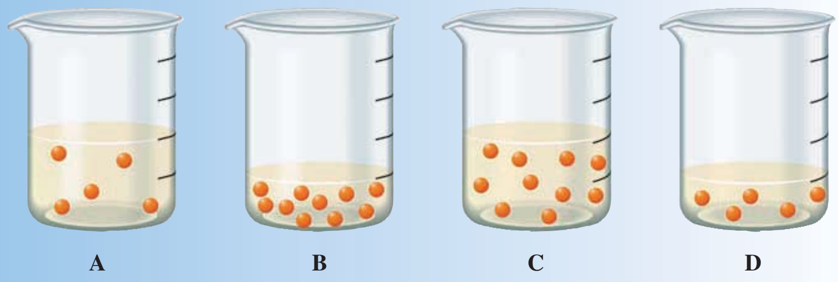
Answer Check When you perform a dilution, the volume of the more concentrated solution should always be less than the volume of the final solution, as it is in the photo. Related to this concept is the fact that the initial concentration of a solution is always greater than the final concentration after dilution. These two concepts will enable you to check the reasonableness of your calculated quantities whenever you use the dilution equation.

Exercise 4.13 You have a solution that is 1.5 M H_2SO_4 (sulfuric acid). How many milliliters of this acid do you need to prepare 100.0 mL of 0.18 M H_2SO_4?

■ See Problems 4.79 and 4.80.

Concept Check 4.4

Consider the following beakers. Each contains a solution of the hypothetical atom X.



a. Arrange the beakers in order of increasing concentration of X.

b. Without adding or removing X, what specific things could you do to make the concentrations of X equal in each beaker? (*Hint:* Think about dilutions.)

Quantitative Analysis

Analytical chemistry deals with the determination of composition of materials—that is, the analysis of materials. The materials that one might analyze include air, water, food, hair, body fluids, pharmaceutical preparations, and so forth. The analysis of materials is divided into qualitative and quantitative analysis. *Qualitative analysis* involves the identification of substances or species present in a material. For instance, you might determine that a sample of water contains lead(II) ion. **Quantitative analysis,** which we will discuss in the last sections of this chapter, involves *the determination of the amount of a substance or species present in a material.* In a quantitative analysis, you might determine that the amount of lead(II) ion in a sample of water is 0.067 mg/L.

4.9 Gravimetric Analysis

Gravimetric analysis is *a type of quantitative analysis in which the amount of a species in a material is determined by converting the species to a product that can be isolated completely and weighed.* Precipitation reactions are frequently used in gravimetric analyses. In these reactions, you determine the amount of an ionic species by precipitating it from solution. The precipitate, or solid formed in the reaction, is then filtered from the solution, dried, and weighed. The advantages of a gravimetric analysis are its simplicity (at least in theory) and its accuracy. The chief disadvantage is that it requires meticulous, time-consuming work. Because of this, whenever possible, chemists use modern instrumental methods.

As an example of a gravimetric analysis, consider the problem of determining the amount of lead in a sample of drinking water. Lead, if it occurs in the water, probably exists as the lead(II) ion, Pb^{2+}. Lead(II) sulfate is a very insoluble compound of lead(II) ion. When sodium sulfate, Na_2SO_4, is added to a solution containing Pb^{2+}, lead(II) sulfate precipitates (that is, $PbSO_4$ comes out of the solution as a fine, crystalline solid). If you assume that the lead is present in solution as lead(II) nitrate, you can write the following equation for the reaction:

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

You can separate the white precipitate of lead(II) sulfate from the solution by filtration. Then you dry and weigh the precipitate. Figure 4.21 shows the laboratory setup used in a similar analysis.

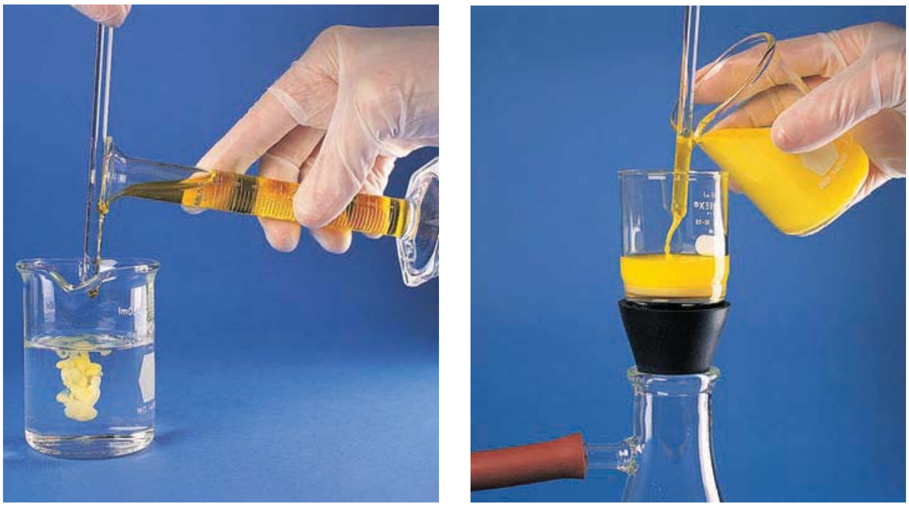


FIGURE 4.21

Gravimetric analysis for barium ion
Left: A solution of potassium chromate (yellow) is poured down a stirring rod into a solution containing an unknown amount of barium ion, Ba^{2+}. The yellow precipitate that forms is barium chromate, $BaCrO_4$. *Right:* The solution is filtered by pouring it into a crucible containing a porous glass partition. Afterward, the crucible is heated to dry the barium chromate. By weighing the crucible before and afterward, you can determine the mass of precipitate.

Example 4.12 Determining the Amount of a Species by Gravimetric Analysis

A 1.000-L sample of polluted water was analyzed for lead(II) ion, Pb^{2+}, by adding an excess of sodium sulfate to it. The mass of lead(II) sulfate that precipitated was 229.8 mg. What is the mass of lead in a liter of the water? Give the answer as milligrams of lead per liter of solution.

Problem Strategy Because an excess of sodium sulfate was added to the solution, you can expect that all of the lead is precipitated as lead(II) sulfate, $PbSO_4$. If you determine the percentage of lead in the $PbSO_4$ precipitate, you can calculate the quantity of lead in the water sample.

Solution Following Example 3.7, you obtain the mass percentage of Pb in $PbSO_4$ by dividing the molar mass of Pb by the molar mass of $PbSO_4$, then multiplying by 100%:

$$\%\ \text{Pb} = \frac{207.2\ \text{g/mol}}{303.3\ \text{g/mol}} \times 100\% = 68.32\%$$

Therefore, the 1.000-L sample of water contains

$$\text{Amount Pb in sample} = 229.8\ \text{mg PbSO}_4 \times 0.6832 = 157.0\ \text{mg Pb}$$

The water sample contains **157.0 mg Pb per liter.**

Answer Check Check to make sure that the mass of the element of interest, 157.0 mg Pb in this case, is less than the total mass of the precipitate, 229.8 mg in this case. If you do not find this to be true, you have made an error.

Exercise 4.14 You are given a sample of limestone, which is mostly $CaCO_3$, to determine the mass percentage of Ca in the rock. You dissolve the limestone in hydrochloric acid, which gives a solution of calcium chloride. Then you precipitate the calcium ion in solution by adding sodium oxalate, $Na_2C_2O_4$. The precipitate is calcium oxalate, CaC_2O_4. You find that a sample of limestone weighing 128.3 mg gives 140.2 mg of CaC_2O_4. What is the mass percentage of calcium in the limestone?

■ See Problems 4.83 and 4.84.

4.10 Volumetric Analysis

As you saw earlier, you can use molarity as a conversion factor, and in this way you can calculate the volume of solution that is equivalent to a given mass of solute (see Example 4.10). This means that you can replace mass measurements in solution reactions by volume measurements. In the next example, we look at the volumes of solutions involved in a given reaction.

Example 4.13 Calculating the Volume of Reactant Solution Needed

Consider the reaction of sulfuric acid, H_2SO_4, with sodium hydroxide, NaOH.

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

Suppose a beaker contains 35.0 mL of 0.175 *M* H_2SO_4. How many milliliters of 0.250 *M* NaOH must be added to react completely with the sulfuric acid?

Problem Strategy This is a stoichiometry problem that involves the reaction of sulfuric acid and sodium hydroxide. You have a known volume and concentration of H_2SO_4 in the beaker, and you want to determine what volume of a known concentration of NaOH is required for complete reaction. If you can determine the number of moles of H_2SO_4 that are contained in the beaker, you can then use the balanced chemical reaction to determine the number of moles of NaOH required to react completely with the H_2SO_4. Finally, you can use the concentration of the NaOH to determine the required volume of NaOH. Following this strategy, you convert from 35.0 mL (or 35.0×10^{-3} L) H_2SO_4 solution to moles H_2SO_4 (using the molarity of H_2SO_4), then to moles NaOH (from the chemical equation). Finally, you convert this to volume of NaOH solution (using the molarity of NaOH).

Solution The calculation is as follows:

$$35.0 \times 10^{-3}\ \cancel{\text{L H}_2\text{SO}_4\text{ soln}} \times \frac{0.175\ \cancel{\text{mol H}_2\text{SO}_4}}{1\ \cancel{\text{L H}_2\text{SO}_4\text{ soln}}} \times \frac{2\ \cancel{\text{mol NaOH}}}{1\ \cancel{\text{mol H}_2\text{SO}_4}} \times$$
$$\frac{1\text{ L NaOH soln}}{0.250\ \cancel{\text{mol NaOH}}} = 4.90 \times 10^{-2}\text{ L NaOH soln (or 49.0 mL NaOH soln)}$$

Thus, 35.0 mL of 0.175 *M* sulfuric acid solution reacts with exactly **49.0 mL** of 0.250 *M* sodium hydroxide solution.

