11

Reactions in Aqueous Solutions II: Calculations

A concentrated NaOH solution added to a CH_3COOH solution that contains a large amount of phenolphthalein indicator.

OUTLINE

OBJECTIVES

After you have studied this chapter, you should be able to

- *Perform molarity calculations*
- *Solve acid–base stoichiometry calculations*
- *Describe titration and standardization*
- *Use the mole method and molarity in acid–base titration reactions*
- *Perform calculations involving equivalent weights and normality of acid and base solutions*
- *Balance oxidation–reduction equations*
- *Perform calculations associated with redox reactions*

AQUEOUS ACID–BASE REACTIONS

Digestive juice is the acidic fluid secreted by glands in the lining of the stomach.

Hydrochloric acid, HCl, is called “stomach acid” because it is the main acid (≈0.10 *M*) in our digestive juices. When the concentration of HCl is too high in humans, problems result. These problems may range from “heartburn” to ulcers that can eat through the lining of the stomach wall. Snakes have very high concentrations of HCl in their digestive juices so that they can digest whole small animals and birds.

Automobile batteries contain 40% H_2SO_4 by mass. When the battery has “run down,” the concentration of H_2SO_4 is significantly lower than 40%. A technician checks an automobile battery by drawing some battery acid into a hydrometer, which indicates the density of the solution. This density is related to the concentration of H_2SO_4.

There are many practical applications of acid–base chemistry in which we must know the concentration of a solution of an acid or a base.

11-1 CALCULATIONS INVOLVING MOLARITY

In Sections 3-6 through 3-8 we introduced methods for expressing concentrations of solutions and discussed some related calculations. Review of those sections will be helpful as we learn more about acid–base reactions in solutions.

In *some cases*, the neutralization reaction involves one mole of an acid reacting with one mole of a base to effect neutralization.

$$\text{HCl} + \text{NaOH} \longrightarrow \text{NaCl} + \text{H}_2\text{O}$$
$$\text{HNO}_3 + \text{KOH} \longrightarrow \text{KNO}_3 + \text{H}_2\text{O}$$

Because one mole of each acid reacts with one mole of each base in these cases, *one liter of a one-molar solution of either of these acids* reacts with *one liter of a one-molar solution of either of these bases.* These acids have only one acidic hydrogen per formula unit, and these bases have one hydroxide ion per formula unit, so one formula unit of base reacts with one formula unit of acid.

The *reaction ratio* is the relative numbers of moles of reactants and products shown in the balanced equation.

Example 11-1 *Acid–Base Reactions*

If 100. mL of 0.100 *M* HCl solution and 100. mL of 0.100 *M* NaOH are mixed, what is the molarity of the salt in the resulting solution? Assume that the volumes are additive.

Experiments have shown that volumes of dilute aqueous solutions are very nearly additive. No significant error is introduced by making this assumption. 0.100 L of NaOH solution mixed with 0.100 L of HCl solution gives 0.200 L of solution.

Plan

We first write the balanced equation for the acid–base reaction and then construct the reaction summary that shows the amounts (moles) of HCl and NaOH. We determine the amount of salt formed from the reaction summary. The final (total) volume is the sum of the volumes mixed. Then we calculate the molarity of the salt.

Solution

The following tabulation shows that equal numbers of moles of HCl and NaOH are mixed and, therefore, all of the HCl and NaOH react. The resulting solution contains only NaCl, the salt formed by the reaction, and water.

	HCl	+	NaOH	$\longrightarrow$	NaCl	+ H_2O
Rxn ratio:	1 mol		1 mol		1 mol	1 mol
Start:	$\left[0.100\ \text{L}\left(\frac{0.100\ \text{mol}}{\text{L}}\right)\right]$		$\left[0.100\ \text{L}\left(\frac{0.100\ \text{mol}}{\text{L}}\right)\right]$		0 mol	
	0.0100 mol HCl		0.0100 mol NaOH			
Change:	−0.0100 mol		−0.0100 mol		+0.0100 mol	
After rxn:	0 mol		0 mol		0.0100 mol	

The amount of water produced by the reaction is negligible.

The HCl and NaOH neutralize each other exactly, and the resulting solution contains 0.0100 mol of NaCl in 0.200 L of solution. Its molarity is

$$\underline{?}\ \frac{\text{mol NaCl}}{\text{L}} = \frac{0.0100\ \text{mol NaCl}}{0.200\ \text{L}} = 0.0500\ M\ \text{NaCl}$$

We often express the volume of a solution in milliliters rather than in liters. Likewise, we may express the amount of solute in millimoles (mmol) rather than in moles. Because one milliliter is 1/1000 of a liter and one millimole is 1/1000 of a mole, molarity also may be expressed as the number of millimoles of solute per milliliter of solution:

1 mol = 1000 mmol
1 L = 1000 mL

$$\text{molarity} = \frac{\text{no. mol}}{\text{L}} = \frac{\text{no. mmol}}{\text{mL}}$$

$$\text{Molarity} = \frac{\text{number of millimoles of solute}}{\text{number of milliliters of solution}}$$

For volumes and concentrations that are commonly used in laboratory experiments, solving problems in terms of millimoles and milliliters often involves more convenient numbers than using moles and liters. We should note also that the reaction ratio that we obtain from any balanced chemical equation is exactly the same whether we express all quantities in moles or in millimoles. We will work many problems in this chapter using millimoles and milliliters. Let us see how we might solve Example 11-1 in these terms.

As in Example 11-1 we first write the balanced equation for the acid–base reaction, and then construct the reaction summary that shows the amounts (millimoles) of NaOH and HCl. We determine the amount of salt formed from the reaction summary. The final (total) volume is the sum of the volumes mixed. Then we can calculate the molarity of the salt.

The following tabulation in the solution would become:

	HCl	+	$NaOH$	$\longrightarrow$	$NaCl$	+	H_2O
Rxn ratio:	1 mmol		1 mmol		1 mmol		1 mmol
Start:	$\left[100.\text{ mL}\left(\frac{0.100\text{ mmol}}{\text{mL}}\right)\right]$		$\left[100.\text{ mL}\left(\frac{0.100\text{ mmol}}{\text{mL}}\right)\right]$		0 mmol		
	= 10.0 mmol HCl		= 10.0 mmol NaOH				
Change:	−10.0 mmol		−10.0 mmol		+10.0 mmol		
After rxn:	0 mmol		0 mmol		10.0 mmol		

$$\underline{?}\ \frac{\text{mmol NaCl}}{\text{mL}} = \frac{10.0\text{ mmol NaCl}}{200.\text{ mL}} = \boxed{0.0500\ M\text{ NaCl}}$$

EXAMPLE 11-2 *Acid–Base Reactions*

If 100. mL of 1.00 *M* HCl and 100. mL of 0.80 *M* NaOH solutions are mixed, what are the molarities of the solutes in the resulting solution?

Plan

We proceed as we did in Example 11-1. This reaction summary shows that NaOH is the limiting reactant and that we have excess HCl.

Solution

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 5-10, Solution Concentration—Molarity.

	HCl	+	$NaOH$	$\longrightarrow$	$NaCl$	+	H_2O
Rxn ratio:	1 mmol		1 mmol		1 mmol		1 mmol
Start:	100. mmol		80. mmol		0 mmol		
Change:	−80. mmol		−80. mmol		+80. mmol		
After rxn:	20. mmol		0 mmol		80. mmol		

Because two solutes are present in the solution after reaction, we must calculate the concentrations of both.

$$\underline{?}\ \frac{\text{mmol HCl}}{\text{mL}} = \frac{20.\ \text{mmol HCl}}{200.\ \text{mL}} = \boxed{0.10\ M\ \text{HCl}}$$

$$\underline{?}\ \frac{\text{mmol NaCl}}{\text{mL}} = \frac{80.\ \text{mmol NaCl}}{200.\ \text{mL}} = \boxed{0.40\ M\ \text{NaCl}}$$

Both HCl and NaCl are strong electrolytes, so the solution is 0.10 M in $H^+(aq)$, $(0.10 + 0.40)$ $M = 0.50\ M$ in Cl^-, and 0.40 M in Na^+ ions.

You should now work Exercises 8 and 16.

Problem-Solving Tip: *Review Limiting Reactant Calculations*

To solve many of the problems in this chapter, you will need to apply the limiting reactant concept (Section 3-3). In Example 11-1, we confirm that the two reactants are initially present in the mole ratio required by the balanced chemical equation; they both react completely, so there is no excess of either one. In Example 11-2, we need to determine which reactant limits the reaction. Before you proceed, be sure you understand how the ideas of Section 3-3 are used in these examples.

In many cases more than one mole of a base will be required to neutralize completely one mole of an acid, or more than one mole of an acid will be required to neutralize completely one mole of a base.

$$\underset{1\ \text{mol}}{H_2SO_4} + \underset{2\ \text{mol}}{2NaOH} \longrightarrow \underset{1\ \text{mol}}{Na_2SO_4} + 2H_2O$$

$$\underset{2\ \text{mol}}{2HCl} + \underset{1\ \text{mol}}{Ca(OH)_2} \longrightarrow \underset{1\ \text{mol}}{CaCl_2} + 2H_2O$$

The first equation shows that one mole of H_2SO_4 reacts with two moles of NaOH. Thus, *two* liters of 1 M NaOH solution are required to neutralize one liter of 1 M H_2SO_4 solution. The second equation shows that two moles of HCl react with one mole of $Ca(OH)_2$. Thus, *two* liters of HCl solution are required to neutralize one liter of $Ca(OH)_2$ solution of equal molarity.

EXAMPLE 11-3 *Volume of Acid to Neutralize Base*

What volume of 0.00300 M HCl solution would just neutralize 30.0 mL of 0.00100 M $Ca(OH)_2$ solution?

Plan

We write the balanced equation for the reaction to determine the reaction ratio. Then we (1) convert milliliters of $Ca(OH)_2$ solution to millimoles of $Ca(OH)_2$ using molarity as a unit factor, 0.00100 mmol $Ca(OH)_2$/1.00 mL $Ca(OH)_2$ solution; (2) convert millimoles of $Ca(OH)_2$ to millimoles of HCl using the unit factor, 2 mmol HCl/1 mmol $Ca(OH)_2$ (the reaction ratio from the balanced equation); and (3) convert millimoles of HCl to milliliters of HCl solution using the unit factor, 1.00 mL HCl/0.00300 mmol HCl, that is, molarity inverted.

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 5-13, Stoichiometry of Reactions in Solution.

$$\begin{array}{c}\text{mL } Ca(OH)_2\\ \text{soln}\end{array} \longrightarrow \begin{array}{c}\text{mmol } Ca(OH)_2\\ \text{present}\end{array} \longrightarrow \begin{array}{c}\text{mmol HCl}\\ \text{needed}\end{array} \longrightarrow \begin{array}{c}\text{mL HCl(aq)}\\ \text{needed}\end{array}$$

Solution

The balanced equation for the reaction is

$$\underset{2\text{ mmol}}{2HCl} + \underset{1\text{ mmol}}{Ca(OH)_2} \longrightarrow \underset{1\text{ mmol}}{CaCl_2} + \underset{2\text{ mmol}}{2H_2O}$$

$\underline{?}$ mL HCl =

$$30.0\text{ mL } Ca(OH)_2 \times \frac{0.00100\text{ mmol } Ca(OH)_2}{1.00\text{ mL } Ca(OH)_2} \times \frac{2\text{ mmol HCl}}{1\text{ mmol } Ca(OH)_2} \times \frac{1.00\text{ mL HCl}}{0.00300\text{ mmol HCl}}$$

$$= 20.0\text{ mL HCl}$$

You should now work Exercise 18.

The balanced chemical equation allows us to construct either a mole ratio or a millimole ratio.

$$\frac{2\text{ mol HCl}}{1\text{ mol } Ca(OH)_2} \text{ or } \frac{2\text{ mmol HCl}}{1\text{ mmol } Ca(OH)_2}$$

In the preceding example we used the unit factor, 2 mol HCl/1 mol $Ca(OH)_2$, to convert moles of $Ca(OH)_2$ to moles of HCl because the balanced equation shows that two moles of HCl are required to neutralize one mole of $Ca(OH)_2$. We must always write the balanced equation and determine the *reaction ratio.*

Problem-Solving Tip: *There Is More Than One Way to Solve Some Problems*

In many problems more than one "plan" can be followed. In Example 11-3 a particular plan was used successfully. Many students can more easily visualize the solution by following a plan like that in Examples 11-1 and 11-4. We suggest that you use the plan that you find most understandable.

EXAMPLE 11-4 *Acid–Base Reactions*

If 100. mL of 1.00 *M* H_2SO_4 solution is mixed with 200. mL of 1.00 *M* KOH, what salt is produced, and what is its molarity?

Plan

We proceed as we did in Example 11-2. We note that the reaction ratio is 1 mmol of H_2SO_4 to 2 mmol of KOH to 1 mmol of K_2SO_4.

Solution

	H_2SO_4	+	2KOH	$\longrightarrow$	K_2SO_4	$+ H_2O$
Rxn ratio:	1 mmol		2 mmol		1 mmol	
Start:	$\left[100.\text{ mL}\left(\frac{1.00\text{ mmol}}{\text{mL}}\right)\right]$		$\left[200.\text{ mL}\left(\frac{1.00\text{ mmol}}{\text{mL}}\right)\right]$			
	= 100. mmol		= 200. mmol		0 mmol	
Change:	−100. mmol		−200. mmol		+100. mmol	
After rxn:	0 mmol		0 mmol		100. mmol	

The reaction produces 100. mmol of potassium sulfate. This is contained in 300. mL of solution, and so the concentration is

$$\underline{?}\ \frac{\text{mmol } K_2SO_4}{\text{mL}} = \frac{100.\ \text{mmol } K_2SO_4}{300.\ \text{mL}} = \boxed{0.333\ M\ K_2SO_4}$$

Because K_2SO_4 is a strong electrolyte, this corresponds to 0.666 M K^+ and 0.333 M SO_4^{2-}.

You should now work Exercises 10 and 14.

11-2 TITRATIONS

In Examples 3-23 and 11-3, we calculated the volume of one solution that is required to react with a given volume of another solution, with the concentrations of *both* solutions given. In the laboratory we often measure the volume of one solution that is required to react with a given volume of another solution of known concentration. Then we calculate the concentration of the first solution. The process is called **titration** (Figure 11-1).