Answer Check Whenever you perform a titration calculation, be sure that you have taken into account the stoichiometry of the reaction between the acid and base (use the balanced chemical equation). In this case, two moles of NaOH are required to neutralize each mole of acid. Furthermore, when performing titration calculations, do not be tempted to apply the dilution equation to solve the problem. If you were to take such an approach here, you would arrive at an incorrect result since the dilution equation fails to take into account the stoichiometry of the reaction.

Exercise 4.15 Nickel sulfate, $NiSO_4$, reacts with sodium phosphate, Na_3PO_4, to give a pale yellow-green precipitate of nickel phosphate, $Ni_3(PO_4)_2$, and a solution of sodium sulfate, Na_2SO_4.

$$3NiSO_4(aq) + 2Na_3PO_4(aq) \longrightarrow Ni_3(PO_4)_2(s) + 3Na_2SO_4(aq)$$

How many milliliters of 0.375 *M* $NiSO_4$ will react with 45.7 mL of 0.265 *M* Na_3PO_4?

■ See Problems 4.89 and 4.90.

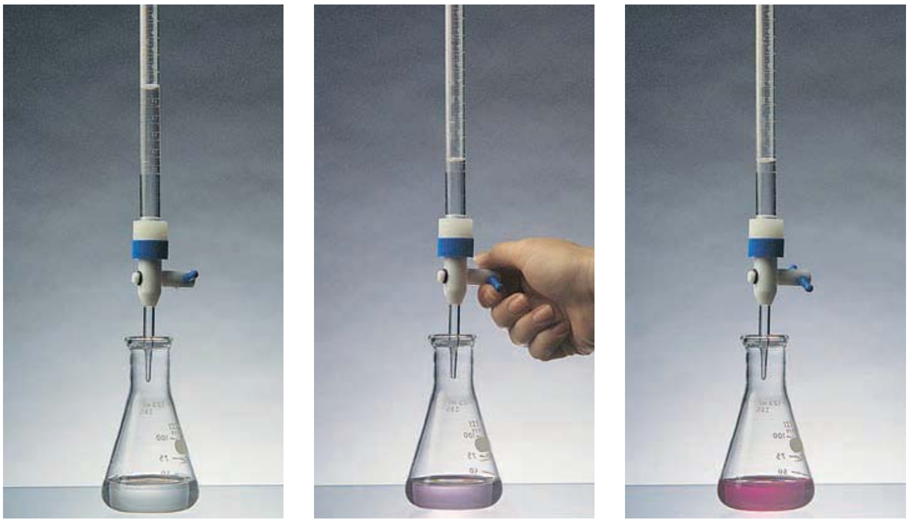


FIGURE 4.22

Titration of an unknown amount of HCl with NaOH
Left: The flask contains HCl and a few drops of phenolphthalein indicator; the buret contains 0.207 *M* NaOH (the buret reading is 44.97 mL). *Center:* NaOH was added to the solution in the flask until a persistent faint pink color was reached, marking the endpoint of the titration (the buret reading is 49.44 mL). The amount of HCl can be determined from the volume of NaOH used (4.47 mL); see Example 4.14.
Right: The addition of several drops of NaOH solution beyond the endpoint gives a deep pink color.

An important method for determining the amount of a particular substance is based on measuring the volume of reactant solution. Suppose substance *A* reacts in solution with substance *B*. If you know the volume and concentration of a solution of *B* that just reacts with substance *A* in a sample, you can determine the amount of *A*. **Titration** is *a procedure for determining the amount of substance* A *by adding a carefully measured volume of a solution with known concentration of* B *until the reaction of* A *and* B *is just complete.* **Volumetric analysis** is *a method of analysis based on titration.*

Figure 4.22 shows a flask containing hydrochloric acid with an unknown amount of HCl being titrated with sodium hydroxide solution, NaOH, of known molarity. The reaction is

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

An indicator is a substance that undergoes a color change when a reaction approaches completion. See Section 4.4.

To the HCl solution are added a few drops of phenolphthalein indicator. < Phenolphthalein is colorless in the hydrochloric acid but turns pink at the completion of the reaction of NaOH with HCl. Sodium hydroxide with a concentration of 0.207 *M* is contained in a *buret,* a glass tube graduated to measure the volume of liquid delivered from the stopcock. The solution in the buret is added to the HCl in the flask until the phenolphthalein just changes from colorless to pink. At this point, the reaction is complete and the volume of NaOH that reacts with the HCl is read from the buret. This volume is then used to obtain the mass of HCl in the original solution.

Example 4.14 Calculating the Quantity of Substance in a Titrated Solution

A flask contains a solution with an unknown amount of HCl. This solution is titrated with 0.207 *M* NaOH. It takes 4.47 mL NaOH to complete the reaction. What is the mass of the HCl?

Problem Strategy First, in order to determine the stoichiometry of the reaction, you start by writing the balanced chemical equation.

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

If you use the numerical information from the problem to determine the moles of NaOH added to the solution, you then can use the stoichiometry of the reaction to determine the

(*continued*)

(continued)

moles of HCl that reacted. Once you know the moles of HCl, you can use the molar mass of HCl to calculate the mass of HCl. Employing this strategy, you convert the volume of NaOH (4.47×10^{-3} L NaOH solution) to moles NaOH (from the molarity of NaOH). Then you convert moles NaOH to moles HCl (from the chemical equation). Finally, you convert moles HCl to grams HCl.

Solution The calculation is as follows:

$$4.47 \times 10^{-3}\ \cancel{\text{L NaOH soln}} \times \frac{0.207\ \cancel{\text{mol NaOH}}}{1\ \cancel{\text{L NaOH soln}}} \times \frac{1\ \cancel{\text{mol HCl}}}{1\ \cancel{\text{mol NaOH}}} \times \frac{36.5\text{ g HCl}}{1\ \cancel{\text{mol HCl}}}$$

$$= \mathbf{0.0338\ g\ HCl}$$

Answer Check Before you perform the titration calculations, always write down the balanced chemical equation.

Exercise 4.16 A 5.00-g sample of vinegar is titrated with 0.108 *M* NaOH. If the vinegar requires 39.1 mL of the NaOH solution for complete reaction, what is the mass percentage of acetic acid, $HC_2H_3O_2$, in the vinegar? The reaction is

$$HC_2H_3O_2(aq) + NaOH(aq) \longrightarrow NaC_2H_3O_2(aq) + H_2O(l)$$

■ See Problems 4.91 and 4.92.

Concept Check 4.5

Consider three flasks, each containing 0.10 mol of acid. You need to learn something about the acids in each of the flasks, so you perform titration using an NaOH solution. Here are the results of the experiment:

Flask A	10 mL of NaOH required for neutralization
Flask B	20 mL of NaOH required for neutralization
Flask C	30 mL of NaOH required for neutralization

a. What have you learned about each of these acids from performing the experiment?

b. Could you use the results of this experiment to determine the concentration of the NaOH? If not, what assumption about the molecular formulas of the acids would allow you to make the concentration determination?

A Checklist for Review

Important Terms

electrolyte (4.1)
nonelectrolyte (4.1)
strong electrolyte (4.1)
weak electrolyte (4.1)
molecular equation (4.2)
complete ionic equation (4.2)
spectator ion (4.2)
net ionic equation (4.2)
precipitate (4.3)
exchange (metathesis) reaction (4.3)
acid–base indicator (4.4)
acid (Arrhenius) (4.4)
base (Arrhenius) (4.4)
acid (Brønsted–Lowry) (4.4)
base (Brønsted–Lowry) (4.4)
strong acid (4.4)
weak acid (4.4)
strong base (4.4)
weak base (4.4)
neutralization reaction (4.4)
salt (4.4)
polyprotic acid (4.4)
oxidation number (oxidation state) (4.5)
oxidation–reduction reaction (redox reaction) (4.5)
half-reaction (4.5)
oxidation (4.5)
reduction (4.5)
oxidizing agent (4.5)
reducing agent (4.5)
combination reaction (4.5)
decomposition reaction (4.5)

displacement reaction (single-replacement reaction) (4.5)
combustion reaction (4.5)
molar concentration (molarity) (*M*) (4.7)
quantitative analysis (4.9)
gravimetric analysis (4.9)
titration (4.10)
volumetric analysis (4.10)

Key Equations

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

$$M_i \times V_i = M_f \times V_f$$

Summary of Facts and Concepts

Reactions often involve ions in aqueous solution. Many of the compounds in such reactions are *electrolytes,* which are substances that dissolve in water to give ions. Electrolytes that exist in solution almost entirely as ions are called *strong electrolytes.* Electrolytes that dissolve in water to give a relatively small percentage of ions are called *weak electrolytes.* The *solubility rules* can be used to predict the extent to which an ionic compound will dissolve in water. Most soluble ionic compounds are strong electrolytes.

We can represent a reaction involving ions in one of three different ways, depending on what information we want to convey. A *molecular equation* is one in which substances are written as if they were molecular, even though they are ionic. This equation closely describes what you actually do in the laboratory. However, this equation does not describe what is happening at the level of ions and molecules. For that purpose, we rewrite the molecular equation as a *complete ionic equation* by replacing the formulas for strong electrolytes by their ion formulas. If you cancel *spectator ions* from the complete ionic equation, you obtain the *net ionic equation.*

Most of the important reactions we consider in this course can be divided into three major classes: (1) precipitation reactions, (2) acid–base reactions, and (3) oxidation–reduction reactions. A *precipitation reaction* occurs in aqueous solution because one product is insoluble. You can decide whether two ionic compounds will result in a precipitation reaction, if you know from solubility rules that one of the potential products is insoluble.

Acids are substances that yield hydrogen ions in aqueous solution or donate protons. *Bases* are substances that yield hydroxide ions in aqueous solution or accept protons. These *acid–base reactions* are proton-transfer reactions. In this chapter, we covered neutralization reactions (reactions of acids and bases to yield salts) and reactions of certain salts with acids to yield a gas.

Oxidation–reduction reactions are reactions involving a transfer of electrons from one species to another or a change in the oxidation number of atoms. The concept of *oxidation numbers* helps us describe this type of reaction. The atom that increases in oxidation number is said to undergo *oxidation;* the atom that decreases in oxidation number is said to undergo *reduction.* Oxidation and reduction must occur together in a reaction. Many oxidation–reduction reactions fall into the following categories: combination reactions, decomposition reactions, displacement reactions, and combustion reactions. Oxidation–reduction reactions can be balanced by the *half-reaction method.*

Molar concentration, or *molarity,* is the moles of solute in a liter of solution. Knowing the molarity allows you to calculate the amount of solute in any volume of solution. Because the moles of solute are constant during the *dilution of a solution,* you can determine to what volume to dilute a concentrated solution to give one of desired molarity.

Quantitative analysis involves the determination of the amount of a species in a material. In *gravimetric analysis,* you determine the amount of a species by converting it to a product you can weigh. In *volumetric analysis,* you determine the amount of a species by titration. *Titration* is a method of chemical analysis in which you measure the volume of solution of known molarity that reacts with a compound of unknown amount. You determine the amount of the compound from this volume of solution.

Media Summary

Visit the **student website at college.hmco.com/pic/ebbing9e** to help prepare for class, study for quizzes and exams, understand core concepts, and visualize molecular-level interactions. The following media activities are available for this chapter:

Prepare for Class

- **Video Lessons** *Mini lectures from chemistry experts*
  - Properties of Solutions
  - CIA Demonstration: The Electrified Pickle
  - CIA Demonstration: Conductivity Apparatus—Ionic Versus Covalent Bonds
  - Precipitation Reactions
  - Acid–Base Reactions
  - CIA Demonstration: The Ammonia Fountain
  - CIA Demonstration: Natural Acid–Base Indicators
  - Strong Acid–Strong Base and Weak Acid–Strong Base Reactions
  - Strong Acid–Weak Base and Weak Acid–Weak Base Reactions
  - Oxidation–Reduction Reactions
  - Balancing Redox Reactions and the Oxidation Number Method
  - Oxidation Numbers
  - CIA Demonstration: The Reaction Between A1 and BR_2
  - The Activity Series of the Elements
  - Balancing Redox Reactions and Using the Half-Reaction Method
  - Concentrations of Solutions
  - CIA Demonstration: Dilutions
  - Gravimetric Analysis
  - Acid–Base Titrations
  - CIA Demonstration: Titrations
  - Solving Titration Problems

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  Electrified Pickle
  Electrolyte Behavior
  Electrolytes
  Solubility Rules
  Precipitation Reactions
  Ammonia Fountain
  Combustion Reaction: Sugar and Potassium Chlorate
  Dilution
  Acid–Base Titration
- **Tutorials** *Animated examples and interactive activities*
  Precipitation Reactions
  Dilution
- **Flashcards** *Key terms and definitions*
  Online Flashcards
- **Self-Assessment Questions** *Additional questions with full worked-out solutions*
  6 Self-Assessment Questions

ACE the Test

Multiple-choice quizzes
3 ACE Practice Tests

Access these resources using the passkey available free with new texts or for purchase separately.

Learning Objectives

4.1 Ionic Theory of Solutions and Solubility Rules

- Describe how an ionic substance can form ions in aqueous solution.
- Explain how an *electrolyte* makes a solution electrically conductive.
- Give examples of substances that are electrolytes.
- Define *nonelectrolyte,* and provide an example of a molecular substance that is a nonelectrolyte.
- Compare the properties of solutions that contain *strong electrolytes* and *weak electrolytes.*
- Learn the *solubility rules* for ionic compounds.
- Use the solubility rules. Example 4.1

4.2 Molecular and Ionic Equations

- Write the *molecular equation* of a chemical reaction.
- From the molecular equation of both strong electrolytes and weak electrolytes, determine the *complete ionic equation.*
- From the complete ionic equation, write the *net ionic equation.*
- Write net ionic equations. Example 4.2

4.3 Precipitation Reactions

- Recognize *precipitation* (*exchange*) reactions.
- Write molecular, complete ionic, and net ionic equations for precipitation reactions.
- Decide whether a precipitation reaction will occur. Example 4.3
- Determine the product of a precipitation reaction.

4.4 Acid–Base Reactions

- Understand how an *acid–base* indicator is used to determine whether a solution is acidic or basic.
- Define *Arrhenius acid* and *Arrhenius base.*
- Write the chemical equation of an Arrhenius base in aqueous solution.
- Define *Brønsted–Lowry acid* and *Brønsted–Lowry base.*
- Write the chemical equation of a Brønsted–Lowry base in aqueous solution.
- Write the chemical equation of an acid in aqueous solution using a *hydronium ion.*
- Learn the common *strong acids* and *strong bases.*
- Distinguish between a strong acid and a *weak acid* and the solutions they form.
- Distinguish between a strong base and a *weak base* and the solutions they form.
- Classify acids and bases as strong or weak. Example 4.4
- Recognize *neutralization reactions.*
- Write an equation for a neutralization reaction. Example 4.5
- Write the reactions for a *polyprotic acid* in aqueous solution.
- Recognize acid–base reactions that lead to gas formation.
- Write an equation for a reaction with gas formation. Example 4.6

4.5 Oxidation–Reduction Reactions

- Define *oxidation–reduction* reaction.
- Learn the oxidation-number rules.
- Assign oxidation numbers. Example 4.7
- Write the *half-reactions* of an oxidation–reduction reaction.
- Determine the species undergoing *oxidation* and *reduction.*
- Recognize *combination reactions, decomposition reactions, displacement reactions,* and *combustion reactions.*
- Use the activity series to predict when displacement reactions will occur.

4.6 Balancing Simple Oxidation–Reduction Equations

- Balance simple oxidation–reduction reactions by the half-reaction method. Example 4.8

4.7 Molar Concentration

- Define *molarity* or *molar concentration* of a solution.
- Calculate the molarity from mass and volume. Example 4.9
- Use molarity as a conversion factor. Example 4.10

4.8 Diluting Solutions

- Describe what happens to the concentration of a solution when it is diluted.
- Perform calculations associated with dilution.
- Diluting a solution. Example 4.11

4.9 Gravimetric Analysis

- Determine the amount of a species by *gravimetric analysis*. Example 4.12

4.10 Volumetric Analysis

- Calculate the volume of reactant solution needed to perform a reaction. Example 4.13
- Understand how to perform a *titration*.
- Calculate the quantity of substance in a titrated solution. Example 4.14

Self-Assessment and Review Questions

4.1 Explain why some electrolyte solutions are strongly conducting, whereas others are weakly conducting.

4.2 Define the terms *strong electrolyte* and *weak electrolyte*. Give an example of each.

4.3 Explain the terms *soluble* and *insoluble*. Use the solubility rules to write the formula of an insoluble ionic compound.

4.4 What are the advantages and disadvantages of using a molecular equation to represent an ionic reaction?

4.5 What is a *spectator ion*? Illustrate with a complete ionic reaction.

4.6 What is a net ionic equation? What is the value in using a net ionic equation? Give an example.

4.7 What are the major types of chemical reactions? Give a brief description and an example of each.

4.8 Describe in words how you would prepare pure crystalline AgCl and $NaNO_3$ from solid $AgNO_3$ and solid NaCl.

4.9 Give an example of a neutralization reaction. Label the acid, base, and salt.

4.10 Give an example of a polyprotic acid and write equations for the successive neutralizations of the acidic hydrogen atoms of the acid molecule to produce a series of salts.

4.11 Why must oxidation and reduction occur together in a reaction?

4.12 Give an example of a displacement reaction. What is the oxidizing agent? What is the reducing agent?

4.13 Why is the product of molar concentration and volume constant for a dilution problem?

4.14 Describe how the amount of sodium hydroxide in a mixture can be determined by titration with hydrochloric acid of known molarity.

4.15 What is the net ionic equation for the following molecular equation?

$$HF(aq) + KOH(aq) \longrightarrow KF(aq) + H_2O(l)$$

Hydrofluoric acid, HF, is a molecular substance and a weak electrolyte.

a. $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$
b. $H^+(aq) + KOH(aq) \longrightarrow K^+(aq) + H_2O(l)$
c. $HF(aq) + KOH(aq) \longrightarrow K^+(aq) + F^-(aq)$
d. $HF(aq) + K^+(aq) + OH^-(aq) \longrightarrow KF(aq) + H_2O(l)$
e. $HF(aq) + OH^-(aq) \longrightarrow F^-(aq) + H_2O(l)$

4.16 An aqueous sodium hydroxide solution mixed with an aqueous magnesium nitrate solution yields which of the following products?

a. magnesium hydroxide(*aq*)
b. magnesium dihydroxide(*s*)
c. magnesium hydroxide(*s*)
d. dimagnesium hydroxide(*s*)
e. sodium nitrate(*l*)

4.17 Which of the following compounds would produce the highest concentration of Cl^- ions when 0.10 mol of each is placed in separate beakers containing equal volumes of water?

a. NaCl
b. $PbCl_2$
c. $HClO_4$
d. $MgCl_2$
e. HCl

4.18 In an aqueous 0.10 *M* HNO_2 solution (HNO_2 is a weak electrolyte), which of the following would you expect to see in the highest concentration?

a. H_3O^+
b. NO_2^-
c. H^+
d. HNO_2
e. OH^-

Concept Explorations

4.19 The Behavior of Substances in Water

Part 1

a. Ammonia, NH_3, is a weak electrolyte. It forms ions in solution by *reacting* with water molecules to form the ammonium ion and hydroxide ion. Write the balanced chemical reaction for this process, including state symbols.

b. From everyday experience you are probably aware that table sugar (sucrose), $C_{12}H_{22}O_{11}$, is soluble in water. When sucrose dissolves in water, it doesn't form ions through any reaction with water. It just *dissolves* without forming ions, so it is a nonelectrolyte. Write the chemical equation for the dissolving of sucrose in water.

c. Both NH_3 and $C_{12}H_{22}O_{11}$ are soluble molecular compounds, yet they behave differently in aqueous solution. Briefly explain why one is a weak electrolyte and the other is a nonelectrolyte.

d. Hydrochloric acid, HCl, is a molecular compound that is a strong electrolyte. Write the chemical reaction of HCl with water.

e. Compare the ammonia reaction with that of hydrochloric acid. Why are both of these substances considered electrolytes?

f. Explain why HCl is a strong electrolyte and ammonia is a weak electrolyte.

g. Classify each of the following substances as either ionic or molecular.