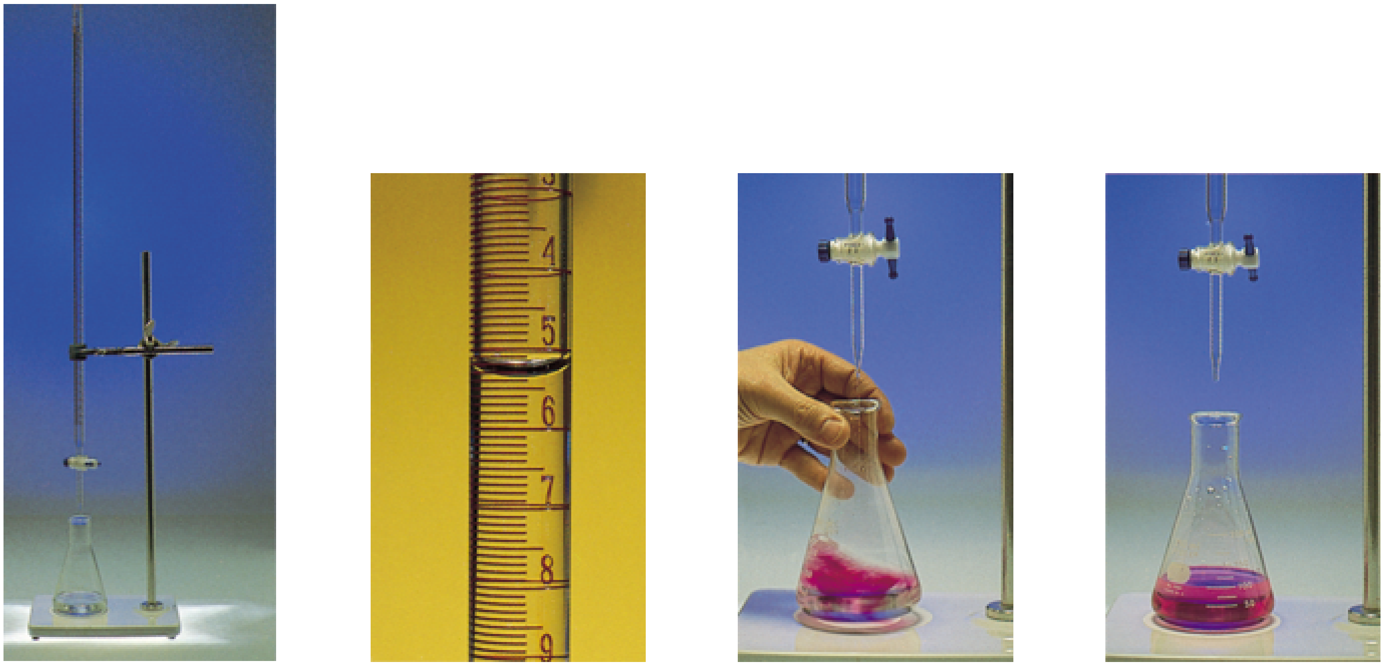

(a) **(b)** **(c)** **(d)**

Figure 11-1 The titration process. (a) A typical setup for titration in a teaching laboratory. The solution to be titrated is placed in an Erlenmeyer flask, and a few drops of indicator are added. The buret is filled with a standard solution (or the solution to be standardized). The volume of solution in the buret is read carefully. (b) The meniscus describes the surface of the liquid in the buret. Aqueous solutions wet glass, so the meniscus of an aqueous solution is always concave. The position of the *bottom* of the meniscus is read and recorded. (c) The solution in the buret is added (dropwise near the end point), with stirring, to the Erlenmeyer flask until the end point is reached. (d) The end point is signaled by the appearance (or change) of color *throughout* the solution being titrated. (A very large excess of indicator was used to make this photograph.) The volume of the liquid is read again—the difference between the final and initial buret readings is the volume of the solution used.

> Titration is the process in which a solution of one reactant, the titrant, is carefully added to a solution of another reactant, and the volume of titrant required for complete reaction is measured.

How does one know when to stop a titration—that is, when is the chemical reaction just complete? In one method, a few drops of an *indicator* solution are added to the solution to be titrated. An **indicator** is a substance that can exist in different forms, with different colors that depend on the concentration of H^+ in the solution. At least one of these forms must be very intensely colored so that even very small amounts of it can be seen.

We can titrate an acid solution of unknown concentration by adding a standardized solution of sodium hydroxide dropwise from a **buret** (see Figure 11-1). A common buret is graduated in large intervals of 1 mL and in smaller intervals of 0.1 mL so that it is possible to estimate the volume of a solution dispensed to within at least ±0.02 mL. (Experienced individuals can often read a buret to ±0.01 mL.) The analyst tries to choose an indicator that changes color clearly at the point at which stoichiometrically equivalent amounts of acid and base have reacted, the **equivalence point.** The point at which the indicator changes color and the titration is stopped is called the **end point.** Ideally, the end point should coincide with the equivalence point. Phenolphthalein is colorless in acidic solution and reddish violet in basic solution. In a titration in which a base is added to an acid, phenolphthalein is often used as an indicator. The end point is signaled by the first appearance of a faint pink coloration that persists for at least 15 seconds as the solution is swirled.

The choice of indicators will be discussed in Section 19.4.

EXAMPLE 11-5 *Titration*

What is the molarity of a hydrochloric acid solution if 36.7 mL of the HCl solution is required to react with 43.2 mL of 0.236 *M* sodium hydroxide solution?

$$\mathrm{HCl + NaOH \longrightarrow NaCl + H_2O}$$

Plan

The balanced equation tells us that the reaction ratio is one millimole of HCl to one millimole of NaOH, which gives the unit factor, 1 mmol HCl/1 mmol NaOH.

$$\underset{1\text{ mmol}}{\mathrm{HCl}} + \underset{1\text{ mmol}}{\mathrm{NaOH}} \longrightarrow \underset{1\text{ mmol}}{\mathrm{NaCl}} + \underset{1\text{ mmol}}{\mathrm{H_2O}}$$

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 5-15, Titration Simulation.

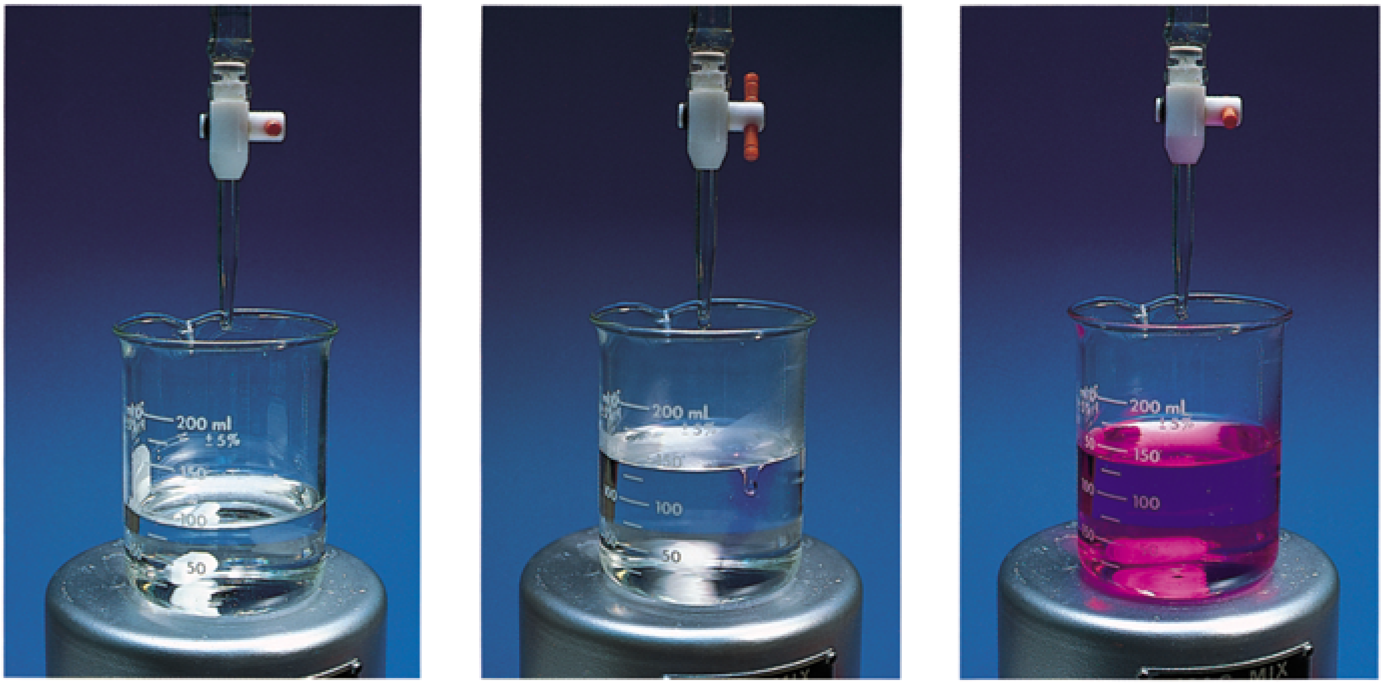
First we find the number of millimoles of NaOH. The reaction ratio is one millimole of HCl to one millimole of NaOH, so the HCl solution must contain the same number of millimoles of HCl. Then we can calculate the molarity of the HCl solution because we know its volume.

Solution

The volume of a solution (in milliliters) multiplied by its molarity gives the number of millimoles of solute.

$$\underline{?}\text{ mmol NaOH} = 43.2\text{ mL NaOH soln} \times \frac{0.236\text{ mmol NaOH}}{1\text{ mL NaOH soln}} = 10.2\text{ mmol NaOH}$$

Because the reaction ratio is one millimole of NaOH to one millimole of HCl, the HCl solution must contain 10.2 millimoles of HCl.



The indicator phenolphthalein changes from colorless, its color in acidic solutions, to pink, its color in basic solutions, when the reaction in Example 11-5 reaches completion. Note the first appearance of a faint pink coloration in the middle beaker; this signals that the end point is near.

$$\underline{?}\text{ mol HCl} = 10.2\text{ mmol NaOH} \times \frac{1\text{ mmol HCl}}{1\text{ mmol NaOH}} = 10.2\text{ mmol HCl}$$

We know the volume of the HCl solution, so we can calculate its molarity.

$$\frac{\underline{?}\text{ mmol HCl}}{\text{mL HCl soln}} = \frac{10.2\text{ mmol HCl}}{36.7\text{ mL HCl soln}} = 0.278\ M\text{ HCl}$$

EXAMPLE 11-6 *Titration*

A 43.2-mL sample of 0.236 *M* sodium hydroxide solution reacts completely with 36.7 mL of a sulfuric acid solution. What is the molarity of the H_2SO_4 solution?

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$$

Plan

The balanced equation tells us that the reaction ratio is one millimole of H_2SO_4 to two millimoles of NaOH, which gives the unit factor, 1 mmol H_2SO_4/2 mmol NaOH.

$$\underset{1\text{ mmol}}{H_2SO_4} + \underset{2\text{ mmol}}{2NaOH} \longrightarrow \underset{1\text{ mmol}}{Na_2SO_4} + \underset{2\text{ mmol}}{2H_2O}$$

First we find the number of millimoles of NaOH. The reaction ratio is one millimole of H_2SO_4 to two millimoles of NaOH, so the number of millimoles of H_2SO_4 must be one half of the number of millimoles of NaOH. Then we can calculate the molarity of the H_2SO_4 solution because we know its volume.

Solution

The volume of a solution (in milliliters) multiplied by its molarity gives the number of millimoles of solute.

$$\underline{?}\text{ mmol NaOH} = 43.2\text{ mL NaOH soln} \times \frac{0.236\text{ mmol NaOH}}{1\text{ mL NaOH soln}} = 10.2\text{ mmol NaOH}$$

Because the reaction ratio is two millimoles of NaOH to one millimole of H_2SO_4, the H_2SO_4 solution must contain 5.10 millimoles of H_2SO_4.

$$\underline{?}\text{ mmol } H_2SO_4 = 10.2\text{ mmol NaOH} \times \frac{1\text{ mmol } H_2SO_4}{2\text{ mmol NaOH}} = 5.10\text{ mmol } H_2SO_4$$

We know the volume of the H_2SO_4 solution, so we can calculate its molarity.

$$\frac{\underline{?}\text{ mmol } H_2SO_4}{\text{mL } H_2SO_4\text{ soln}} = \frac{5.10\text{ mmol } H_2SO_4}{36.7\text{ mL } H_2SO_4\text{ soln}} = 0.139\ M\ H_2SO_4$$

Notice the similarity between Examples 11-5 and 11-6 in which 43.2 mL of 0.236 *M* NaOH solution is used. In Example 11-5 the reaction ratio is 1 mmol acid/1 mmol base, whereas in Example 11-6 the reaction ratio is 1 mmol acid/2 mmol base, and so the molarity of the HCl solution (0.278 *M*) is twice the molarity of the H_2SO_4 solution (0.139 *M*).

You should now work Exercise 40.

Solutions of accurately known concentrations are called **standard solutions.** Often we prepare solutions of such substances and then determine their concentrations by titration with a standard solution.

Standardization is the process by which one determines the concentration of a solution by measuring accurately the volume of the solution required to react with an exactly known amount of a **primary standard.** The standardized solution is then known as a **secondary standard** and is used in the analysis of unknowns.

The properties of an ideal *primary standard* include the following.

CO_2, H_2O, and O_2 are present in the atmosphere. They react with many substances.

1. It must not react with or absorb the components of the atmosphere, such as water vapor, oxygen, and carbon dioxide.
2. It must react according to one invariable reaction.
3. It must have a high percentage purity.
4. It should have a high formula weight to minimize the effect of error in weighing.
5. It must be soluble in the solvent of interest.
6. It should be nontoxic.
7. It should be readily available (inexpensive).
8. It should be environmentally friendly.

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 5-14, Titrations.

The first five of these characteristics are essential to minimize the errors involved in analytical methods. The last three characteristics are just as important as the first five in most analytical laboratories. Because primary standards are often costly and difficult to prepare, secondary standards are often used in day-to-day work.

11-3 THE MOLE METHOD AND MOLARITY

Let us now describe the use of a few primary standards for acids and bases. One primary standard for solutions of acids is sodium carbonate, Na_2CO_3, a solid compound.

$$\underset{1\text{ mol}}{H_2SO_4} + \underset{1\text{ mol}}{Na_2CO_3} \longrightarrow \underset{1\text{ mol}}{Na_2SO_4} + \underset{1\text{ mol}}{CO_2} + \underset{1\text{ mol}}{H_2O}$$

$$1\text{ mol } Na_2CO_3 = 106.0\text{ g} \qquad \text{and} \qquad 1\text{ mmol } Na_2CO_3 = 0.1060\text{ g}$$

Refer to the Brønsted–Lowry theory. (Section 10-4).