KCl NH_3 CO_2 $MgBr_2$ HCl $Ca(OH)_2$ PbS $HC_2H_3O_2$

h. For those compounds above that you classified as ionic, use the solubility rules to determine which are soluble.

i. The majority of ionic substances are solids at room temperature. Describe what you would observe if you placed a soluble ionic compound and an insoluble ionic compound in separate beakers of water.

j. Write the chemical equation(s), including state symbols, for what happens when each soluble ionic compound that you identified above is placed in water. Are these substances reacting with water when they are added to water?

k. How would you classify the soluble ionic compounds: strong electrolyte, weak electrolyte, or nonelectrolyte? Explain your answer.

l. Sodium chloride, NaCl, is a strong electrolyte, as is hydroiodic acid, HI. Write the chemical equations for what happens when these substances are added to water.

m. Are NaCl and HI strong electrolytes because they have similar behavior in aqueous solution? If not, describe, using words and equations, the different chemical process that takes place in each case.

Part 2: You have two hypothetical molecular compounds, AX and AY. AX is a strong electrolyte and AY is a weak electrolyte. The compounds undergo the following chemical reactions when added to water.

$$AX(aq) + H_2O(l) \longrightarrow AH_2O^+(aq) + X^-(aq)$$

$$AY(aq) + H_2O(l) \longrightarrow AH_2O^+(aq) + Y^-(aq)$$

a. Explain how the relative amounts of AX(*aq*) and AY(*aq*) would compare if you had a beaker of water with AX and a beaker of water with AY.

b. How would the relative amounts of $X^-(aq)$ and $Y^-(aq)$ in the two beakers compare? Be sure to explain your answer.

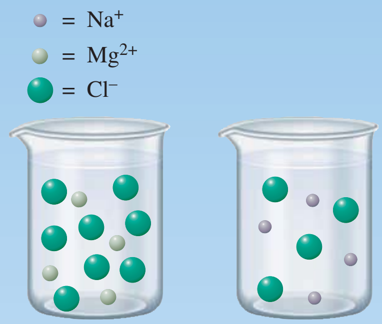
4.20 Working with Concentration (Molarity Concepts)

Note: You should be able to answer all of the following questions without using a calculator.

Part 1

a. Both NaCl and $MgCl_2$ are soluble ionic compounds. Write the balanced chemical equations for these two substances dissolving in water.

b. Consider the pictures below. These pictures represent 1.0-L solutions of 1.0 *M* NaCl(*aq*) and 1.0 *M* $MgCl_2(aq)$. The representations of the ions in solution are the correct relative amounts. Water molecules have been omitted for clarity. Correctly label each of the beakers, provide a key to help identify the ions, and give a brief explanation of how you made your assignments.



Keeping in mind that the pictures represent the relative amounts of ions in the solution and that the numerical information about these solutions is presented above, answer the following questions c through f.

c. How many moles of NaCl and $MgCl_2$ are in each beaker?

d. How many moles of chloride ions are in each beaker? How did you arrive at this answer?

e. What is the concentration of chloride ions in each beaker? Without using mathematical equations, briefly explain how you obtained your answer.

f. Explain how it is that the concentrations of chloride ions in these beakers are different even though the concentrations of each substance (compound) are the same.

Part 2: Say you were to dump out half of the $MgCl_2$ solution from the beaker above.

a. What would be the concentration of the $MgCl_2(aq)$ ion and of the chloride ions in the remaining solution?

b. How many moles of the $MgCl_2$ and of the chloride ions would remain in the beaker?

c. Explain why the concentration of $MgCl_2(aq)$ *would not* change, whereas the number of moles of $MgCl_2$ *would* change when solution was removed from the beaker. As part of your answer, you are encouraged to use pictures.

Part 3: Consider the beaker containing 1.0 L of the 1.0 *M* NaCl(*aq*) solution. You now add 1.0 L of water to this beaker.

a. What is the concentration of this NaCl(*aq*) solution?

b. How many moles of NaCl are present in the 2.0 L of NaCl(*aq*) solution?

c. Explain why the concentration of NaCl(*aq*) *does* change with the addition of water, whereas the number of moles *does not* change. Here again, you are encouraged to use pictures to help answer the question.

Conceptual Problems

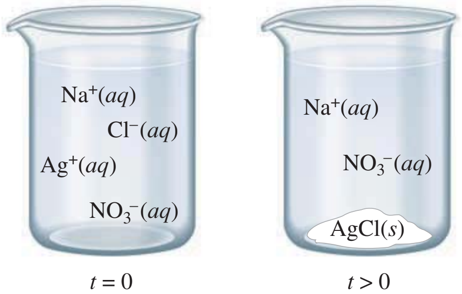
4.21 You need to perform gravimetric analysis of a water sample in order to determine the amount of Ag^+ present.

a. List three aqueous solutions that would be suitable for mixing with the sample to perform the analysis.

b. Would adding $KNO_3(aq)$ allow you to perform the analysis?

c. Assume you have performed the analysis and the silver solid that formed is moderately soluble. How might this affect your analysis results?

4.22 In this problem you need to draw two pictures of solutions in beakers at different points in time. Time zero ($t = 0$) will be the *hypothetical* instant at which the reactants dissolve in the solution (*if* they dissolve) *before* they react. Time after mixing ($t > 0$) will be the time required to allow sufficient interaction of the materials. For now, we assume that insoluble solids have no ions in solution and do not worry about representing the stoichiometric amounts of the dissolved ions. Here is an example: Solid NaCl and solid $AgNO_3$ are added to a beaker containing 250 mL of water.



Note that we are not showing the H_2O, and we are representing only the ions and solids in solution. Using the same conditions as the example (adding the solids to H_2O), draw pictures of the following:

a. Solid lead(II) nitrate and solid ammonium chloride at $t = 0$ and $t > 0$

b. $FeS(s)$ and $NaNO_3(s)$ at $t = 0$ and $t > 0$

c. Solid lithium iodide and solid sodium carbonate at $t = 0$ and $t > 0$

4.23 You come across a beaker that contains water, aqueous ammonium acetate, and a precipitate of calcium phosphate.

a. Write the balanced molecular equation for a reaction between two solutions containing ions that could produce this solution.

b. Write the complete ionic equation for the reaction in part a.

c. Write the net ionic equation for the reaction in part a.

4.24 Three acid samples are prepared for titration by 0.01 *M* NaOH:

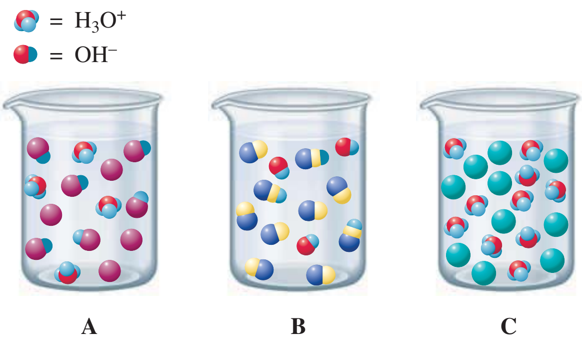
1. Sample 1 is prepared by dissolving 0.01 mol of HCl in 50 mL of water.
2. Sample 2 is prepared by dissolving 0.01 mol of HCl in 60 mL of water.
3. Sample 3 is prepared by dissolving 0.01 mol of HCl in 70 mL of water.

a. Without performing a formal calculation, compare the concentrations of the three acid samples (rank them from highest to lowest).

b. When the titration is performed, which sample, if any, will require the largest volume of the 0.01 *M* NaOH for neutralization?

4.25 Would you expect a precipitation reaction between an ionic compound that is an electrolyte and an ionic compound that is a nonelectrolyte? Justify your answer.

4.26 Equal quantities of the hypothetical strong acid HX, weak acid HA, and weak base BZ, are added to separate beakers of water, producing the solutions depicted in the drawings. In the drawings, the relative amounts of each substance present in the solution (neglecting the water) are shown. Identify the acid or base that was used to produce each of the solutions (HX, HA, or BZ).



4.27 Try and answer the following questions without using a calculator.

a. A solution is made by mixing 1.0 L of 0.5 *M* NaCl and 0.5 L of 1.0 *M* $CaCl_2$. Which ion is at the highest concentration in the solution?

b. Another solution is made by mixing 0.50 L of 1.0 *M* KBr and 0.50 L of 1.0 *M* K_3PO_4. What is the concentration of each ion in the solution?

4.28 If one mole of the following compounds were each placed into separate beakers containing the same amount of water, rank the $Cl^-(aq)$ concentrations from highest to lowest (some may be equivalent): KCl, $AlCl_3$, $PbCl_2$, NaCl, HCl, NH_3, KOH, and HCN.

Practice Problems

Solubility Rules

4.29 Using solubility rules, predict the solubility in water of the following ionic compounds.

a. PbS **b.** $AgNO_3$
c. Na_2CO_3 **d.** CaI_2

4.30 Using solubility rules, predict the solubility in water of the following ionic compounds.

a. $Al(OH)_3$ **b.** Li_3P
c. NH_4Cl **d.** NaOH

4.31 Using solubility rules, decide whether the following ionic solids are soluble or insoluble in water. If they are soluble, indicate what ions you would expect to be present in solution.

a. AgBr **b.** Li_2SO_4
c. $Ca_3(PO_4)_2$ **d.** Na_2CO_3

4.32 Using solubility rules, decide whether the following ionic solids are soluble or insoluble in water. If they are soluble, indicate what ions you would expect to be present in solution.

a. $(NH_4)_2SO_4$ **b.** $BaCO_3$
c. $PbSO_4$ **d.** $Ca(NO_3)_2$

Ionic Equations

4.33 Write net ionic equations for the following molecular equations. HBr is a strong electrolyte.

a. $HBr(aq) + KOH(aq) \longrightarrow KBr(aq) + H_2O(l)$
b. $AgNO_3(aq) + NaBr(aq) \longrightarrow AgBr(s) + NaNO_3(aq)$
c. $K_2S(aq) + 2HBr(aq) \longrightarrow 2KBr(aq) + H_2S(g)$
d. $NaOH(aq) + NH_4Br(aq) \longrightarrow NaBr(aq) + NH_3(g) + H_2O(l)$

4.34 Write net ionic equations for the following molecular equations. HBr is a strong electrolyte.

a. $HBr(aq) + NH_3(aq) \longrightarrow NH_4Br(aq)$
b. $2HBr(aq) + Ba(OH)_2(aq) \longrightarrow 2H_2O(l) + BaBr_2(aq)$
c. $Pb(NO_3)_2(aq) + 2NaBr(aq) \longrightarrow PbBr_2(s) + 2NaNO_3(aq)$
d. $MgCO_3(s) + H_2SO_4(aq) \longrightarrow MgSO_4(aq) + H_2O(l) + CO_2(g)$

4.35 Lead(II) nitrate solution and sodium sulfate solution are mixed. Crystals of lead(II) sulfate come out of solution, leaving a solution of sodium nitrate. Write the molecular equation and the net ionic equation for the reaction.

4.36 Potassium carbonate solution reacts with aqueous hydrobromic acid to give a solution of potassium bromide, carbon dioxide gas, and water. Write the molecular equation and the net ionic equation for the reaction.

Precipitation

4.37 Write the molecular equation and the net ionic equation for each of the following aqueous reactions. If no reaction occurs, write *NR* after the arrow.

a. $FeSO_4 + NaCl \longrightarrow$
b. $Na_2CO_3 + MgBr_2 \longrightarrow$
c. $MgSO_4 + NaOH \longrightarrow$
d. $NiCl_2 + NaBr \longrightarrow$

4.38 Write the molecular equation and the net ionic equation for each of the following aqueous reactions. If no reaction occurs, write *NR* after the arrow.

a. $AgNO_3 + NaI \longrightarrow$
b. $Ba(NO_3)_2 + K_2SO_4 \longrightarrow$
c. $Mg(NO_3)_2 + K_2SO_4 \longrightarrow$
d. $CaCl_2 + Al(NO_3)_3 \longrightarrow$

4.39 For each of the following, write molecular and net ionic equations for any precipitation reaction that occurs. If no reaction occurs, indicate this.

a. Solutions of barium nitrate and lithium sulfate are mixed.
b. Solutions of sodium bromide and calcium nitrate are mixed.
c. Solutions of aluminum sulfate and sodium hydroxide are mixed.
d. Solutions of calcium bromide and sodium phosphate are mixed.

4.40 For each of the following, write molecular and net ionic equations for any precipitation reaction that occurs. If no reaction occurs, indicate this.

a. Zinc chloride and sodium sulfide are dissolved in water.
b. Sodium sulfide and calcium chloride are dissolved in water.
c. Magnesium sulfate and potassium bromide are dissolved in water.
d. Magnesium sulfate and potassium carbonate are dissolved in water.

Strong and Weak Acids and Bases

4.41 Classify each of the following as a strong or weak acid or base.

a. HF **b.** KOH **c.** $HClO_4$ **d.** HIO

4.42 Classify each of the following as a strong or weak acid or base.

a. NH_3 **b.** HCNO **c.** $Sr(OH)_2$ **d.** HI

Neutralization Reactions

4.43 Complete and balance each of the following molecular equations (in aqueous solution); include phase labels. Then, for each, write the net ionic equation.

a. $NaOH + HNO_3 \longrightarrow$
b. $HCl + Ba(OH)_2 \longrightarrow$
c. $HC_2H_3O_2 + Ca(OH)_2 \longrightarrow$
d. $NH_3 + HNO_3 \longrightarrow$

4.44 Complete and balance each of the following molecular equations (in aqueous solution); include phase labels. Then, for each, write the net ionic equation.

a. $Al(OH)_3 + HCl \longrightarrow$
b. $HBr + Sr(OH)_2 \longrightarrow$
c. $Ba(OH)_2 + HC_2H_3O_2 \longrightarrow$
d. $HNO_3 + KOH \longrightarrow$

4.45 For each of the following, write the molecular equation, including phase labels. Then write the net ionic equation. Note that the salts formed in these reactions are soluble.

a. the neutralization of hydrobromic acid with calcium hydroxide solution
b. the reaction of solid aluminum hydroxide with nitric acid
c. the reaction of aqueous hydrogen cyanide with calcium hydroxide solution
d. the neutralization of lithium hydroxide solution by aqueous hydrogen cyanide

4.46 For each of the following, write the molecular equation, including phase labels. Then write the net ionic equation. Note that the salts formed in these reactions are soluble.

a. the neutralization of lithium hydroxide solution by aqueous perchloric acid
b. the reaction of barium hydroxide solution and aqueous nitrous acid
c. the reaction of sodium hydroxide solution and aqueous nitrous acid
d. the neutralization of aqueous hydrogen cyanide by aqueous strontium hydroxide

4.47 Complete the right side of each of the following molecular equations. Then write the net ionic equations. Assume all salts formed are soluble. Acid salts are possible.

a. $2KOH(aq) + H_3PO_4(aq) \longrightarrow$
b. $3H_2SO_4(aq) + 2Al(OH)_3(s) \longrightarrow$
c. $2HC_2H_3O_2(aq) + Ca(OH)_2(aq) \longrightarrow$
d. $H_2SO_3(aq) + NaOH(aq) \longrightarrow$

4.48 Complete the right side of each of the following molecular equations. Then write the net ionic equations. Assume all salts formed are soluble. Acid salts are possible.

a. $Ca(OH)_2(aq) + 2H_2SO_4(aq) \longrightarrow$
b. $2H_3PO_4(aq) + Ca(OH)_2(aq) \longrightarrow$
c. $NaOH(aq) + H_2SO_4(aq) \longrightarrow$
d. $Sr(OH)_2(aq) + 2H_2CO_3(aq) \longrightarrow$

4.49 Write molecular and net ionic equations for the successive neutralizations of each acidic hydrogen of sulfurous acid by aqueous calcium hydroxide. $CaSO_3$ is insoluble; the acid salt is soluble.

4.50 Write molecular and net ionic equations for the successive neutralizations of each acidic hydrogen of phosphoric acid by calcium hydroxide solution. $Ca_3(PO_4)_2$ is insoluble; assume that the acid salts are soluble.

Reactions Evolving a Gas

4.51 The following reactions occur in aqueous solution. Complete and balance the molecular equations using phase labels. Then write the net ionic equations.

a. $CaS + HBr \longrightarrow$
b. $MgCO_3 + HNO_3 \longrightarrow$
c. $K_2SO_3 + H_2SO_4 \longrightarrow$

4.52 The following reactions occur in aqueous solution. Complete and balance the molecular equations using phase labels. Then write the net ionic equations.

a. $BaCO_3 + HNO_3 \longrightarrow$
b. $K_2S + HCl \longrightarrow$
c. $CaSO_3(s) + HI \longrightarrow$

4.53 Write the molecular equation and the net ionic equation for the reaction of solid iron(II) sulfide and hydrochloric acid. Add phase labels.

4.54 Write the molecular equation and the net ionic equation for the reaction of solid barium carbonate and hydrogen bromide in aqueous solution. Add phase labels.

Oxidation Numbers

4.55 Obtain the oxidation number for the element noted in each of the following.

a. Ga in Ga_2O_3 **b.** Nb in NbO_2
c. Br in $KBrO_4$ **d.** Mn in K_2MnO_4

4.56 Obtain the oxidation number for the element noted in each of the following.

a. Cr in CrO_3 **b.** Hg in Hg_2Cl_2
c. Ga in $Ga(OH)_3$ **d.** P in Na_3PO_4

4.57 Obtain the oxidation number for the element noted in each of the following.

a. N in NH_2^- **b.** I in IO_3^-
c. Al in $Al(OH)_4^-$ **d.** Cl in $HClO_4$

4.58 Obtain the oxidation number for the element noted in each of the following.

a. N in NO_2^- **b.** Cr in CrO_4^{2-}
c. Zn in $Zn(OH)_4^{2-}$ **d.** As in $H_2AsO_3^-$

4.59 Determine the oxidation numbers of all the elements in each of the following compounds. (*Hint:* Look at the ions present.)

a. $Mn(ClO_3)_2$ **b.** $Fe_2(CrO_4)_3$
c. $HgCr_2O_7$ **d.** $Co_3(PO_4)_2$

4.60 Determine the oxidation numbers of all the elements in each of the following compounds. (*Hint:* Look at the ions present.)

a. $Hg_2(BrO_3)_2$ **b.** $Cr_2(SO_4)_3$
c. $CoSeO_4$ **d.** $Pb(OH)_2$

Describing Oxidation–Reduction Reactions

4.61 In the following reactions, label the oxidizing agent and the reducing agent.

a. $P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}(s)$
b. $Co(s) + Cl_2(g) \longrightarrow CoCl_2(s)$

4.62 In the following reactions, label the oxidizing agent and the reducing agent.

a. $ZnO(s) + C(s) \longrightarrow Zn(g) + CO(g)$
b. $8Fe(s) + S_8(s) \longrightarrow 8FeS(s)$

4.63 In the following reactions, label the oxidizing agent and the reducing agent.

a. $2Al(s) + 3F_2(g) \longrightarrow 2AlF_3(s)$
b. $Hg^{2+}(aq) + NO_2^-(aq) + H_2O(l) \longrightarrow Hg(s) + 2H^+(aq) + NO_3^-(aq)$

4.64 In the following reactions, label the oxidizing agent and the reducing agent.

a. $Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$
b. $PbS(s) + 4H_2O_2(aq) \longrightarrow PbSO_4(s) + 4H_2O(l)$

Balancing Oxidation–Reduction Reactions

4.65 Balance the following oxidation–reduction reactions by the half-reaction method.

a. $CuCl_2(aq) + Al(s) \longrightarrow AlCl_3(aq) + Cu(s)$
b. $Cr^{3+}(aq) + Zn(s) \longrightarrow Cr(s) + Zn^{2+}(aq)$

4.66 Balance the following oxidation–reduction reactions by the half-reaction method.

a. $FeI_3(aq) + Mg(s) \longrightarrow Fe(s) + MgI_2(aq)$
b. $H_2(g) + Ag^+(aq) \longrightarrow Ag(s) + H^+(aq)$

Molarity

4.67 A sample of 0.0512 mol of iron(III) chloride, $FeCl_3$, was dissolved in water to give 25.0 mL of solution. What is the molarity of the solution?