Sodium carbonate is a salt. Because a base can be broadly defined as a substance that reacts with hydrogen ions, in *this* reaction Na_2CO_3 can be thought of as a base.

EXAMPLE 11-7 *Standardization of an Acid Solution*

Calculate the molarity of a solution of H_2SO_4 if 40.0 mL of the solution neutralizes 0.364 gram of Na_2CO_3.

Plan

We know from the balanced equation that 1 mol of H_2SO_4 reacts with 1 mol of Na_2CO_3, 106.0 g. This provides the unit factors that convert 0.364 g of Na_2CO_3 to the corresponding number of moles of H_2SO_4, from which we can calculate molarity.

g Na_2CO_3 available ⟶ mol Na_2CO_3 present ⟶ mol H_2SO_4 used ⟶ molarity of H_2SO_4

Solution

$$\underline{?}\text{ mol } H_2SO_4 = 0.364\text{ g } Na_2CO_3 \times \frac{1\text{ mol } Na_2CO_3}{106.0\text{ g } Na_2CO_3} \times \frac{1\text{ mol } H_2SO_4}{1\text{ mol } Na_2CO_3}$$

$$= 0.00343\text{ mol } H_2SO_4 \quad \text{(present in 40.0 mL of solution)}$$

Now we calculate the molarity of the H_2SO_4 solution

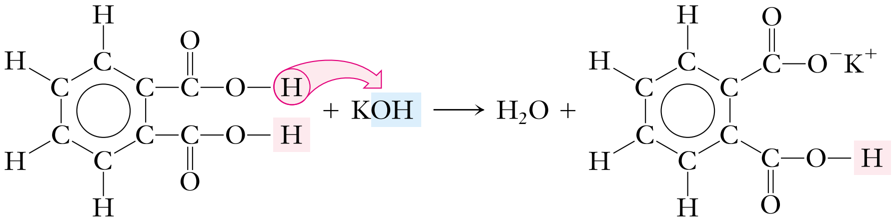
$$\frac{\underline{?}\text{ mol } H_2SO_4}{\text{L}} = \frac{0.00343\text{ mol } H_2SO_4}{0.0400\text{ L}} = \boxed{0.0858\ M\ H_2SO_4}$$

You should now work Exercise 28.

Sodium carbonate is often used as a primary standard for acids.

Most inorganic bases are metal hydroxides, all of which are solids. Even in the solid state, however, most inorganic bases react rapidly with CO_2 (an acid anhydride) from the atmosphere. Most metal hydroxides also absorb H_2O from the air. These properties make it *very* difficult to accurately weigh out samples of pure metal hydroxides. Chemists obtain solutions of bases of accurately known concentration by standardizing the solutions against an acidic salt, potassium hydrogen phthalate, $KC_6H_4(COO)(COOH)$. This is produced by neutralization of one of the two ionizable hydrogens of an organic acid, phthalic acid.

The "ph" in *phthalate* is silent. Phthalate is pronounced "thalate."



$C_6H_4(COOH)_2$
phthalic acid

$KC_6H_4(COO)(COOH)$
potassium hydrogen
phthalate (KHP)

This acidic salt, known simply as KHP, has one acidic hydrogen (highlighted) that reacts with bases. KHP is easily obtained in a high state of purity, and is soluble in water. It is used as a primary standard for bases.

The P in KHP stands for the phthalate ion, $C_6H_4(COO)_2^{2-}$, *not* phosphorus.

EXAMPLE 11-8 *Standardization of Base Solution*

A 20.00-mL sample of a solution of NaOH reacts with 0.3641 gram of KHP. Calculate the molarity of the NaOH solution.

Very pure KHP is readily available.

Plan

We first write the balanced equation for the reaction between NaOH and KHP. We then calculate the number of moles of NaOH in 20.00 mL of solution from the amount of KHP that reacts with it. Then we can calculate the molarity of the NaOH solution.

g KPH available ⟶ mol KHP available ⟶ mol NaOH required ⟶ molarity of NaOH

Solution

$$\underset{1\text{ mol}}{\text{NaOH}} + \underset{1\text{ mol}}{\text{KHP}} \longrightarrow \underset{1\text{ mol}}{\text{NaKP}} + \underset{1\text{ mol}}{\text{H}_2\text{O}}$$

We see that NaOH and KHP react in a 1 : 1 mole ratio. One mole of KHP is 204.2 g.

$$\underline{?}\text{ mol NaOH} = 0.3641\text{ g KHP} \times \frac{1\text{ mol KHP}}{204.2\text{ g KHP}} \times \frac{1\text{ mol NaOH}}{1\text{ mol KHP}} = 0.001783\text{ mol NaOH}$$

Then we calculate the molarity of the NaOH solution.

$$\frac{\underline{?}\text{ mol NaOH}}{\text{L}} = \frac{0.001783\text{ mol NaOH}}{0.02000\text{ L}} = \boxed{0.08915\ M\text{ NaOH}}$$

You should now work Exercise 30.

Impure samples of acids can be titrated with standard solutions of bases. The results can be used to determine percentage purity of the samples.

EXAMPLE 11-9 *Determination of Percent Acid*

Oxalic acid, $(COOH)_2$, is used to remove rust stains and some ink stains from fabrics. A 0.1743-gram sample of *impure* oxalic acid required 39.82 mL of 0.08915 *M* NaOH solution for complete neutralization. No acidic impurities were present. Calculate the percentage purity of the $(COOH)_2$.

Plan

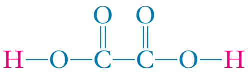
We write the balanced equation for the reaction and calculate the number of moles of NaOH in the standard solution. Then we calculate the mass of $(COOH)_2$ in the sample, which gives us the information we need to calculate percentage purity.

Solution

The equation for the complete neutralization of $(COOH)_2$ with NaOH is

$$\underset{2\text{ mol}}{2\text{NaOH}} + \underset{1\text{ mol}}{(\text{COOH})_2} \longrightarrow \underset{1\text{ mol}}{\text{Na}_2(\text{COO})_2} + \underset{2\text{ mol}}{2\text{H}_2\text{O}}$$

Each molecule of $(COOH)_2$ contains two acidic H's.



$$\text{H—O—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—O—H}$$

1 mol = 90.04 g

Two moles of NaOH neutralizes completely one mole of $(COOH)_2$. The number of moles of NaOH that react is the volume times the molarity of the solution.

$$\underline{?}\text{ mol NaOH} = 0.03982\text{ L} \times \frac{0.08915\text{ mol NaOH}}{\text{L}} = 0.003550\text{ mol NaOH}$$

Now we calculate the mass of $(COOH)_2$ that reacts with 0.003550 mol NaOH.

$$\underline{?}\text{ g }(\text{COOH})_2 = 0.003550\text{ mol NaOH} \times \frac{1\text{ mol }(\text{COOH})_2}{2\text{ mol NaOH}} \times \frac{90.04\text{ g }(\text{COOH})_2}{1\text{ mol }(\text{COOH})_2}$$

$$= 0.1598\text{ g }(\text{COOH})_2$$

The 0.1743-g sample contained 0.1598 g of $(\text{COOH})_2$, so its percentage purity was

$$\%\text{ purity} = \frac{0.1598\text{ g }(\text{COOH})_2}{0.1743\text{ g sample}} \times 100\% = \boxed{91.68\%\text{ pure }(\text{COOH})_2}$$

You should now work Exercise 36.

11-4 EQUIVALENT WEIGHTS AND NORMALITY

Because one mole of an acid does not necessarily neutralize one mole of a base, some chemists prefer a method of expressing concentration other than molarity to retain a one-to-one relationship. Concentrations of solutions of acids and bases are frequently expressed as *normality* (N). The **normality** of a solution is defined as the number of equivalent weights, or simply equivalents (eq), of solute per liter of solution. Normality may be represented symbolically as

Any calculation that can be carried out with equivalent weights and normality can also be done by the mole method using molarity. The methods of this section are widely used, however, in health-related fields and in many industrial laboratories.

$$\text{Normality} = \frac{\text{number of equivalent weights of solute}}{\text{liter of solution}} = \frac{\text{no. eq}}{\text{L}}$$

An **equivalent weight** is often referred to simply as an **equivalent** (eq).

By definition there are 1000 milliequivalent weights (meq) in one equivalent weight of an acid or base. Normality may also be represented as

$$\text{Normality} = \frac{\text{number of milliequivalent weights of solute}}{\text{milliliter of solution}} = \frac{\text{no. meq}}{\text{mL}}$$

A **milliequivalent weight** is often referred to simply as a **milliequivalent** (meq).

In acid–base reactions, one **equivalent weight,** or **equivalent (eq), of an acid** is defined as the mass of the acid (expressed in grams) that could furnish 6.022×10^{23} hydrogen ions (1 mol) or that could react with 6.022×10^{23} hydroxide ions (1 mol). One mole of an acid contains 6.022×10^{23} formula units of the acid. Consider hydrochloric acid as a typical monoprotic acid.

$$\begin{array}{cccc}
\text{HCl} & \xrightarrow{\text{H}_2\text{O}} \ \text{H}^+(aq) & + & \text{Cl}^-(aq) \\
1\text{ mol} & 1\text{ mol} & & 1\text{ mol} \\
36.46\text{ g} & 1.008\text{ g} & & 35.45\text{ g} \\
6.022 \times 10^{23} & 6.022 \times 10^{23} & & 6.022 \times 10^{23} \\
\text{formula units} & \text{formula units} & & \text{formula units}
\end{array}$$

We see that one mole of HCl can produce 6.022×10^{23} H^+ ions, and so *one mole of HCl is one equivalent.* The same is true for all monoprotic acids.

TABLE 11-1 *Equivalent Weights* of Some Acids and Bases*

Acids		Bases	
Symbolic representation	*One eq*	*Symbolic representation*	*One eq*
$\frac{HNO_3}{1} = \frac{63.02\ g}{1}$	$= 63.02\ g\ HNO_3$	$\frac{NaOH}{1} = \frac{40.00\ g}{1}$	$= 40.00\ g\ NaOH$
$\frac{CH_3COO\underline{H}}{1} = \frac{60.03\ g}{1}$	$= 60.03\ g\ CH_3COO\underline{H}$	$\frac{NH_3}{1} = \frac{17.04\ g}{1}$	$= 17.04\ g\ NH_3$
$\frac{K\underline{H}P}{1} = \frac{204.2\ g}{1}$	$= 204.2\ g\ K\underline{H}P$	$\frac{Ca(OH)_2}{2} = \frac{74.10\ g}{2}$	$= 37.05\ g\ Ca(OH)_2$
$\frac{H_2SO_4}{2} = \frac{98.08\ g}{2}$	$= 49.04\ g\ H_2SO_4$	$\frac{Ba(OH)_2}{2} = \frac{171.36\ g}{2}$	$= 85.68\ g\ Ba(OH)_2$

**Complete neutralization is assumed.*

One mole of H_2SO_4 is two equivalent weights of H_2SO_4.

Sulfuric acid is a diprotic acid. One molecule of H_2SO_4 can furnish $2H^+$ ions.

$$\begin{array}{ccccc} H_2SO_4 & \xrightarrow{H_2O} & 2H^+(aq) & + & SO_4{}^{2-}(aq) \\ \text{1 mol} & & \text{2 mol} & & \text{1 mol} \\ \text{98.08 g} & & \text{2(1.008 g)} & & \text{96.06 g} \\ 6.022 \times 10^{23} & & 2(6.022 \times 10^{23}) & & 6.022 \times 10^{23} \\ \text{formula units} & & \text{formula units} & & \text{formula units} \end{array}$$

This equation shows that one mole of H_2SO_4 can produce $2(6.022 \times 10^{23})\ H^+$; therefore, one mole of H_2SO_4 is *two* equivalent weights in all reactions in which *both* acidic hydrogen atoms react.

One **equivalent weight of a base** is defined as the mass of the base (expressed in grams) that will furnish 6.022×10^{23} hydroxide ions or the mass of the base that will react with 6.022×10^{23} hydrogen ions.

The equivalent weight of an *acid* is obtained by dividing its formula weight in grams either by the number of acidic hydrogens that could be furnished by one formula unit of the acid *or* by the number of hydroxide ions with which one formula unit of the acid reacts. The equivalent weight of a *base* is obtained by dividing its formula weight in grams either by the number of hydroxide ions furnished by one formula unit *or* by the number of hydrogen ions with which one formula unit of the base reacts. Equivalent weights of some common acids and bases are given in Table 11-1.

EXAMPLE 11-10 *Concentration of a Solution*

Calculate the normality of a solution of 4.202 grams of HNO_3 in 600. mL of solution.

Plan

We convert grams of HNO_3 to moles of HNO_3 and then to equivalents of HNO_3, which lets us calculate the normality.

$$\frac{g\ HNO_3}{L} \longrightarrow \frac{mol\ HNO_3}{L} \longrightarrow \frac{eq\ HNO_3}{L} = N\ HNO_3$$

Solution

$$N = \frac{\text{no. eq HNO}_3}{\text{L}}$$

$$\underline{?}\ \frac{\text{eq HNO}_3}{\text{L}} = \underbrace{\frac{4.202\text{ g HNO}_3}{0.600\text{ L}} \times \frac{1\text{ mol HNO}_3}{63.02\text{ g HNO}_3}}_{M_{\text{HNO}_3}} \times \frac{1\text{ eq HNO}_3}{\text{mol HNO}_3} = \boxed{0.111\ N\ \text{HNO}_3}$$

Because normality is equal to molarity times the number of equivalents per mole of solute, a solution's normality is always equal to or greater than its molarity.

$$\text{Normality} = \text{molarity} \times \frac{\text{no. eq}}{\text{mol}} \quad \text{or} \quad N = M \times \frac{\text{no. eq}}{\text{mol}}$$

EXAMPLE 11-11 *Concentration of a Solution*

Calculate (a) the molarity and (b) the normality of a solution that contains 9.50 grams of barium hydroxide in 2000. mL of solution.

Plan

(a) We use the same kind of logic we used in Example 11-10.