4.68 A 50.0-mL volume of $AgNO_3$ solution contains 0.0285 mol $AgNO_3$ (silver nitrate). What is the molarity of the solution?

4.69 An aqueous solution is made from 0.798 g of potassium permanganate, $KMnO_4$. If the volume of solution is 50.0 mL, what is the molarity of $KMnO_4$ in the solution?

4.70 A sample of oxalic acid, $H_2C_2O_4$, weighing 1.192 g is placed in a 100.0-mL volumetric flask, which is then filled to the mark with water. What is the molarity of the solution?

4.71 What volume of 0.120 *M* $CuSO_4$ is required to give 0.150 mol of copper(II) sulfate, $CuSO_4$?

4.72 How many milliliters of 0.126 *M* $HClO_4$ (perchloric acid) are required to give 0.102 mol $HClO_4$?

4.73 An experiment calls for 0.0353 g of potassium hydroxide, KOH. How many milliliters of 0.0176 *M* KOH are required?

4.74 What is the volume (in milliliters) of 0.215 *M* H_2SO_4 (sulfuric acid) containing 0.949 g H_2SO_4?

4.75 Heme, obtained from red blood cells, binds oxygen, O_2. How many moles of heme are there in 150 mL of 0.0019 *M* heme solution?

4.76 Insulin is a hormone that controls the use of glucose in the body. How many moles of insulin are required to make up 28 mL of 0.0048 *M* insulin solution?

4.77 How many grams of sodium dichromate, $Na_2Cr_2O_7$, should be added to a 100.0-mL volumetric flask to prepare 0.025 *M* $Na_2Cr_2O_7$ when the flask is filled to the mark with water?

4.78 Describe how you would prepare 2.50×10^2 mL of 0.20 *M* Na_2SO_4. What mass (in grams) of sodium sulfate, Na_2SO_4, is needed?

4.79 You wish to prepare 0.12 *M* HNO_3 from a stock solution of nitric acid that is 15.8 *M*. How many milliliters of the stock solution do you require to make up 1.00 L of 0.12 *M* HNO_3?

4.80 A chemist wants to prepare 0.50 *M* HCl. Commercial hydrochloric acid is 12.4 *M*. How many milliliters of the commercial acid does the chemist require to make up 1.50 L of the dilute acid?

4.81 A 3.50 g sample of KCl is dissolved in 10.0 mL of water. The resulting solution is then added to 60.0 mL of a 0.500 *M* $CaCl_2(aq)$ solution. Assuming that the volumes are additive, calculate the concentrations of each ion present in the final solution.

4.82 Calculate the concentrations of each ion present in a solution that results from mixing 50.0 mL of a 0.20 *M* $NaClO_3(aq)$ solution with 25.0 mL of a 0.20 *M* $Na_2SO_4(aq)$. Assume that the volumes are additive.

Gravimetric Analysis

4.83 A chemist added an excess of sodium sulfate to a solution of a soluble barium compound to precipitate all of the barium ion as barium sulfate, $BaSO_4$. How many grams of barium ion are in a 458-mg sample of the barium compound if a solution of the sample gave 513 mg $BaSO_4$ precipitate? What is the mass percentage of barium in the compound?

4.84 A soluble iodide was dissolved in water. Then an excess of silver nitrate, $AgNO_3$, was added to precipitate all of the iodide ion as silver iodide, AgI. If 1.545 g of the soluble iodide gave 2.185 g of silver iodide, how many grams of iodine are in the sample of soluble iodide? What is the mass percentage of iodine, I, in the compound?

4.85 Copper has compounds with copper(I) ion or copper(II) ion. A compound of copper and chlorine was treated with a solution of silver nitrate, $AgNO_3$, to convert the chloride ion in the compound to a precipitate of AgCl. A 59.40-mg sample of the copper compound gave 86.00 mg AgCl.

a. Calculate the percentage of chlorine in the copper compound.

b. Decide whether the formula of the compound is CuCl or $CuCl_2$.

4.86 Gold has compounds containing gold(I) ion or gold(III) ion. A compound of gold and chlorine was treated with a solution of silver nitrate, $AgNO_3$, to convert the chloride ion in the compound to a precipitate of AgCl. A 162.7-mg sample of the gold compound gave 100.3 mg AgCl.

a. Calculate the percentage of the chlorine in the gold compound.

b. Decide whether the formula of the compound is AuCl or $AuCl_3$.

4.87 A compound of iron and chlorine is soluble in water. An excess of silver nitrate was added to precipitate the chloride ion as silver chloride. If a 134.8-mg sample of the compound gave 304.8 mg AgCl, what is the formula of the compound?

4.88 A 1.345-g sample of a compound of barium and oxygen was dissolved in hydrochloric acid to give a solution of barium ion, which was then precipitated with an excess of potassium chromate to give 2.012 g of barium chromate, $BaCrO_4$. What is the formula of the compound?

Volumetric Analysis

4.89 What volume of 0.250 *M* HNO_3 (nitric acid) reacts with 44.8 mL of 0.150 *M* Na_2CO_3 (sodium carbonate) in the following reaction?

$$2HNO_3(aq) + Na_2CO_3(aq) \longrightarrow 2NaNO_3(aq) + H_2O(l) + CO_2(g)$$

4.90 A flask contains 49.8 mL of 0.150 *M* $Ca(OH)_2$ (calcium hydroxide). How many milliliters of 0.350 *M* Na_2CO_3 (sodium carbonate) are required to react completely with the calcium hydroxide in the following reaction?

$$Na_2CO_3(aq) + Ca(OH)_2(aq) \longrightarrow CaCO_3(s) + 2NaOH(aq)$$

4.91 How many milliliters of 0.150 *M* H_2SO_4 (sulfuric acid) are required to react with 8.20 g of sodium hydrogen carbonate, $NaHCO_3$, according to the following equation?

$$H_2SO_4(aq) + 2NaHCO_3(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O(l) + 2CO_2(g)$$

4.92 How many milliliters of 0.250 *M* $KMnO_4$ are needed to react with 3.36 g of iron(II) sulfate, $FeSO_4$? The reaction is as follows:

$$10FeSO_4(aq) + 2KMnO_4(aq) + 8H_2SO_4(aq) \longrightarrow 5Fe_2(SO_4)_3(aq) + 2MnSO_4(aq) + K_2SO_4(aq) + 8H_2O(l)$$

4.93 A solution of hydrogen peroxide, H_2O_2, is titrated with a solution of potassium permanganate, $KMnO_4$. The reaction is

$$5H_2O_2(aq) + 2KMnO_4(aq) + 3H_2SO_4(aq) \longrightarrow 5O_2(g) + 2MnSO_4(aq) + K_2SO_4(aq) + 8H_2O(l)$$

It requires 51.7 mL of 0.145 M $KMnO_4$ to titrate 20.0 g of the solution of hydrogen peroxide. What is the mass percentage of H_2O_2 in the solution?

4.94 A 3.33-g sample of iron ore is transformed to a solution of iron(II) sulfate, $FeSO_4$, and this solution is titrated with 0.150 M $K_2Cr_2O_7$ (potassium dichromate). If it requires 43.7 mL of potassium dichromate solution to titrate the iron(II) sulfate solution, what is the percentage of iron in the ore? The reaction is

$$6FeSO_4(aq) + K_2Cr_2O_7(aq) + 7H_2SO_4(aq) \longrightarrow 3Fe_2(SO_4)_3(aq) + Cr_2(SO_4)_3(aq) + 7H_2O(l) + K_2SO_4(aq)$$

General Problems

4.95 Magnesium metal reacts with hydrobromic acid to produce hydrogen gas and a solution of magnesium bromide. Write the molecular equation for this reaction. Then write the corresponding net ionic equation.

4.96 Aluminum metal reacts with perchloric acid to produce hydrogen gas and a solution of aluminum perchlorate. Write the molecular equation for this reaction. Then write the corresponding net ionic equation.

4.97 Nickel(II) sulfate solution reacts with lithium hydroxide solution to produce a precipitate of nickel(II) hydroxide and a solution of lithium sulfate. Write the molecular equation for this reaction. Then write the corresponding net ionic equation.

4.98 Potassium sulfate solution reacts with barium bromide solution to produce a precipitate of barium sulfate and a solution of potassium bromide. Write the molecular equation for this reaction. Then write the corresponding net ionic equation.