(b) Because each mole of $Ba(OH)_2$ produces 2 moles of OH^- ions, 1 mole of $Ba(OH)_2$ is 2 equivalents. Thus,

$$N = M \times \frac{2\text{ eq}}{\text{mol}} \quad \text{or} \quad M = \frac{N}{2\text{ eq/mol}}$$

Solution

(a) $\underline{?}\ \frac{\text{mol Ba(OH)}_2}{\text{L}} = \frac{9.50\text{ g Ba(OH)}_2}{2.00\text{ L}} \times \frac{1\text{ mol Ba (OH)}_2}{171.36\text{ g Ba(OH)}_2} = \boxed{0.0277\ M\ \text{Ba(OH)}_2}$

(b) $\underline{?}\ \frac{\text{eq Ba(OH)}_2}{\text{L}} = \frac{0.0277\text{ mol Ba(OH)}_2}{\text{L}} \times \frac{2\text{ eq Ba(OH)}_2}{1\text{ mol Ba(OH)}_2} = \boxed{0.0554\ N\ \text{Ba(OH)}_2}$

You should now work Exercises 42 through 44.

Because each formula unit of $Ba(OH)_2$ contains two OH^- ions,

$$1\text{ mol Ba(OH)}_2 = 2\text{ eq Ba(OH)}_2$$

Thus, molarity is one half of normality for $Ba(OH)_2$ solutions.

From the definitions of one equivalent of an acid and of a base, we see that *one equivalent of an acid reacts with one equivalent of any base.* It is *not* true that one mole of any acid reacts with one mole of any base in any specific chemical reaction that goes to completion. As a consequence of the definition of equivalents, 1 eq acid ≅ 1 eq base. We may write the following for *all* acid–base reactions that go to completion.

The notation ≅ is read "is equivalent to."

Number of equivalents of acid = number of equivalents of base

The product of the volume of a solution, in liters, and its normality is equal to the number of equivalents of solute contained in the solution. For a solution of an acid,

$$\text{L}_{\text{acid}} \times N_{\text{acid}} = \text{L}_{\text{acid}} \times \frac{\text{eq acid}}{\text{L}_{\text{acid}}} = \text{eq acid}$$

Remember that the product of volume and concentration equals the amount of solute.

Similar relationships can be written for a solution of a base. Because 1 eq of acid *always* reacts with 1 eq of base, we may write

$$\text{Number of equivalents of acid} = \text{number of equivalents of base}$$

so

$$\text{L}_{\text{acid}} \times N_{\text{acid}} = \text{L}_{\text{base}} \times N_{\text{base}} \qquad \text{or} \qquad \text{mL}_{\text{acid}} \times N_{\text{acid}} = \text{mL}_{\text{base}} \times N_{\text{base}}$$

The conversion factors needed to convert liters to milliliters on each side of this equation will cancel.

EXAMPLE 11-12 *Volume Required for Neutralization*

What volume of 0.100 N HNO_3 solution is required to neutralize completely 50.0 mL of a 0.150 N solution of $Ba(OH)_2$?

Plan

We know three of the four variables in the relationship

$$\text{mL}_{\text{acid}} \times N_{\text{acid}} = \text{mL}_{\text{base}} \times N_{\text{base}}, \text{ and so we solve for } \text{mL}_{\text{acid}}.$$

Solution

$$\underline{?}\ \text{mL}_{\text{acid}} = \frac{\text{mL}_{\text{base}} \times N_{\text{base}}}{N_{\text{acid}}} = \frac{50.0\ \text{mL} \times 0.150\ N}{0.100\ N} = \boxed{75.0\ \text{mL of } HNO_3 \text{ solution}}$$

You should now work Exercise 48.

In Example 11-13 let us again solve Example 11-7, this time using normality rather than molarity. The balanced equation for the reaction of H_2SO_4 with Na_2CO_3, interpreted in terms of equivalent weights, is

$$\begin{array}{ccccccccc} H_2SO_4 & + & Na_2CO_3 & \longrightarrow & Na_2SO_4 & + & CO_2 & + & H_2O \\ \text{1 mol} & & \text{1 mol} & & \text{1 mol} & & \text{1 mol} & & \text{1 mol} \\ \text{2 eq} & & \text{2 eq} & & \text{2 eq} & & \text{2 eq} & & \text{2 eq} \\ \text{98.08 g} & & \text{106.0 g} & & & & & & \end{array}$$

By definition, there must be equal numbers of equivalents of all reactants and products in a balanced chemical equation.

So, 1 eq Na_2CO_3 = 53.0 g

EXAMPLE 11-13 *Standardization of Acid Solution*

Calculate the normality of a solution of H_2SO_4 if 40.0 mL of the solution reacts completely with 0.364 gram of Na_2CO_3.

Plan

We refer to the balanced equation. We are given the mass of Na_2CO_3, so we convert grams of Na_2CO_3 to equivalents of Na_2CO_3, then to equivalents of H_2SO_4, which lets us calculate the normality of the H_2SO_4 solution.

$$\boxed{\begin{array}{c}\text{g } Na_2CO_3 \\ \text{present}\end{array}} \longrightarrow \boxed{\begin{array}{c}\text{eq } Na_2CO_3 \\ \text{present}\end{array}} \longrightarrow \boxed{\begin{array}{c}\text{eq } H_2SO_4 \\ \text{needed}\end{array}} \longrightarrow \boxed{\frac{\text{eq } H_2SO_4}{\text{L}}}$$

Automatic titrators are used in modern analytical laboratories. Such titrators rely on electrical properties of the solutions. Methyl red indicator changes from yellow to red at the end point of this titration.

Solution

First we calculate the number of equivalents of Na_2CO_3 in the sample.

$$\text{no. eq } Na_2CO_3 = 0.364 \text{ g } Na_2CO_3 \times \frac{1 \text{ eq } Na_2CO_3}{53.0 \text{ g } Na_2CO_3} = 6.87 \times 10^{-3} \text{ eq } Na_2CO_3$$

Because no. eq H_2SO_4 = no. eq Na_2CO_3, we can write

$$L_{H_2SO_4} \times N_{H_2SO_4} = 6.87 \times 10^{-3} \text{ eq } H_2SO_4$$

$$N_{H_2SO_4} = \frac{6.87 \times 10^{-3} \text{ eq } H_2SO_4}{L_{H_2SO_4}} = \frac{6.87 \times 10^{-3} \text{ eq } H_2SO_4}{0.040 \text{ L}} = \boxed{0.172\ N\ H_2SO_4}$$

You should now work Exercise 50.

The starting values in this example are the same as those in Example 11-7. The normality of this H_2SO_4 solution is twice the molarity obtained in Example 11-7 because 1 mol of H_2SO_4 is 2 eq.

OXIDATION–REDUCTION REACTIONS

Our rules for assigning oxidation numbers are constructed so that in all redox reactions

> the total increase in oxidation numbers must equal the total decrease in oxidation numbers.

This equivalence provides the basis for balancing redox equations. Although there is no single "best method" for balancing all redox equations, two methods are particularly useful: (1) the half-reaction method, which is used extensively in electrochemistry (Chapter 21) and (2) the change-in-oxidation-number method. Many redox equations can be balanced by simple inspection, but you should master one of these systematic methods so it can be used to balance difficult equations.

Most redox equations can be balanced by both methods, but in some instances one may be easier to use than the other.

All balanced equations must satisfy two criteria.

1. There must be mass balance. That is, the same number of atoms of each kind must appear in reactants and products.
2. There must be charge balance. The sums of actual charges on the left and right sides of the equation must equal each other. In a balanced *formula unit equation*, the total charge on each side will be equal to zero. In a balanced *net ionic equation*, the total charge on each side might not be zero, but it still must be equal on the two sides of the equation.

11-5 THE HALF-REACTION METHOD

In the half-reaction method we separate and completely balance equations describing oxidation and reduction **half-reactions.** Then we equalize the numbers of electrons gained and lost in each. Finally, we add the resulting half-reactions to give the overall balanced equation. The general procedure follows.

For brevity, we will refer to this as the HR method. It is sometimes referred to as the ion–electron method.

1. Write as much of the overall unbalanced equation as possible, omitting spectator ions.
2. Construct unbalanced oxidation and reduction half-reactions (these are usually incomplete as well as unbalanced). Show complete formulas for polyatomic ions and molecules.
3. Balance by inspection all elements in each half-reaction, except H and O. Then use the chart in Section 11-6 to balance H and O in each half-reaction.
4. Balance the charge in each half-reaction by adding electrons as “products” or “reactants.”
5. Balance the electron transfer by multiplying the balanced half-reactions by appropriate integers.
6. Add the resulting half-reactions and eliminate any common terms.

EXAMPLE 11-14 *Balancing Redox Equations (HR method)*

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 21-3, Balancing Equations for Redox Reactions.

A useful analytical procedure involves the oxidation of iodide ions to free iodine. The free iodine is then titrated with a standard solution of sodium thiosulfate, $Na_2S_2O_3$. Iodine oxidizes $S_2O_3^{2-}$ ions to tetrathionate ions, $S_4O_6^{2-}$, and is reduced to I^- ions. Write the balanced net ionic equation for this reaction.

Plan

We are given the formulas for two reactants and two products. We use these to write as much of the equations as possible. We construct and balance the appropriate half-reactions using the rules just described. Then we add the half-reactions and eliminate common terms.

Solution

$$
\begin{aligned}
I_2 + S_2O_3^{2-} &\longrightarrow I^- + S_4O_6^{2-} & & \\
I_2 &\longrightarrow I^- & & \text{(red. half-reaction)} \\
I_2 &\longrightarrow 2I^- & & \\
I_2 + 2e^- &\longrightarrow 2I^- & & \text{(balanced red. half-reaction)}
\end{aligned}
$$

$$
\begin{aligned}
S_2O_3^{2-} &\longrightarrow S_4O_6^{2-} & & \text{(ox. half-reaction)} \\
2S_2O_3^{2-} &\longrightarrow S_4O_6^{2-} & & \\
2S_2O_3^{2-} &\longrightarrow S_4O_6^{2-} + 2e^- & & \text{(balanced ox. half-reaction)}
\end{aligned}
$$

Each I_2 gains $2e^-$. I_2 is reduced; it is the oxidizing agent.

Each $S_2O_3^{2-}$ ion loses an e^-. $S_2O_3^{2-}$ is oxidized; it is the reducing agent.

Each balanced half-reaction involves a transfer of two electrons. We add these half-reactions and cancel the electrons.

$$
\begin{aligned}
I_2 + 2e^- &\longrightarrow 2I^- \\
2S_2O_3^{2-} &\longrightarrow S_4O_6^{2-} + 2e^- \\
\hline
I_2(s) + 2S_2O_3^{2-}(aq) &\longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)
\end{aligned}
$$

11-6 ADDING H⁺, OH⁻, OR H₂O TO BALANCE OXYGEN OR HYDROGEN

Frequently we need more oxygen or hydrogen to complete the mass balance for a reaction or half-reaction in aqueous solution. We must be careful, however, not to introduce other changes in oxidation number or to use species that could not actually be present in the solution. We cannot add H_2 or O_2 to equations because these species are not present in aqueous solutions. Acidic solutions do not contain significant concentrations of OH^- ions. Basic solutions do not contain significant concentrations of H^+ ions.

In acidic solution:	We add only H^+ or H_2O (*not* OH^- in acidic solution).
In basic solution:	We add only OH^- or H_2O (*not* H^+ in basic solution).

The following chart shows how to balance hydrogen and oxygen.

	To balance O:		To balance H:
In Acidic Solution:	Add H_2O	and $\longrightarrow$ then	Add H^+
In Basic Solution:	For *each* O needed, (1) add *two* OH^- to side needing O and (2) add *one* H_2O to other side	and $\longrightarrow$ then	For *each* H needed, (1) add *one* H_2O to side needing H and (2) add *one* OH^- to other side

When balancing redox equations, we often find it convenient to omit the spectator ions (Section 4-3) so that we can focus on the oxidation and reduction processes. We use the methods presented in this chapter to balance the net ionic equation. If necessary we add the spectator ions and combine species to write the balanced formula unit equation. Examples 11-15 and 11-16 illustrate this approach.

In Section 4-3, we first wrote the *formula unit equation.* We separated any ionized or dissociated species into ions to obtain the *total ionic equation.* Then we eliminated the spectator ions to obtain the *net ionic equation.* In Examples 11-15 and 11-16, we reverse the procedure.

EXAMPLE 11-15 *Net Ionic Equations*

Permanganate ions oxidize iron(II) to iron(III) in sulfuric acid solution. Permanganate ions are reduced to manganese(II) ions. Write the balanced net ionic equation for this reaction.

Plan

We use the given information to write as much of the equation as possible. Then we follow steps 2 through 6 in Section 11-5. The reaction occurs in H_2SO_4 solution; we can add H^+ and H_2O as needed to balance H and O in the half-reactions (Step 3).

Solution

$$\mathrm{Fe^{2+} + MnO_4^- \longrightarrow Fe^{3+} + Mn^{2+}}$$

$$\mathrm{Fe^{2+} \longrightarrow Fe^{3+}} \qquad \text{(ox. half-reaction)}$$

$$\mathrm{Fe^{2+} \longrightarrow Fe^{3+} + 1}e^- \qquad \text{(balanced ox. half-reaction)}$$

$$\mathrm{MnO_4^- \longrightarrow Mn^{2+}} \qquad \text{(red. half-reaction)}$$

$$\mathrm{MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O}$$

$$\mathrm{MnO_4^- + 8H^+ + 5}e^- \mathrm{\longrightarrow Mn^{2+} + 4H_2O} \qquad \text{(balanced red. half-reaction)}$$

The oxidation half-reaction involves one electron, and the reduction half-reaction involves five electrons. Now we balance the electron transfer and then add the two equations term by term. This gives the balanced net ionic equation.

$$\begin{array}{rcl} 5(\mathrm{Fe^{2+}} & \longrightarrow & \mathrm{Fe^{3+}} + 1e^-) \\ 1(\mathrm{MnO_4^-} + 8\mathrm{H^+} + 5e^- & \longrightarrow & \mathrm{Mn^{2+}} + 4\mathrm{H_2O}) \\ \hline 5\mathrm{Fe^{2+}(aq)} + \mathrm{MnO_4^-(aq)} + 8\mathrm{H^+(aq)} & \longrightarrow & 5\mathrm{Fe^{3+}(aq)} + \mathrm{Mn^{2+}(aq)} + 4\mathrm{H_2O}(\ell) \end{array}$$

EXAMPLE 11-16 *Total Ionic and Formula Unit Equations*

Write the balanced total ionic and the formula unit equations for the reaction in Example 11-15, given that the reactants were $KMnO_4$, $FeSO_4$, and H_2SO_4.

Plan

The K^+ is the cationic spectator ion, and the anionic spectator ion is SO_4^{2-}. The Fe^{3+} ion will need to occur twice in the product $Fe_2(SO_4)_3$, so there must be an even number of Fe atoms. So the net ionic equation is multiplied by two. It now becomes:

$$10\mathrm{Fe^{2+}(aq)} + 2\mathrm{MnO_4^-(aq)} + 16\mathrm{H^+(aq)} \longrightarrow 10\mathrm{Fe^{3+}(aq)} + 2\mathrm{Mn^{2+}(aq)} + 8\mathrm{H_2O}(\ell)$$

Based on the $10Fe^{2+}$ and the $16H^+$, we add $18SO_4^{2-}$ to the reactant side of the equation; we must also add them to the product side to keep the equation balanced. Based on the $2MnO_4^-$, we add $2K^+$ to each side of the equation.

Solution

Total ionic equation

$$\begin{aligned}&10[Fe^{2+}(aq) + SO_4{}^{2-}(aq)] + 2[K^+(aq) + MnO_4{}^-(aq)] + 8[2H^+(aq) + SO_4{}^{2-}(aq)] \longrightarrow\\ &\qquad 5[2Fe^{3+}(aq) + 3SO_4{}^{2-}(aq)] + 2[Mn^{2+}(aq) + SO_4{}^{2-}(aq)] + 8H_2O(\ell)\\ &\qquad\qquad + [2\ K^+(aq) + SO_4{}^{2-}(aq)]\end{aligned}$$

Balanced formula unit equation

$$\begin{aligned}&10FeSO_4(aq) + 2KMnO_4(aq) + 8H_2SO_4(aq) \longrightarrow\\ &\qquad 5Fe_2(SO_4)_3(aq) + 2MnSO_4(aq) + K_2SO_4(aq) + 8H_2O(\ell)\end{aligned}$$

You should now work Exercise 62.

Bleaches sold under trade names such as Clorox and Purex are 5% solutions of sodium hypochlorite. The hypochlorite ion is a very strong oxidizing agent in basic solution. It oxidizes many stains to colorless substances.

These common household chemicals, ammonia and bleach, should never be mixed because they react to form chloramine (NH_2Cl), a very poisonous volatile compound.

$$NH_3(aq) + ClO^-(aq) \longrightarrow NH_2Cl(aq) + OH^-(aq)$$

EXAMPLE 11-17 *Balancing Redox Equations (HR method)*

In basic solution, hypochlorite ions, ClO^-, oxidize chromite ions, $CrO_2{}^-$, to chromate ions, $CrO_4{}^{2-}$, and are reduced to chloride ions. Write the balanced net ionic equation for this reaction.

Plan

We are given the formulas for two reactants and two products; we write as much of the equations as possible. The reaction occurs in basic solution; we can add OH^- and H_2O as needed. We construct and balance the appropriate half-reactions, equalize the electron transfer, add the half-reactions, and eliminate common terms.

Solution

$$\begin{aligned}CrO_2{}^- + ClO^- &\longrightarrow CrO_4{}^{2-} + Cl^- &&\\ CrO_2{}^- &\longrightarrow CrO_4{}^{2-} &&\text{(ox. half-rxn)}\\ CrO_2{}^- + 4OH^- &\longrightarrow CrO_4{}^{2-} + 2H_2O &&\\ CrO_2{}^- + 4OH^- &\longrightarrow CrO_4{}^{2-} + 2H_2O + 3e^- &&\text{(balanced ox. half-rxn)}\end{aligned}$$

$$\begin{aligned}ClO^- &\longrightarrow Cl^- &&\text{(red. half-rxn)}\\ ClO^- + H_2O &\longrightarrow Cl^- + 2OH^- &&\\ ClO^- + H_2O + 2e^- &\longrightarrow Cl^- + 2OH^- &&\text{(balanced red. half-rxn)}\end{aligned}$$

The oxidation half-reaction involves three electrons, and the reduction half-reaction involves two electrons. We balance the electron transfer and add the half-reactions term by term.

$$\begin{array}{rcl} 2(CrO_2^- + 4OH^- & \longrightarrow & CrO_4^{2-} + 2H_2O + 3e^-) \\ 3(ClO^- + H_2O + 2e^- & \longrightarrow & Cl^- + 2OH^-) \\ \hline 2CrO_2^- + 8OH^- + 3ClO^- + 3H_2O & \longrightarrow & 2CrO_4^{2-} + 4H_2O + 3Cl^- + 6OH^- \end{array}$$

We see 6 OH^- and 3 H_2O that can be eliminated from both sides to give the balanced net ionic equation.

$$2CrO_2^-(aq) + 2OH^-(aq) + 3ClO^-(aq) \longrightarrow 2CrO_4^{2-}(aq) + H_2O(\ell) + 3Cl^-(aq)$$

You should now work Exercise 58.

These common household chemicals, vinegar and bleach, should never be mixed because they react to form chlorine, a very poisonous gas.

$$2H^+(aq) + ClO^-(aq) + Cl^-(aq) \longrightarrow Cl_2(g) + H_2O(\ell)$$

✓ Problem-Solving Tip: *Converting Ionic to Formula Unit Equations*

We learned in Section 4-3 how to convert the formula unit equation to the net ionic equation. To do this, we convert the formulas for all *strong electrolytes* into their ions, and then cancel *spectator ions* from both sides of the equation. In Example 11-16 we reverse this procedure. To balance this excess charge, we must add negatively charged spectator ions to combine with the positively charged reactants, and we add positively charged spectator ions to combine with the negatively charged reactants. Any spectator ions added to the reactant side of the equation must also be added to the product side. Then we combine species to give complete formula units. Now we can write total ionic and formula unit equations for Exercise 11-17 if we know what spectator ions are present. Just for practice, consider the spectator ions to be Na^+.

11-7 CHANGE-IN-OXIDATION-NUMBER METHOD

For brevity, we will refer to this as the CON method.

The next few examples illustrate this method, which is based on *equal total increases and decreases in oxidation numbers.* The general procedure follows.

1. Write as much of the overall *unbalanced* equation as possible.
2. Assign oxidation numbers (Section 4-4) to find the elements that undergo changes in oxidation numbers.
3. **a.** Draw a bracket to connect atoms of the element that is oxidized. Show the increase in oxidation number *per atom.* Draw a bracket to connect atoms of the element that is reduced. Show the decrease in oxidation number *per atom.*
   b. Determine the factors that will make the *total* increase and decrease in oxidation numbers equal.

4. Insert coefficients into the equation to make the total increase and decrease in oxidation numbers equal.
5. Balance the other atoms by inspection. The chart in Section 11-6 will help with the balancing of H's and O's in aqueous solutions.

See the *Saunders Interactive General Chemistry CD-ROM,* Screen 21-3, Balancing Equations for Redox Reactions.

EXAMPLE 11-18 *Balancing Redox Equations (CON method)*

Iron(II) chloride reacts with tin(IV) chloride to form iron(III) chloride and tin(II) chloride. Balance the formula unit equation, and identify the oxidizing and reducing agents.

Plan

We follow the five-step procedure, one step at a time.

Solution

The unbalanced formula unit equation and oxidation numbers (steps 1 and 2) are

$$\overset{\textcircled{+2}\,\textcircled{-1}}{\text{FeCl}_2} + \overset{\textcircled{+4}\,\textcircled{-1}}{\text{SnCl}_4} \longrightarrow \overset{\textcircled{+2}\,\textcircled{-1}}{\text{SnCl}_2} + \overset{\textcircled{+3}\,\textcircled{-1}}{\text{FeCl}_3}$$

The oxidation number of Fe increases from +2 to +3. Fe^{2+} is the reducing agent; it is oxidized. The oxidation number of Sn decreases from +4 to +2. Sn^{4+} is the oxidizing agent; it is reduced.

$$\underbrace{\overset{\textcircled{+2}}{\text{FeCl}_2} + \underbrace{\overset{\textcircled{+4}}{\text{SnCl}_4} \longrightarrow \overset{\textcircled{+2}}{\text{SnCl}_2}}_{-2} + \overset{\textcircled{+3}}{\text{FeCl}_3}}_{+1} \qquad \text{(Step 3a)}$$

We make the *total* increase and decrease in oxidation numbers equal (step 3b).

Oxidation Numbers	Change/Atom	Equalizing Changes Gives
$\text{Fe} = +2 \longrightarrow \text{Fe} = +3$	+1	$2(+1) = +2$
$\text{Sn} = +4 \longrightarrow \text{Sn} = +2$	−2	$1(-2) = -2$

$2(+1) = +2$ (total increase) $1(-2) = -2$ (total decrease)

We need 2 Fe^{2+} on each side of the equation (step 4). All elements are now balanced, so Step 5 is not required.

$$\boxed{2\text{FeCl}_2 + \text{SnCl}_4 \longrightarrow \text{SnCl}_2 + 2\text{FeCl}_3}$$

EXAMPLE 11-19 *Balancing Redox Equations (CON method)*

Copper is a widely used metal. Before it is welded (brazed), copper is cleaned by dipping it into nitric acid. HNO_3 oxidizes Cu to Cu^{2+} ions and is reduced to NO. The other product is H_2O. Write the balanced net ionic and formula unit equations for the reaction. Excess HNO_3 is present.

Plan

In writing ionic equations, we recall that strong acids, strong bases, and most soluble salts are strong electrolytes. Then we apply our five-step procedure for redox equations.

Solution

We write the unbalanced net ionic equation and assign oxidation numbers. HNO_3 is a strong acid.

$$\overset{+1}{H^+}(aq) + \overset{+5}{N}\overset{-2}{O_3^-}(aq) + \overset{0}{Cu}(s) \longrightarrow \overset{+2}{Cu^{2+}}(aq) + \overset{+2}{N}\overset{-2}{O}(g) + \overset{+1}{H_2}\overset{-2}{O}(\ell)$$

We see that copper is oxidized; it is the reducing agent. Nitrate ions are reduced; they are the oxidizing agent.

$$H^+ + \underbrace{\overset{+5}{N}O_3^- + \underbrace{\overset{0}{Cu} \longrightarrow \overset{+2}{Cu^{2+}}}_{+2} + \overset{+2}{N}O}_{-3} + H_2O$$

We make the *total* increase and decrease in oxidation numbers equal.

Oxidation Numbers	Change/Atom	Equalizing Changes Gives
$Cu = 0 \longrightarrow Cu = +2$	$+2$	$3(+2) = +6$
$N = +5 \longrightarrow N = +2$	-3	$2(-3) = -6$

Copper is cleaned by dipping it into nitric acid.

Now we balance the *redox part* of the reaction.

$$H^+ + 2NO_3^- + 3Cu \longrightarrow 3Cu^{2+} + 2NO + H_2O$$

There are 6 O on the left in NO_3^- ions. A coefficient of 4 before H_2O balances O and gives 8 H on the right. So we need 8 H^+ ions on the left to balance the net ionic equation.

$$8H^+(aq) + 2NO_3^-(aq) + 3Cu(s) \longrightarrow 3Cu^{2+}(aq) + 2NO(g) + 4H_2O(\ell)$$

This solution contains excess HNO_3, so NO_3^- is the only anion present in significant concentration. Therefore, we add six more NO_3^- ions to each side to give the total ionic equation.

$$8[H^+(aq) + NO_3^-(aq)] + 3Cu(s) \longrightarrow 3[Cu^{2+}(aq) + 2NO_3^-(aq)] + 2NO(g) + 4H_2O(\ell)$$

Now we can write the balanced formula unit equation.

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

You should now work Exercise 52.

The Drāno reaction.

EXAMPLE 11-20 *Balancing Redox Equations (CON method)*

Drāno drain cleaner is solid sodium hydroxide that contains some aluminum chips. When Drāno is added to water, the NaOH dissolves rapidly with the evolution of a lot of heat. The Al reduces H_2O in the basic solution to produce $[Al(OH)_4]^-$ ions and H_2 gas, which gives the bubbling action. Write the balanced net ionic and formula unit equations for this reaction.

Plan

We are given formulas for reactants and products. Recall that NaOH is a strong soluble base (OH^- and H_2O can be added to either side as needed). We apply our five-step procedure.

Solution

We write the unbalanced net ionic equation and assign oxidation numbers.

$$OH^-(aq) + \overset{0}{Al}(s) + \overset{+1}{H_2}O(\ell) \longrightarrow [\overset{+3}{Al}(OH)_4]^-(aq) + \overset{0}{H_2}(g)$$

Aluminum is oxidized; it is the reducing agent. H_2O is reduced; it is the oxidizing agent.

$$OH^- + \overset{\textcircled{+1}}{H_2}O + \overset{\textcircled{0}}{Al} \longrightarrow [\overset{\textcircled{+3}}{Al}(OH)_4]^- + \overset{\textcircled{0}}{H_2}$$

$$+3$$

$$-1$$

We make the *total* increase and decrease in oxidation numbers equal.

Oxidation Numbers	Change/Atom	Equalizing Changes Gives
$Al = 0 \longrightarrow Al = +3$	$+3$	$1(+3) = +3$
$H = +1 \longrightarrow H = 0$	-1	$3(-1) = -3$

Each change must be multiplied by two because there are 2 H in each H_2.

$2(+3) = +6$ (total increase) $2(-3) = -6$ (total decrease)

Now we balance the redox part of the equation. We need 2 Al on each side. Because only one H in each H_2O molecule is reduced (the other H is in OH^-), we show 6 H_2O on the left and 3 H_2 on the right.

$$OH^- + 6H_2O + 2Al \longrightarrow 2[Al(OH)_4]^- + 3H_2$$

The net charge on the right is 2−, and so we need 2 OH^- on the left to balance the net ionic equation.

$$2OH^-(aq) + 6H_2O(\ell) + 2Al(s) \longrightarrow 2[Al(OH)_4]^-(aq) + 3H_2(g)$$

This reaction occurs in excess NaOH solution. We need 2 Na^+(aq) on each side to balance the negative charges.

$$2NaOH(aq) + 6H_2O(\ell) + 2Al(s) \longrightarrow 2Na[Al(OH)_4](aq) + 3H_2(g)$$

You should now work Exercise 58.

EXAMPLE 11-21 *Balancing Redox Equations (CON method)*

The breathalyzer detects the presence of ethanol (ethyl alcohol) in the breath of persons suspected of drunken driving. It utilizes the oxidation of ethanol to acetaldehyde by dichromate ions in acidic solution. The $Cr_2O_7^{2-}$(aq) ion is orange (see Example 11-23). The Cr^{3+}(aq) ion is green. The appearance of a green color signals alcohol in the breath that exceeds the legal limit. Balance the net ionic equation for this reaction.

$$H^+(aq) + Cr_2O_7^{2-}(aq) + C_2H_5OH(\ell) \longrightarrow Cr^{3+}(aq) + C_2H_4O(\ell) + H_2O(\ell)$$

Plan

We are given the unbalanced equation, which includes H^+. This tells us that the reaction occurs in acidic solution. We apply our five-step procedure.