4.99 Decide whether a reaction occurs for each of the following. If it does not, write *NR* after the arrow. If it does, write the balanced molecular equation; then write the net ionic equation.

a. $LiOH + HCN \longrightarrow$
b. $Li_2CO_3 + HNO_3 \longrightarrow$
c. $LiCl + AgNO_3 \longrightarrow$
d. $LiCl + MgSO_4 \longrightarrow$

4.100 Decide whether a reaction occurs for each of the following. If it does not, write *NR* after the arrow. If it does, write the balanced molecular equation; then write the net ionic equation.

a. $Al(OH)_3 + HNO_3 \longrightarrow$
b. $NaBr + HClO_4 \longrightarrow$
c. $CaCl_2 + NaNO_3 \longrightarrow$
d. $MgSO_4 + Ba(NO_3)_2 \longrightarrow$

4.101 Complete and balance each of the following molecular equations, including phase labels, if a reaction occurs. Then write the net ionic equation. If no reaction occurs, write *NR* after the arrow.

a. $Sr(OH)_2 + HC_2H_3O_2 \longrightarrow$
b. $NH_4I + CsCl \longrightarrow$
c. $NaNO_3 + CsCl \longrightarrow$
d. $NH_4I + AgNO_3 \longrightarrow$

4.102 Complete and balance each of the following molecular equations, including phase labels, if a reaction occurs. Then write the net ionic equation. If no reaction occurs, write *NR* after the arrow.

a. $HClO_4 + BaCO_3 \longrightarrow$
b. $H_2CO_3 + Sr(OH)_2 \longrightarrow$
c. $K_3PO_4 + MgCl_2 \longrightarrow$
d. $FeSO_4 + MgCl_2 \longrightarrow$

4.103 Describe in words how you would do each of the following preparations. Then give the molecular equation for each preparation.

a. $CuCl_2(s)$ from $CuSO_4(s)$
b. $Ca(C_2H_3O_2)_2(s)$ from $CaCO_3(s)$
c. $NaNO_3(s)$ from $Na_2SO_3(s)$
d. $MgCl_2(s)$ from $Mg(OH)_2(s)$

4.104 Describe in words how you would do each of the following preparations. Then give the molecular equation for each preparation.

a. $MgCl_2(s)$ from $MgCO_3(s)$
b. $NaNO_3(s)$ from $NaCl(s)$
c. $Al(OH)_3(s)$ from $Al(NO_3)_3(s)$
d. $HCl(aq)$ from $H_2SO_4(aq)$

4.105 Classify each of the following reactions as a combination reaction, decomposition reaction, displacement reaction, or combustion reaction.

a. When they are heated, ammonium dichromate crystals, $(NH_4)_2Cr_2O_7$, decompose to give nitrogen, water vapor, and solid chromium(III) oxide, Cr_2O_3.
b. When aqueous ammonium nitrite, NH_4NO_2, is heated, it gives nitrogen and water vapor.
c. When gaseous ammonia, NH_3, reacts with hydrogen chloride gas, HCl, fine crystals of ammonium chloride, NH_4Cl, are formed.
d. Aluminum added to an aqueous solution of sulfuric acid, H_2SO_4, forms a solution of aluminum sulfate, $Al_2(SO_4)_3$. Hydrogen gas is released.

4.106 Classify each of the following reactions as a combination reaction, decomposition reaction, displacement reaction, or combustion reaction.

a. When solid calcium oxide, CaO, is exposed to gaseous sulfur trioxide, SO_3, solid calcium sulfate, $CaSO_4$, is formed.
b. Calcium metal (solid) reacts with water to produce a solution of calcium hydroxide, $Ca(OH)_2$, and hydrogen gas.
c. When solid sodium hydrogen sulfite, $NaHSO_3$, is heated, solid sodium sulfite, Na_2SO_3, sulfur dioxide gas, SO_2, and water vapor are formed.
d. Magnesium reacts with bromine to give magnesium bromide, $MgBr_2$.

4.107 Consider the reaction of all pairs of the following compounds in water solution: $Ba(OH)_2$, $Pb(NO_3)_2$, H_2SO_4, $NaNO_3$, $MgSO_4$.

a. Which pair (or pairs) forms one insoluble compound and one soluble compound (not water)?
b. Which pair (or pairs) forms two insoluble compounds?
c. Which pair (or pairs) forms one insoluble compound and water?

4.108 Consider the reaction of all pairs of the following compounds in water solution: $Sr(OH)_2$, $AgNO_3$, H_3PO_4, KNO_3, $CuSO_4$.

a. Which pair (or pairs) forms one insoluble compound and one soluble compound (not water)?
b. Which pair (or pairs) forms two insoluble compounds?
c. Which pair (or pairs) forms one insoluble compound and water?

4.109 An aqueous solution contains 4.50 g of calcium chloride, $CaCl_2$, per liter. What is the molarity of $CaCl_2$? When calcium chloride dissolves in water, the calcium ions, Ca^{2+}, and chloride ions, Cl^-, in the crystal go into the solution. What is the molarity of each ion in the solution?

4.110 An aqueous solution contains 3.45 g of iron(III) sulfate, $Fe_2(SO_4)_3$, per liter. What is the molarity of $Fe_2(SO_4)_3$? When the compound dissolves in water, the Fe^{3+} ions and SO_4^{2-} ions in the crystal go into the solution. What is the molar concentration of each ion in the solution?

4.111 A stock solution of potassium dichromate, $K_2Cr_2O_7$, is made by dissolving 89.3 g of the compound in 1.00 L of solution. How many milliliters of this solution are required to prepare 1.00 L of 0.100 M $K_2Cr_2O_7$?

4.112 A 71.2-g sample of oxalic acid, $H_2C_2O_4$, was dissolved in 1.00 L of solution. How would you prepare 1.00 L of 0.150 M $H_2C_2O_4$ from this solution?

4.113 A solution contains 6.00% (by mass) NaBr (sodium bromide). The density of the solution is 1.046 g/cm^3. What is the molarity of NaBr?

4.114 An aqueous solution contains 4.00% NH_3 (ammonia) by mass. The density of the aqueous ammonia is 0.979 g/mL. What is the molarity of NH_3 in the solution?

4.115 A barium mineral was dissolved in hydrochloric acid to give a solution of barium ion. An excess of potassium sulfate was added to 50.0 mL of the solution, and 1.128 g of barium sulfate precipitate formed. Assume that the original solution was barium chloride. What was the molarity of $BaCl_2$ in this solution?

4.116 Bone was dissolved in hydrochloric acid, giving 50.0 mL of solution containing calcium chloride, $CaCl_2$. To precipitate the calcium ion from the resulting solution, an excess of potassium oxalate was added. The precipitate of calcium oxalate, CaC_2O_4, weighed 1.437 g. What was the molarity of $CaCl_2$ in the solution?

4.117 You have a sample of a rat poison whose active ingredient is thallium(I) sulfate. You analyze this sample for the mass percentage of active ingredient by adding potassium iodide to precipitate yellow thallium(I) iodide. If the sample of rat poison weighed 759.0 mg and you obtained 212.2 mg of the dry precipitate, what is the mass percentage of the thallium(I) sulfate in the rat poison?

4.118 An antacid tablet has calcium carbonate as the active ingredient; other ingredients include a starch binder. You dissolve the tablet in hydrochloric acid and filter off insoluble material. You add potassium oxalate to the filtrate (containing calcium ion) to precipitate calcium oxalate. If a tablet weighing 0.680 g gave 0.629 g of calcium oxalate, what is the mass percentage of active ingredient in the tablet?

4.119 A sample of $CuSO_4 \cdot 5H_2O$ was heated to 110°C, where it lost water and gave another hydrate of copper(II) ion that contains 32.50% Cu. A 98.77-mg sample of this new hydrate gave 116.66 mg of barium sulfate precipitate when treated with a barium nitrate solution. What is the formula of the new hydrate?

4.120 A sample of $CuSO_4 \cdot 5H_2O$ was heated to 100°C, where it lost water and gave another hydrate of copper(II) ion that contained 29.76% Cu. An 85.42-mg sample of this new hydrate gave 93.33 mg of barium sulfate precipitate when treated with a barium nitrate solution. What is the formula of the new hydrate?

4.121 A water-soluble compound of gold and chlorine is treated with silver nitrate to convert the chlorine completely to silver chloride, AgCl. In an experiment, 328 mg of the compound gave 464 mg of silver chloride. Calculate the percentage of Cl in the compound. What is its empirical formula?

4.122 A solution of scandium chloride was treated with silver nitrate. The chlorine in the scandium compound was converted to silver chloride, AgCl. A 58.9-mg sample of scandium chloride gave 167.4 mg of silver chloride. What are the mass percentages of Sc and Cl in scandium chloride? What is its empirical formula?

4.123 A 0.608-g sample of fertilizer contained nitrogen as ammonium sulfate, $(NH_4)_2SO_4$. It was analyzed for nitrogen by heating with sodium hydroxide.

$$(NH_4)_2SO_4(s) + 2NaOH(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O(l) + 2NH_3(g)$$

The ammonia was collected in 46.3 mL of 0.213 M HCl (hydrochloric acid), with which it reacted.

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

This solution was titrated for excess hydrochloric acid with 44.3 mL of 0.128 M NaOH.

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

What is the percentage of nitrogen in the fertilizer?

4.124 An antacid tablet contains sodium hydrogen carbonate, $NaHCO_3$, and inert ingredients. A 0.500-g sample of powdered tablet was mixed with 50.0 mL of 0.190 M HCl (hydrochloric acid). The mixture was allowed to stand until it reacted.

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

The excess hydrochloric acid was titrated with 47.1 mL of 0.128 M NaOH (sodium hydroxide).

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

What is the percentage of sodium hydrogen carbonate in the antacid?

Strategy Problems

4.125 You order a glass of juice in a restaurant, only to discover that it is warm and too sweet. The sugar concentration of the juice is 3.47 *M*, but you would like it reduced to a concentration of 1.78 *M*. How many grams of ice should you add to 100 mL of juice, knowing that only a third of the ice will melt before you take the first sip? (The density of water is 1.00 g/mL.)

4.126 If 45.1 mL of a solution containing 8.30 g of silver nitrate is added to 30.6 mL of 0.511 *M* sodium carbonate solution, calculate the molarity of silver ion in the resulting solution. (Assume volumes are additive.)

4.127 If 38.2 mL of 0.248 *M* aluminum sulfate solution is diluted with deionized water to a total volume of 0.639 L, how many grams of aluminum ion are present in the diluted solution?

4.128 An aluminum nitrate solution is labeled 0.256 *M*. If 31.6 mL of this solution is diluted to a total of 63.7 mL, calculate the molarity of nitrate ion in the resulting solution.