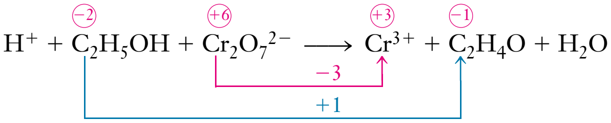
Solution

We first assign oxidation numbers to the elements that change.

$$H^+ + \overset{\textcircled{-2}}{C_2}H_5OH + \overset{\textcircled{+6}}{Cr_2}O_7^{2-} \longrightarrow \overset{\textcircled{+3}}{Cr^{3+}} + \overset{\textcircled{-1}}{C_2}H_4O + H_2O(\ell)$$

Many breathalyzers have been developed over the years. This model has proved to be effective.

We see that ethanol is oxidized; it is the reducing agent. $Cr_2O_7^{2-}$ ions are reduced; they are the oxidizing agent.



Oxidation Numbers	Change/Atom	Equalizing Changes Gives
$Cr = +6 \longrightarrow Cr = +3$	-3	$1(-3) = -3$
$C = -2 \longrightarrow C = -1$	$+1$	$3(+1) = +3$

Each change must be multiplied by two because there are 2 Cr in each $Cr_2O_7^{2-}$ and 2 C in C_2H_5OH.

$$2(-3) = -6 \text{ (total decrease)} \qquad 2(+3) = +6 \text{ (total increase)}$$

We need 2 Cr and 6 C on each side of the equation to balance the redox part.

$$H^+ + 3C_2H_5OH + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 3C_2H_4O + H_2O$$

Now we balance H and O using our chart. There are 10 O on the left and only 4 O on the right. So we add 6 *more* H_2O molecules on the right.

$$H^+ + 3C_2H_5OH + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 3C_2H_4O + 7H_2O$$

Now there are 26 H on the right and only 19 on the left. So we add 7 *more* H^+ ions on the left to give the balanced net ionic equation.

$$8H^+(aq) + 3C_2H_5OH(aq) + Cr_2O_7^{2-}(aq) \longrightarrow 2Cr^{3+}(aq) + 3C_2H_4O(aq) + 7H_2O(\ell)$$

You should now work Exercise 54.

Every balanced equation must have both mass balance and charge balance. Once the redox part of an equation has been balanced, we must next count *either* atoms or charges. After we balanced the redox part in Example 11-21, we had

$$H^+ + 3C_2H_5OH + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 3C_2H_4O + H_2O$$

The net charge on the left side is $(1 + 2-) = 1-$. On the right, it is $2(3+) = 6+$. Because H^+ is the *only charged species whose coefficient isn't known*, we add 7 *more* H^+ to give a net charge of 6+ on both sides.

$$8H^+ + 3C_2H_5OH + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 3C_2H_4O + H_2O$$

Now we have 10 O on the left and only 4 O on the right. We add six *more* H_2O molecules to give the balanced net ionic equation.

$$8H^+(aq) + 3C_2H_5OH(\ell) + Cr_2O_7^{2-}(aq) \longrightarrow 2Cr^{3+}(aq) + 3C_2H_4O(\ell) + 7H_2O(\ell)$$

How can you tell whether to balance atoms or charges first? Look at the equation *after you have balanced the redox part.* Decide which is simpler, and do that. In the preceding equation, it is easier to balance charges than to balance atoms.

11-8 STOICHIOMETRY OF REDOX REACTIONS

One method of analyzing samples quantitatively for the presence of *oxidizable* or *reducible* substances is by **redox titration.** In such analyses, the concentration of a solution is determined by allowing it to react with a carefully measured amount of a *standard* solution of an oxidizing or reducing agent.

As in other kinds of chemical reactions, we must pay particular attention to the mole ratio in which oxidizing agents and reducing agents react.

Potassium permanganate, $KMnO_4$, is a strong oxidizing agent. Through the years it has been the "workhorse" of redox titrations. For example, in acidic solution, $KMnO_4$ reacts with iron(II) sulfate, $FeSO_4$, according to the balanced equation in the following example. A strong acid, such as H_2SO_4, is used in such titrations (Example 11-15).

A word about terminology. The reaction involves MnO_4^- ions and Fe^{2+} ions in acidic solution. The source of MnO_4^- ions usually is the soluble ionic compound $KMnO_4$. We often refer to "permanganate solutions." Such solutions also contain cations—in this case, K^+. Likewise, we often refer to "iron(II) solutions" without specifying what the anion is.

Because it has an intense purple color, $KMnO_4$ acts as its own indicator. One drop of 0.020 M $KMnO_4$ solution imparts a pink color to a liter of pure water. When $KMnO_4$ solution is added to a solution of a reducing agent, the end point in the titration is taken as the point at which a pale pink color appears in the solution being titrated and persists for at least 30 seconds.

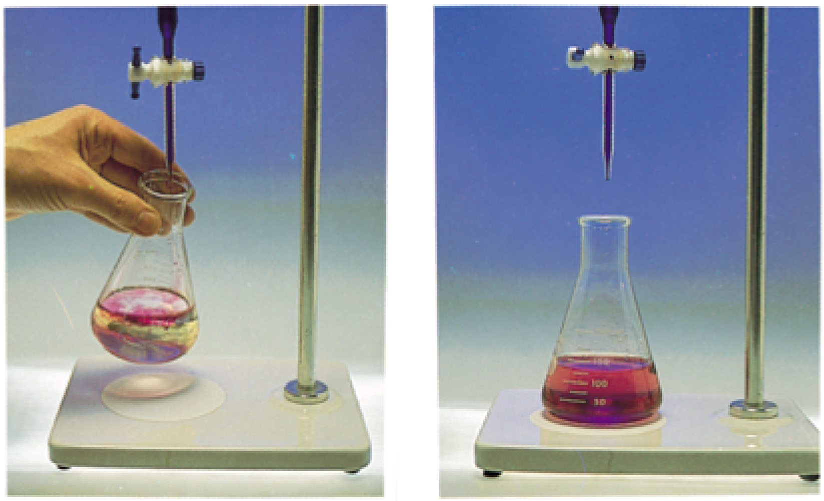
EXAMPLE 11-22 *Redox Titration*

What volume of 0.0200 M $KMnO_4$ solution is required to oxidize 40.0 mL of 0.100 M $FeSO_4$ in sulfuric acid solution (Figure 11-2)?

Plan

The balanced equation in Example 11-15 gives the reaction ratio, 1 mol MnO_4^-/5 mol Fe^{2+}. Then we calculate the number of moles of Fe^{2+} to be titrated, which lets us find the number of moles of MnO_4^- required *and* the volume in which this number of moles of $KMnO_4$ is contained.

One mole of $KMnO_4$ contains one mole of MnO_4^- ions. The number of moles of $KMnO_4$ is therefore *always* equal to the number of moles of MnO_4^- ions required in a reaction. Similarly, one mole of $FeSO_4$ contains 1 mole of Fe^{2+} ions.



(a) **(b)**

Figure 11-2 (a) Nearly colorless $FeSO_4$ solution is titrated with deep-purple $KMnO_4$. (b) The end point is the point at which the solution becomes pink, owing to a *very small* excess of $KMnO_4$. Here a considerable excess of $KMnO_4$ was added so that the pink color could be reproduced photographically.

Solution

The reaction ratio is

$$\begin{array}{lcl} & MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \longrightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(\ell) \\ \text{rxn ratio:} & \text{1 mol} \qquad\qquad\qquad\qquad \text{5 mol} & \end{array}$$

The number of moles of Fe^{2+} to be titrated is

$$\underline{?}\text{ mol } Fe^{2+} = 40.0\text{ mL} \times \frac{0.100\text{ mol } Fe^{2+}}{1000\text{ mL}} = 4.00 \times 10^{-3}\text{ mol } Fe^{2+}$$

We use the balanced equation to find the number of moles of MnO_4^- required.

$$\underline{?}\text{ mol } MnO_4^- = 4.00 \times 10^{-3}\text{ mol } Fe^{2+} \times \frac{1\text{ mol } MnO_4^-}{5\text{ mol } Fe^{2+}} = 8.00 \times 10^{-4}\text{ mol } MnO_4^-$$

Each formula unit of $KMnO_4$ contains one MnO_4^- ion, and so

$$1\text{ mol } KMnO_4 \cong 1\text{ mol } MnO_4^-$$

The volume of 0.0200 M $KMnO_4$ solution that contains 8.00×10^{-4} mol of $KMnO_4$ is

$$\begin{aligned} \underline{?}\text{ mL } KMnO_4\text{ soln} &= 8.00 \times 10^{-4}\text{ mol } KMnO_4 \times \frac{1000\text{ mL } KMnO_4\text{ soln}}{0.0200\text{ mol } KMnO_4} \\ &= 40.0\text{ mL } KMnO_4\text{ soln} \end{aligned}$$

You should now work Exercises 66 and 68.

Potassium dichromate, $K_2Cr_2O_7$, is another frequently used oxidizing agent. However, an indicator must be used when reducing agents are titrated with dichromate solutions. $K_2Cr_2O_7$ is orange, and its reduction product, Cr^{3+}, is green.

Consider the oxidation of sulfite ions, SO_3^{2-}, to sulfate ions, SO_4^{2-}, by $Cr_2O_7^{2-}$ ions in the presence of a strong acid such as sulfuric acid. We shall balance the equation by the half-reaction method.

$$\begin{array}{rcll}
Cr_2O_7^{2-} & \longrightarrow & Cr^{3+} & \text{(red. half-rxn)} \\
Cr_2O_7^{2-} & \longrightarrow & 2Cr^{3+} & \\
14H^+ + Cr_2O_7^{2-} & \longrightarrow & 2Cr^{3+} + 7H_2O & \\
6e^- + 14H^+ + Cr_2O_7^{2-} & \longrightarrow & 2Cr^{3+} + 7H_2O & \text{(balanced red. half-rxn)} \\
\hdashline
SO_3^{2-} & \longrightarrow & SO_4^{2-} & \text{(ox. half-rxn)} \\
SO_3^{2-} + H_2O & \longrightarrow & SO_4^{2-} + 2H^+ & \\
SO_3^{2-} + H_2O & \longrightarrow & SO_4^{2-} + 2H^+ + 2e^- & \text{(balanced ox. half-rxn)}
\end{array}$$

We now equalize the electron transfer, add the balanced half-reactions, and eliminate common terms.

$$\begin{array}{rcll}
(6e^- + 14H^+ + Cr_2O_7^{2-} & \longrightarrow & 2Cr^{3+} + 7H_2O) & \text{(reduction)} \\
3(SO_3^{2-} + H_2O & \longrightarrow & SO_4^{2-} + 2H^+ + 2e^-) & \text{(oxidation)} \\
\hline
8H^+(aq) + Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) & \longrightarrow & 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + 4H_2O(\ell) &
\end{array}$$

The balanced equation tells us that the reaction ratio is 3 mol SO_3^{2-}/mol $Cr_2O_7^{2-}$ or 1 mol $Cr_2O_7^{2-}$/3 mol SO_3^{2-}. Potassium dichromate is the usual source of $Cr_2O_7^{2-}$ ions, and Na_2SO_3 is the usual source of SO_3^{2-} ions. Thus, the preceding reaction ratio could also be expressed as 1 mol $K_2Cr_2O_7$/3 mol Na_2SO_3.

EXAMPLE 11-23 *Redox Titration*

A 20.00-mL sample of Na_2SO_3 was titrated with 36.30 mL of 0.05130 *M* $K_2Cr_2O_7$ solution in the presence of H_2SO_4. Calculate the molarity of the Na_2SO_3 solution.

Plan

We can calculate the number of millimoles of $Cr_2O_7^{2-}$ in the standard solution. Then we refer to the balanced equation in the preceding discussion, which gives us the reaction ratio, 3 mmol SO_3^{2-}/1 mmol $Cr_2O_7^{2-}$. The reaction ratio lets us calculate the number of millimoles of SO_3^{2-} (Na_2SO_3) that reacted and the molarity of the solution.

$$\text{mL } Cr_2O_7^{2-} \text{ soln} \longrightarrow \text{mmol } Cr_2O_7^{2-} \longrightarrow \text{mmol } SO_3^{2-} \longrightarrow M\ SO_3^{2-} \text{ soln}$$

Solution

From the preceding discussion we know the balanced equation and the reaction ratio.

$$\underset{3\text{ mmol}}{3SO_3^{2-}} + \underset{1\text{ mmol}}{Cr_2O_7^{2-}} + 8H^+ \longrightarrow 3SO_4^{2-} + 2Cr^{3+} + 4H_2O$$

The number of millimoles of $Cr_2O_7^{2-}$ used is

$$\underline{?}\ \text{mmol } Cr_2O_7^{2-} = 36.30\text{ mL} \times \frac{0.05130\text{ mmol } Cr_2O_7^{2-}}{\text{mL}} = 1.862\text{ mmol } Cr_2O_7^{2-}$$

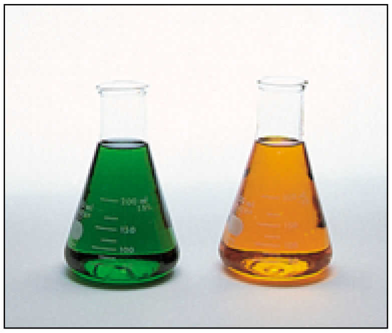
The number of millimoles of SO_3^{2-} that reacted with 1.862 mmol of $Cr_2O_7^{2-}$ is

$$\underline{?}\ \text{mmol } SO_3^{2-} = 1.862\text{ mmol } Cr_2O_7^{2-} \times \frac{3\text{ mmol } SO_3^{2-}}{1\text{ mmol } Cr_2O_7^{2-}} = 5.586\text{ mmol } SO_3^{2-}$$

The Na_2SO_3 solution contained 5.586 mmol of SO_3^{2-} (or 5.586 mmol of Na_2SO_3). Its molarity is

$$\underline{?}\ \frac{\text{mmol } Na_2SO_3}{\text{mL}} = \frac{5.586\text{ mmol } Na_2SO_3}{20.00\text{ mL}} = \boxed{0.2793\ M\ Na_2SO_3}$$

You should now work Exercise 70.



$Cr_2(SO_4)_3$ is green in acidic solution. $K_2Cr_2O_7$ is orange in acidic solution.

Key Terms

Buret A piece of volumetric glassware, usually graduated in 0.1-mL intervals, that is used in titrations to deliver solutions in a quantitative (dropwise) manner.

End point The point at which an indicator changes color and a titration is stopped.

Equivalence point The point at which chemically equivalent amounts of reactants have reacted.

Equivalent weight in acid–base reactions The mass of an acid or base that furnishes or reacts with 6.022×10^{23} H_3O^+ or OH^- ions.

Half-reaction Either the oxidation part or the reduction part of a redox reaction.

Indicator For acid–base titrations, an organic compound that exhibits its different colors in solutions of different acidities; used to determine the point at which the reaction between two solutes is complete.

Millimole 1/1000 mole.

Molarity (*M*) The number of moles of solute per liter of solution or the number of millimoles of solute per milliliter of solution.

Normality (*N*) The number of equivalent weights (equivalents) of solute per liter of solution.

Oxidation An algebraic increase in oxidation number; may correspond to a loss of electrons.

Oxidation–reduction reaction A reaction in which oxidation and reduction occur; also called redox reaction.

Oxidizing agent The substance that oxidizes another substance and is reduced.

Primary standard A substance of a known high degree of purity that undergoes one invariable reaction with the other reactant of interest.

Redox reaction An oxidation-reduction reaction.

Redox titration The quantitative analysis of the amount or concentration of an oxidizing or reducing agent in a sample by observing its reaction with a known amount or concentration of a reducing or oxidizing agent.

Reducing agent The substance that reduces another substance and is oxidized.

Reduction An algebraic decrease in oxidation number; may correspond to a gain of electrons.

Secondary standard A solution that has been titrated against a primary standard. A standard solution in a secondary standard.

Standard solution A solution of accurately known concentration.

Standardization The process by which the concentration of a solution is accurately determined by titrating it against an accurately known amount of a primary standard.

Titration The process by which the volume of a standard solution required to react with a specific amount of a substance is determined.

Exercises

Molarity

1. Why can we describe molarity as a “method of convenience” for expressing concentrations of solutions?
2. Why is the molarity of a solution the same number whether we describe it in mol/L or in mmol/mL?
3. Calculate the molarities of solutions that contain the following masses of solute in the indicated volumes: (a) 45 g of H_3AsO_4 in 500. mL of solution; (b) 8.3 g of $(COOH)_2$ in 600. mL of solution; (c) 8.25 g of $(COOH)_2 \cdot 2H_2O$ in 750. mL of solution.
4. What is the molarity of a solution made by dissolving 132.6 g of magnesium sulfate in sufficient water to produce a total of 3.500 L?
5. There is 75.0 g of iron(II) nitrate present in 750. mL of a solution. Calculate the molarity of that solution.
6. Calculate the molarity of a solution that is 39.77% H_2SO_4 by mass. The specific gravity of the solution is 1.305.
7. Calculate the molarity of a solution that is 19.0% HNO_3 by mass. The specific gravity of the solution is 1.11.
8. If 150. mL of 4.32 M HCl solution is added to 300. mL of 2.16 M NaOH solution, the resulting solution will be ______ molar in NaCl.
9. What is the molarity of the salt solution produced when 500. mL of 3.00 M HCl and 500. mL of 3.00 M LiOH are mixed? (Assume that the volumes are additive.) Give the name and formula of the salt formed.
10. Potassium iodide is sometimes used as a sodium chloride replacement for those people who cannot tolerate table salt. Calculate the molarity of potassium iodide solution produced when 25.0 mL of 9.00 M HI and 25.0 mL of 9.00 M KOH are mixed.
11. Calculate the molarity of the salt solution produced when 3.60 mL of 0.00100 M $Mg(OH)_2$ and 3.60 mL of 0.00100 M H_2SO_4 are mixed. Give the name and formula of the salt formed.
12. What is the concentration of the salt solution produced when 32.5 mL of 2.00 M H_2SO_4 and 32.5 mL of 4.00 M NaOH are mixed? Give the name and formula of the salt formed.
13. What is the salt concentration produced if we mix 8.00 mL of 3.00 M HCl with 3.00 mL of 4.00 M $Ba(OH)_2$? Give the name and formula of the salt formed.
14. What is the concentration of barium iodide produced by mixing 5.00 mL of 0.125 M $Ba(OH)_2$ with 12.0 mL of 0.0650 M HI?
15. What is the concentration of the ammonium chloride produced when 44.0 mL of 12.0 M HCl and 37.0 mL of 8.00 M NH_3 are mixed?
16. If 225 mL of 3.68 M H_3PO_4 solution is added to 775 mL of 3.68 M NaOH solution, the resulting solution will be ______ molar in Na_3PO_4 and ______ molar in ______.
17. If 400 mL of 0.200 M HCl solution is added to 800. mL of 0.0400 M $Ba(OH)_2$ solution, the resulting solution will be ______ molar in $BaCl_2$ and ______ molar in ______.
18. What volume of 0.0150 M acetic acid solution would completely neutralize 18.7 mL of 0.0105 M $Ba(OH)_2$ solution?
19. What volume of 0.300 M potassium hydroxide solution would completely neutralize 35.0 mL of 0.100 M H_2SO_4 solution?
20. A vinegar solution is 5.11% acetic acid. Its density is 1.007 g/mL. What is its molarity?
21. A household ammonia solution is 5.03% ammonia. Its density is 0.979 g/mL. What is its molarity?
22. (a) What volumes of 1.50 M NaOH and 3.00 M H_3PO_4 solutions would be required to form 1.00 mol of Na_3PO_4? (b) What volumes of the solutions would be required to form 1.00 mol of Na_2HPO_4?

Standardization and Acid–Base Titrations: Mole Method

23. Define and illustrate the following terms clearly and concisely: (a) standard solution; (b) titration; (c) primary standard; (d) secondary standard.

24. Describe the preparation of a standard solution of NaOH, a compound that absorbs both CO_2 and H_2O from the air.

25. Distinguish between the *net ionic equation* and the *formula unit equation.*

26. (a) What is potassium hydrogen phthalate, KHP? (b) For what is it used?

27. Why can sodium carbonate be used as a primary standard for solutions of acids?

28. Calculate the molarity of a solution of HNO_3 if 35.72 mL of the solution neutralizes 0.302 g of Na_2CO_3.

29. If 41.38 mL of a sulfuric acid solution reacts completely with 0.3545 g of Na_2CO_3, what is the molarity of the sulfuric acid solution?

30. A solution of sodium hydroxide is standardized against potassium hydrogen phthalate. From the following data, calculate the molarity of the NaOH solution.

mass of KHP	0.6536
buret reading before titration	0.23 mL
buret reading after titration	31.26 mL

31. Calculate the molarity of a KOH solution if 40.68 mL of the KOH solution reacted with 0.4084 g of potassium hydrogen phthalate, KHP.

32. Calcium carbonate tablets can be used as an antacid and a source of dietary calcium. A bottle of generic antacid tablets states that each tablet contains 500. mg calcium carbonate. What volume of 6.0 *M* HNO_3 could be neutralized by the calcium carbonate in one tablet?

33. What volume of 18.0 *M* H_2SO_4 is required to react with 100. mL of 6.00 *M* NaOH to produce a Na_2SO_4 solution? What volume of water must be added to the resulting solution to obtain a 1.25 *M* Na_2SO_4 solution?

34. (a) What are the properties of an ideal primary standard? (b) What is the importance of each property?

35. The secondary standard solution of NaOH of Exercise 30 was used to titrate a solution of unknown concentration of HCl. A 30.00-mL sample of the HCl solution required 34.21 mL of the NaOH solution for complete neutralization. What is the molarity of the HCl solution?

***36.** An impure sample of $(COOH)_2 \cdot 2H_2O$ that had a mass of 2.00 g was dissolved in water and titrated with standard NaOH solution. The titration required 38.32 mL of 0.198 *M* NaOH solution. Calculate the percent $(COOH)_2 \cdot 2H_2O$ in the sample. Assume that the sample contains no acidic impurities.

***37.** A 50.0-mL sample of 0.0500 *M* $Ca(OH)_2$ is added to 10.0 mL of 0.200 *M* HNO_3. (a) Is the resulting solution acidic or basic? (b) How many moles of excess acid or base are present? (c) How many additional mL of 0.0500 *M* $Ca(OH)_2$ or 0.200 *M* HNO_3 would be required to completely neutralize the solution?

***38.** An antacid tablet containing calcium carbonate as an active ingredient required 24.5 mL of 0.0932 *M* HCl for complete neutralization. What mass of $CaCO_3$ did the tablet contain?

***39.** Butyric acid, whose empirical formula is C_2H_4O, is the acid responsible for the odor of rancid butter. The acid has one ionizable hydrogen per molecule. A 1.000-g sample of butyric acid is neutralized by 54.42 mL of 0.2088 *M* NaOH solution. What are (a) the molecular weight and (b) the molecular formula of butyric acid?

40. What is the molarity of a solution of sodium hydroxide, NaOH, if 36.2 mL of this solution is required to react with 25.0 mL of 0.0513 *M* nitric acid solution according to the following reaction?

$$HNO_3 + NaOH \longrightarrow NaNO_3 + H_2O$$

41. What is the molarity of a solution of sodium hydroxide, NaOH, if 36.9 mL of this solution is required to react with 35.2 mL of 0.101 *M* hydrochloric acid solution according to the following reaction?

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

Standardization and Acid–Base Titrations: Equivalent Weight Method

In answering Exercises 42–51, assume that the acids and bases will be completely neutralized.

42. What is the normality of each of the following acid or base solutions? (a) 0.35 *M* HCl; (b) 0.35 *M* H_2SO_4; (c) 0.35 *M* H_3PO_4; (d) 0.35 *M* NaOH.

43. What is the normality of each of the following acid or base solutions? (a) 0.105 *M* $Ca(OH)_2$; (b) 0.105 *M* $Al(OH)_3$; (c) 0.105 *M* HNO_3; (d) 0.105 *M* H_2Se.

44. What is the normality of a solution that contains 7.08 g of H_3PO_4 in 185 mL of solution?

45. Calculate the molarity and the normality of a solution that was prepared by dissolving 24.2 g of barium hydroxide in enough water to make 4000. mL of solution.

46. Calculate the molarity and the normality of a solution that contains 19.6 g of arsenic acid, H_3AsO_4, in enough water to make 500. mL of solution.

47. What are the molarity and normality of a sulfuric acid solution that is 19.6% H_2SO_4 by mass? The density of the solution is 1.14 g/mL.

48. A 25.0-mL sample of 0.206 normal nitric acid solution required 35.2 mL of barium hydroxide solution for neutralization. Calculate the molarity of the barium hydroxide solution.

49. Vinegar is an aqueous solution of acetic acid, CH_3COOH. Suppose you titrate a 25.00-mL sample of vinegar with

17.62 mL of a standardized 0.1060 *N* solution of NaOH. (a) What is the normality of acetic acid in this vinegar? (b) What is the mass of acetic acid contained in 1.000 L of vinegar?

50. Calculate the normality and molarity of an HCl solution if 43.1 mL of the solution reacts with 0.318 g of Na_2CO_3.

$$2HCl + Na_2CO_3 \longrightarrow 2NaCl + CO_2 + H_2O$$

51. Calculate the normality and molarity of an H_2SO_4 solution if 40.0 mL of the solution reacts with 0.424 g of Na_2CO_3.

$$H_2SO_4 + Na_2CO_3 \longrightarrow Na_2SO_4 + CO_2 + H_2O$$

Balancing Redox Equations

In Exercises 52 and 53, write balanced formula unit equations for the reactions described by words.

52. (a) Iron reacts with hydrochloric acid to form aqueous iron(II) chloride and gaseous hydrogen. (b) Chromium reacts with sulfuric acid to form aqueous chromium(III) sulfate and gaseous hydrogen. (c) Tin reacts with concentrated nitric acid to form tin(IV) oxide, nitrogen dioxide, and water.

53. (a) Carbon reacts with hot concentrated nitric acid to form carbon dioxide, nitrogen dioxide, and water. (b) Sodium reacts with water to form aqueous sodium hydroxide and gaseous hydrogen. (c) Zinc reacts with sodium hydroxide solution to form aqueous sodium tetrahydroxozincate and gaseous hydrogen. (The tetrahydroxozincate ion is $[Zn(OH)_4]^{2-}$.)

54. Balance the following equations. For each equation tell what is oxidized, what is reduced, what is the oxidizing agent, and what is the reducing agent.

(a) $Zn(s) + HClO_4(aq) \longrightarrow Zn(ClO_4)_2(aq) + H_2(g)$
(b) $K(s) + H_2O(\ell) \longrightarrow KOH(aq) + H_2(g)$
(c) $NaClO_3(s) \xrightarrow{\text{heat}} NaCl(s) + O_2(g)$

55. Balance the following equations. For each equation tell what is oxidized, what is reduced, what is the oxidizing agent, and what is the reducing agent.

(a) $Cu(NO_3)_2(s) \xrightarrow{\text{heat}} CuO(s) + NO_2(g) + O_2(g)$
(b) $Hg_2Cl_2(s) + NH_3(aq) \longrightarrow Hg(\ell) + HgNH_2Cl(s) + NH_4^+(aq) + Cl^-(aq)$
(c) $Ba(s) + H_2O(\ell) \longrightarrow Ba(OH)_2(aq) + H_2(g)$

56. Balance the following equations. For each equation tell what is oxidized, what is reduced, what is the oxidizing agent, and what is the reducing agent.

(a) $MnO_4^-(aq) + H^+(aq) + Br^-(aq) \longrightarrow Mn^{2+}(aq) + Br_2(\ell) + H_2O(\ell)$
(b) $Cr_2O_7^{2-}(aq) + H^+(aq) + I^-(aq) \longrightarrow Cr^{3+}(aq) + I_2(s) + H_2O(\ell)$
(c) $MnO_4^-(aq) + SO_3^{2-}(aq) + H^+(aq) \longrightarrow Mn^{2+}(aq) + SO_4^{2-}(aq) + H_2O(\ell)$
(d) $Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) + H^+(aq) \longrightarrow Cr^{3+}(aq) + Fe^{3+}(aq) + H_2O(\ell)$

57. Balance the following ionic equations. For each equation tell what is oxidized, what is reduced, what is the oxidizing agent, and what is the reducing agent.

(a) $C_2H_4(g) + MnO_4^-(aq) + H^+(aq) \rightarrow CO_2(g) + Mn^{2+}(aq) + H_2O(\ell)$
(b) $H_2S(aq) + H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq) + S(s) + H_2O(\ell)$
(c) $ClO_3^-(aq) + H_2O(\ell) + I_2(s) \rightarrow IO_3^-(aq) + Cl^-(aq) + H^+(aq)$
(d) $Cu(s) + H^+(aq) + SO_4^{2-}(aq) \rightarrow Cu^{2+}(aq) + H_2O(\ell) + SO_2(g)$

58. Balance the following ionic equations. For each equation tell what is oxidized, what is reduced, what is the oxidizing agent, and what is the reducing agent.