4.129 Zinc acetate is sometimes prescribed by physicians for the treatment of Wilson's disease, which is a genetically caused condition wherein copper accumulates to toxic levels in the body. If you were to analyze a sample of zinc acetate and find that it contains 3.33×10^{23} acetate ions, how many grams of zinc acetate must be present in the sample?

4.130 Arsenic acid, H_3AsO_4, is a poisonous acid that has been used in the treatment of wood to prevent insect damage. Arsenic acid has three acidic protons. Say you take a 26.14-mL sample of arsenic acid and prepare it for titration with NaOH by adding 25.00 mL of water. The complete neutralization of this solution requires the addition of 53.07 mL of 0.6441 *M* NaOH solution. Write the balanced chemical reaction for the titration, and calculate the molarity of the arsenic acid sample.

4.131 When the following equation is balanced by the half-reaction method using the smallest set of whole-number stoichiometric coefficients possible, how many electrons are canceled when the two half-reactions are added together?

$$K(s) + N_2(g) \Rightarrow K_3N(s)$$

4.132 Identify each of the following reactions as being a neutralization, precipitation, or oxidation–reduction reaction.

a. $Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$

b. $Na_2SO_4(aq) + Hg(NO_3)_2(aq) \longrightarrow HgSO_4(s) + 2NaNO_3(aq)$

c. $CsOH(aq) + HClO_4(aq) \longrightarrow Cs^+(aq) + 2H_2O(l) + ClO_4^-(aq)$

d. $Mg(NO_3)_2(g) + Na_2S(aq) \longrightarrow MgS(s) + 2NaNO_3(aq)$

4.133 A 414-mL sample of 0.196 *M* $MgBr_2$ solution is prepared in a large flask. A 43.0-mL portion of the solution is then placed into an empty 100.0-mL beaker. What is the concentration of the solution in the beaker?

4.134 Three 1.0-g samples of $PbCl_2$, KCl, and $CaCl_2$ are placed in separate 500-mL beakers. In each case, enough 25°C water is added to bring the total volume of the mixture to 250 mL. Each of the mixtures is then stirred for five minutes. Which of the mixtures will have the highest concentration of chloride (Cl^-) ion?

Cumulative-Skills Problems

4.135 Lead(II) nitrate reacts with cesium sulfate in an aqueous precipitation reaction. What are the formulas of lead(II) nitrate and cesium sulfate? Write the molecular equation and net ionic equation for the reaction. What are the names of the products? Give the molecular equation for another reaction that produces the same precipitate.

4.136 Silver nitrate reacts with strontium chloride in an aqueous precipitation reaction. What are the formulas of silver nitrate and strontium chloride? Write the molecular equation and net ionic equation for the reaction. What are the names of the products? Give the molecular equation for another reaction that produces the same precipitate.

4.137 Elemental bromine is the source of bromine compounds. The element is produced from certain brine solutions that occur naturally. These brines are essentially solutions of calcium bromide that, when treated with chlorine gas, yield bromine in a displacement reaction. What are the molecular equation and net ionic equation for the reaction? A solution containing 40.0 g of calcium bromide requires 14.2 g of chlorine to react completely with it, and 22.2 g of calcium chloride is produced in addition to whatever bromine is obtained. How many grams of calcium bromide are required to produce 10.0 pounds of bromine?

4.138 Barium carbonate is the source of barium compounds. It is produced in an aqueous precipitation reaction from barium sulfide and sodium carbonate. (Barium sulfide is a soluble compound obtained by heating the mineral barite, which is barium sulfate, with carbon.) What are the molecular equation and net ionic equation for the precipitation reaction? A solution containing 33.9 g of barium sulfide requires 21.2 g of sodium carbonate to react completely with it, and 15.6 g of sodium sulfide is produced in addition to whatever barium carbonate is obtained. How many grams of barium sulfide are required to produce 5.00 tons of barium carbonate? (One ton equals 2000 pounds.)

4.139 Mercury(II) nitrate is treated with hydrogen sulfide, H_2S, forming a precipitate and a solution. Write the molecular equation and the net ionic equation for the reaction. An acid is formed; is it strong or weak? Name each of the products. If 81.15 g of mercury(II) nitrate and 8.52 g of hydrogen sulfide are mixed in 550.0 g of water to form 58.16 g of precipitate, what is the mass of the solution after the reaction?

4.140 Mercury(II) nitrate is treated with hydrogen sulfide, H_2S, forming a precipitate and a solution. Write the molecular equation and the net ionic equation for the reaction. An acid is formed; is it strong or weak? Name each of the products. If 65.65 g of mercury(II) nitrate and 4.26 g of hydrogen sulfide are mixed in 395.0 g of water to form 54.16 g of precipitate, what is the mass of the solution after the reaction?

4.141 Iron forms a sulfide with the approximate formula Fe_7S_8. Assume that the oxidation state of sulfur is -2 and that iron atoms exist in both $+2$ and $+3$ oxidation states. What is the ratio of Fe(II) atoms to Fe(III) atoms in this compound?

4.142 A transition metal X forms an oxide of formula X_2O_3. It is found that only 50% of X atoms in this compound are in the $+3$ oxidation state. The only other stable oxidation states of X are $+2$ and $+5$. What percentage of X atoms are in the $+2$ oxidation state in this compound?

4.143 What volume of a solution of ethanol, C_2H_6O, that is 94.0% ethanol by mass contains 0.200 mol C_2H_6O? The density of the solution is 0.807 g/mL.

4.144 What volume of a solution of ethylene glycol, $C_2H_6O_2$, that is 56.0% ethylene glycol by mass contains 0.350 mol $C_2H_6O_2$? The density of the solution is 1.072 g/mL.

4.145 A 10.0-mL sample of potassium iodide solution was analyzed by adding an excess of silver nitrate solution to produce silver iodide crystals, which were filtered from the solution.

$$KI(aq) + AgNO_3(aq) \longrightarrow KNO_3(aq) + AgI(s)$$

If 2.183 g of silver iodide was obtained, what was the molarity of the original KI solution?

4.146 A 25.0-mL sample of sodium sulfate solution was analyzed by adding an excess of barium chloride solution to produce barium sulfate crystals, which were filtered from the solution.

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

If 5.719 g of barium sulfate was obtained, what was the molarity of the original Na_2SO_4 solution?

4.147 A metal, M, was converted to the sulfate, $M_2(SO_4)_3$. Then a solution of the sulfate was treated with barium chloride to give barium sulfate crystals, which were filtered off.

$$M_2(SO_4)_3(aq) + 3BaCl_2(aq) \longrightarrow 2MCl_3(aq) + 3BaSO_4(s)$$

If 1.200 g of the metal gave 6.026 g of barium sulfate, what is the atomic weight of the metal? What is the metal?

4.148 A metal, M, was converted to the chloride, MCl_2. Then a solution of the chloride was treated with silver nitrate to give silver chloride crystals, which were filtered from the solution.

$$MCl_2(aq) + 2AgNO_3(aq) \longrightarrow M(NO_3)_2(aq) + 2AgCl(s)$$

If 2.434 g of the metal gave 7.964 g of silver chloride, what is the atomic weight of the metal? What is the metal?

4.149 Phosphoric acid is prepared by dissolving phosphorus(V) oxide, P_4O_{10}, in water. What is the balanced equation for this reaction? How many grams of P_4O_{10} are required to make 1.50 L of aqueous solution containing 5.00% phosphoric acid by mass? The density of the solution is 1.025 g/mL.

4.150 Iron(III) chloride can be prepared by reacting iron metal with chlorine. What is the balanced equation for this reaction? How many grams of iron are required to make 3.00 L of aqueous solution containing 9.00% iron(III) chloride by mass? The density of the solution is 1.067 g/mL.

4.151 An alloy of aluminum and magnesium was treated with sodium hydroxide solution, in which only aluminum reacts.

$$2Al(s) + 2NaOH(aq) + 6H_2O(l) \longrightarrow 2NaAl(OH)_4(aq) + 3H_2(g)$$

If a sample of alloy weighing 1.118 g gave 0.1068 g of hydrogen, what is the percentage of aluminum in the alloy?

4.152 An alloy of iron and carbon was treated with sulfuric acid, in which only iron reacts.

$$2Fe(s) + 3H_2SO_4(aq) \longrightarrow Fe_2(SO_4)_3(aq) + 3H_2(g)$$

If a sample of alloy weighing 2.358 g gave 0.1152 g of hydrogen, what is the percentage of iron in the alloy?

4.153 Determine the volume of sulfuric acid solution needed to prepare 37.4 g of aluminum sulfate, $Al_2(SO_4)_3$, by the reaction

$$2Al(s) + 3H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 3H_2(g)$$

The sulfuric acid solution, whose density is 1.104 g/mL, contains 15.0% H_2SO_4 by mass.

4.154 Determine the volume of sodium hydroxide solution needed to prepare 26.2 g sodium phosphate, Na_3PO_4, by the reaction

$$3NaOH(aq) + H_3PO_4(aq) \longrightarrow Na_3PO_4(aq) + 3H_2O(l)$$

The sodium hydroxide solution, whose density is 1.133 g/mL, contains 12.0% NaOH by mass.

4.155 The active ingredients of an antacid tablet contained only magnesium hydroxide and aluminum hydroxide. Complete neutralization of a sample of the active ingredients required 48.5 mL of 0.187 *M* hydrochloric acid. The chloride salts from this neutralization were obtained by evaporation of the filtrate from the titration; they weighed 0.4200 g. What was the percentage by mass of magnesium hydroxide in the active ingredients of the antacid tablet?

4.156 The active ingredients in an antacid tablet contained only calcium carbonate and magnesium carbonate. Complete reaction of a sample of the active ingredients required 41.33 mL of 0.08750 *M* hydrochloric acid. The chloride salts from the reaction were obtained by evaporation of the filtrate from this titration; they weighed 0.1900 g. What was the percentage by mass of the calcium carbonate in the active ingredients of the antacid tablet?