(a) $Al(s) + NO_3^-(aq) + OH^-(aq) + H_2O \rightarrow Al(OH)_4^-(aq) + NH_3(g)$
(b) $NO_2(g) + OH^-(aq) \rightarrow NO_3^-(aq) + NO_2^-(aq) + H_2O(\ell)$
(c) $MnO_4^-(aq) + H_2O(\ell) + NO_2^-(aq) \rightarrow MnO_2(s) + NO_3^-(aq) + OH^-(aq)$

59. Balance the following ionic equations. For each equation tell what is oxidized, what is reduced, what is the oxidizing agent, and what is the reducing agent.

(a) $Cr(OH)_4^-(aq) + OH^-(aq) + H_2O_2(aq) \rightarrow CrO_4^{2-}(aq) + H_2O(\ell)$
(b) $MnO_2(s) + H^+(aq) + NO_2^-(aq) \rightarrow NO_3^-(aq) + Mn^{2+}(aq) + H_2O(\ell)$
(c) $Sn(OH)_3^-(aq) + Bi(OH)_3(s) + OH^-(aq) \rightarrow Sn(OH)_6^{2-}(aq) + Bi(s)$
(d) $CrO_4^{2-}(aq) + H_2O(\ell) + HSnO_2^-(aq) \rightarrow CrO_2^-(aq) + OH^-(aq) + HSnO_3^-(aq)$

60. Balance the following ionic equations for reactions in acidic solution. H^+ or H_2O (but not OH^-) may be added as necessary.

(a) $Fe^{2+}(aq) + MnO_4^-(aq) \rightarrow Fe^{3+}(aq) + Mn^{2+}(aq)$
(b) $Br_2(\ell) + SO_2(g) \rightarrow Br^-(aq) + SO_4^{2-}(aq)$
(c) $Cu(s) + NO_3^-(aq) \rightarrow Cu^{2+}(aq) + NO_2(g)$
(d) $PbO_2(s) + Cl^-(aq) \rightarrow PbCl_2(s) + Cl_2(g)$
(e) $Zn(s) + NO_3^-(aq) \rightarrow Zn^{2+}(aq) + N_2(g)$

61. Balance the following ionic equations for reactions in acidic solution. H^+ or H_2O (but not OH^-) may be added as necessary.

(a) $P_4(s) + NO_3^-(aq) \rightarrow H_3PO_4(aq) + NO(g)$
(b) $H_2O_2(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + O_2(g)$
(c) $HgS(s) + Cl^-(aq) + NO_3^-(aq) \rightarrow HgCl_4^{2-}(aq) + NO_2(g) + S(s)$
(d) $HBrO(aq) \rightarrow Br^-(aq) + O_2(g)$

62. Write the balanced net ionic equations for the reactions given. Then, using the reactants shown in parentheses convert each balanced net ionic equation to a balanced formula unit equation.

(a) $MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow Mn^{2+} + CO_2 + H_2O$ ($KMnO_4$, HCl, and $K_2C_2O_4$)
(b) $Zn + NO_3^- + H^+ \rightarrow Zn^{2+} + NH_4^+ + H_2O$ (Zn(s) and HNO_3)

63. Write the balanced net ionic equations for the reactions given. Then, using the reactants shown in parentheses convert each balanced net ionic equation to a balanced formula unit equation.
(a) $I_2 + S_2O_3^{2-} \rightarrow I^- + S_4O_6^{2-}$ (I_2 and $Na_2S_2O_3$)
(b) $IO_3^- + N_2H_4 + Cl^- + H^+ \rightarrow N_2 + ICl_2^- + H_2O$ ($NaIO_3 + N_2H_4$, and HCl)

64. Write the balanced net ionic equations for the reactions given. Then, using the reactants shown in parentheses convert each balanced net ionic equation to a balanced formula unit equation.
(a) $Zn + Cu^{2+} \rightarrow Cu + Zn^{2+}$ (Zn and $CuSO_4$)
(b) $Cr + H^+ \rightarrow Cr^{3+} + H_2$ (Cr and H_2SO_4)

65. Write the balanced net ionic equations for the reactions given. Then, using the reactants shown in parentheses convert each balanced net ionic equation to a balanced formula unit equation.
(a) $Cl_2 + OH^- \rightarrow ClO_3^- + Cl^- + H_2O$ (Cl_2 and hot NaOH)
(b) $Pb + H^+ + Br^- \rightarrow PbBr_2(s) + H_2$ (Pb(s) and HBr)

Redox Titrations: Mole Method and Molarity

66. What volume of 0.150 *M* $KMnO_4$ would be required to oxidize 25.0 mL of 0.100 *M* $FeSO_4$ in acidic solution? Refer to Example 11-22.

67. What volume of 0.150 *M* $K_2Cr_2O_7$ would be required to oxidize 70.0 mL of 0.100 *M* Na_2SO_3 in acidic solution? The products include Cr^{3+} and SO_4^{2-} ions. Refer to Example 11-23.

68. What volume of 0.200 *M* $KMnO_4$ would be required to oxidize 40.0 mL of 0.100 *M* KI in acidic solution? Products include Mn^{2+} and I_2.

69. What volume of 0.200 *M* $K_2Cr_2O_7$ would be required to oxidize 50.0 mL of 0.150 *M* KI in acidic solution? Products include Cr^{3+} and I_2.

70. (a) A solution of sodium thiosulfate, $Na_2S_2O_3$, is 0.1442 *M*. 40.00 mL of this solution reacts with 26.36 mL of I_2 solution. Calculate the molarity of the I_2 solution.

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

(b) 25.32 mL of the I_2 solution is required to titrate a sample containing As_2O_3. Calculate the mass of As_2O_3 (197.8 g/mol) in the sample.

$$As_2O_3 + 5H_2O + 2I_2 \longrightarrow 2\ H_3AsO_4 + 4HI$$

71. Copper(II) ions, Cu^{2+}, can be determined by the net reaction

$$2Cu^{2+} + 2I^- + 2S_2O_3^{2-} \longrightarrow 2CuI(s) + S_4O_6^{2-}$$

A 2.075-g sample containing $CuSO_4$ and excess KI is titrated with 32.55 mL of 0.1214 *M* solution of $Na_2S_2O_3$. What is the percent $CuSO_4$ (159.6 g/mol) in the sample?

72. What volume of 3.0 *M* nitrate ion solution would be required to react with 25. mL of 0.80 *M* sulfide ion solution? (*Hint:* The equation is not balanced.)

$$NO_3^- + S^{2-} \rightarrow NO + S \qquad \text{(acidic solution)}$$

***73.** The iron in a 5.675-g sample containing some Fe_2O_3 is reduced to Fe^{2+}. The Fe^{2+} is titrated with 12.02 mL of 0.1467 *M* $K_2Cr_2O_7$ in an acid solution.

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

Find (a) the mass of Fe and (b) the percentage of Fe in the sample.

74. Calculate the molarity of a solution that contains 12.6 g of $KMnO_4$ in 500. mL of solution to be used in the reaction that produces MnO_4^{2-} ions as the reduction product.

***75.** A 0.783-g sample of an ore of iron is dissolved in acid and converted to Fe(II). The sample is oxidized by 38.50 mL of 0.161 *M* ceric sulfate, $Ce(SO_4)_2$, solution; the cerium(IV) ion, Ce^{4+}, is reduced to Ce^{3+} ion. (a) Write a balanced equation for the reaction. (b) What is the percent iron in the ore?

Mixed Exercises

76. Calculate the molarity of a hydrochloric acid solution if 32.75 mL of it reacts with 0.4011 g of sodium carbonate.

77. Calculate the molarity and the normality of a sulfuric acid solution if 32.75 mL of it reacts with 0.4011 g of sodium carbonate.

78. Find the number of mmols of HCl that reacts with 25.5 mL of 0.110 *M* NaOH. What volume of 0.303 *M* HCl is needed to furnish this amount of HCl?

79. What is the composition of the final solution when 25.5 mL of 0.110 *M* NaOH and 25.5 mL of 0.205 *M* HCl solutions are mixed?

80. What volume of 0.1123 *M* HCl is needed to neutralize completely 1.58 g of $Ca(OH)_2$?

81. What mass of NaOH is needed to neutralize 45.50 mL of 0.1036 *M* HCl? If the NaOH is available as a 0.1333 *M* aqueous solution, what volume will be required?

82. What volume of 0.246 *M* H_2SO_4 solution would be required to neutralize completely 39.4 mL of 0.302 *M* KOH solution?

83. What volume of 0.388 *N* H_2SO_4 solution would be required to neutralize completely 37.4 mL of 0.302 *N* KOH solution?

84. What volume of 0.1945 normal sodium hydroxide would be required to neutralize completely 38.38 mL of 0.1023 normal H_2SO_4 solution?

85. Benzoic acid, C_6H_5COOH, is sometimes used as a primary standard for the standardization of solutions of bases. A 1.862-g sample of the acid is neutralized by 33.00 mL of NaOH solution. What is the molarity of the base solution?

$$C_6H_5COOH(s) + NaOH(aq) \longrightarrow C_6H_5COONa(aq) + H_2O(\ell)$$

86. Find the volume of 0.250 M HI solution required to titrate
(a) 25.0 mL of 0.100 M NaOH
(b) 5.03 g of $AgNO_3$ ($Ag^+ + I^- \rightarrow AgI(s)$)
(c) 0.621 g $CuSO_4$ ($2Cu^{2+} + 4I^- \rightarrow 2CuI(s) + I_2(s)$)

CONCEPTUAL EXERCISES

87. Describe how you could prepare 1.00 L of 1.00×10^{-6} M NaCl solution by using a balance that can only measure masses to 0.01 g.

88. Ascorbic acid (vitamin C), along with many other reputed properties, acts as an antioxidant. The following equation illustrates its antioxidant properties.

$$H_2C_6H_6O_6 \longrightarrow C_6H_6O_6 + H_2$$

What is an antioxidant? Assign oxidation numbers. Is vitamin C oxidized or reduced in this reaction?

BUILDING YOUR KNOWLEDGE

89. For the formation of 1.00 mol of water, which reaction uses the most nitric acid?
(a) $3Cu(s) + 8HNO_3(aq) \rightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(\ell)$
(b) $Al_2O_3(s) + 6HNO_3(aq) \rightarrow 2Al(NO_3)_3(aq) + 3H_2O(\ell)$
(c) $4Zn(s) + 10HNO_3(aq) \rightarrow 4Zn(NO_3)_2(aq) + NH_4NO_3(aq) + 3H_2O(\ell)$

90. Limonite is an ore of iron that contains $2Fe_2O_3{\cdot}3H_2O$. A 0.5166-g sample of limonite is dissolved in acid and treated so that all the iron is converted to ferrous ions, Fe^{2+}. This sample requires 42.96 mL of 0.02130 M sodium dichromate solution, $Na_2Cr_2O_7$, for titration. Fe^{2+} is oxidized to Fe^{3+}, and $Cr_2O_7{}^{2-}$ is reduced to Cr^{3+}. What is the percent iron in the limonite? If your answer had been over 100% limonite, what conclusion could you make, presuming that the analytical data are correct?

91. One of the troublesome products of a water treatment plant in some areas of the country is $Mg(OH)_2$, a gelatinous precipitate formed during water softening. A suggestion was made that instead of shoveling the precipitate out of the pool during cleaning, the $Mg(OH)_2$ could be neutralized with hydrochloric acid to produce a soluble compound, $MgCl_2$. Then the pool could be flushed out with fresh water. Calculate the volume of 12.0 M HCl necessary to neutralize 4750 L of solution containing 1.50 g of $Mg(OH)_2$ per liter.

92. Silver nitrate and calcium chloride solutions produce a heavy, white precipitate when mixed. Chemical analysis indicates that the precipitate is silver chloride. What mass of silver chloride would be produced if 45 mL of 6.0 M silver nitrate is mixed with 45 mL of 6.0 M calcium chloride?

93. A 0.500-g sample of a crystalline monoprotic acid was dissolved in sufficient water to produce 100. mL of solution. Neutralization of the resulting solution required 75.0 mL of 0.150 M NaOH. How many moles of the acid were present in the initial acid solution?

94. The typical concentration of HCl in stomach acid (digestive juice) is a concentration of about 8.0×10^{-2} M. One experiences "acid stomach" when the stomach contents reach about 1.0×10^{-1} M HCl. One antacid tablet contains 334 mg of active ingredient, $NaAl(OH)_2CO_3$. Assume that you have acid stomach and that your stomach contains 800. mL of 1.0×10^{-1} M HCl. Calculate the number of mmol of HCl in the stomach and the number of mmol of HCl that the tablet *can* neutralize. Which is greater? (The neutralization reaction produces NaCl, $AlCl_3$, CO_2, and H_2O.)

95. Refer to Exercises 20 and 21. Notice that the percent by mass of solute is nearly the same for both solutions. How many moles of solute are present per liter of each solution? Are the moles of solute per liter also nearly equal? Why or why not?

96. The etching of glass by hydrofluoric acid may be represented by the simplified reaction of silica with HF.

$$SiO_2(s) + HF(aq) \longrightarrow H_2SiF_6(aq) + H_2O(\ell)$$

This is an acid–base reaction in which a weak acid is used to produce an even weaker acid. Is it also an oxidation–reduction reaction? Balance the equation.

97. Write a Lewis formula for the anion $SiF_6{}^{2-}$ that would be produced from the weak acid H_2SiF_6. Use the VSEPR theory to predict the shape of $SiF_6{}^{2-}$.

98. Baking soda, $NaHCO_3$, used to be a common remedy for "acid stomach." What weight of baking soda would be required to neutralize 85 mL of digestive juice, corresponding in acidity to 0.17 M HCl?

99. Oxalic acid, a poisonous compound, is found in certain vegetables such as spinach and rhubarb, but in concentrations well below toxic limits. The manufacturers of a spinach juice concentration routinely test their product using an oxalic acid analysis to avoid any problems from an unexpectedly high concentration of this chemical. A titration with potassium permanganate is used for the oxalic acid assay, according to the following net equation.

$$5H_2C_2O_4 + 2MnO_4{}^- + 6H^+ \longrightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

Calculate the molarity of an oxalic acid solution requiring 23.2 mL of 0.127 M permanganate for a 25.0 mL portion of the solution.