Chapter 4

Stoichiometry of Chemical Reactions



Figure 4.1 Many modern rocket fuels are solid mixtures of substances combined in carefully measured amounts and ignited to yield a thrust-generating chemical reaction. (credit: modification of work by NASA)

Chapter Outline

- 4.1 Writing and Balancing Chemical Equations
- 4.2 Classifying Chemical Reactions
- 4.3 Reaction Stoichiometry
- 4.4 Reaction Yields
- 4.5 Quantitative Chemical Analysis

Introduction

Solid-fuel rockets are a central feature in the world's space exploration programs, including the new Space Launch System being developed by the National Aeronautics and Space Administration (NASA) to replace the retired Space Shuttle fleet (Figure 4.1). The engines of these rockets rely on carefully prepared solid mixtures of chemicals combined in precisely measured amounts. Igniting the mixture initiates a vigorous chemical reaction that rapidly generates large amounts of gaseous products. These gases are ejected from the rocket engine through its nozzle, providing the thrust needed to propel heavy payloads into space. Both the nature of this chemical reaction and the relationships between the amounts of the substances being consumed and produced by the reaction are critically important considerations that determine the success of the technology. This chapter will describe how to symbolize chemical reactions using chemical equations, how to classify some common chemical reactions by identifying patterns of reactivity, and how to determine the quantitative relations between the amounts of substances involved in chemical reactions—that is, the reaction *stoichiometry*.

4.1 Writing and Balancing Chemical Equations

By the end of this section, you will be able to:

- Derive chemical equations from narrative descriptions of chemical reactions.
- Write and balance chemical equations in molecular, total ionic, and net ionic formats.

An earlier chapter of this text introduced the use of element symbols to represent individual atoms. When atoms gain or lose electrons to yield ions, or combine with other atoms to form molecules, their symbols are modified or combined to generate chemical formulas that appropriately represent these species. Extending this symbolism to represent both the identities and the relative quantities of substances undergoing a chemical (or physical) change involves writing and balancing a **chemical equation**. Consider as an example the reaction between one methane molecule (CH_4) and two diatomic oxygen molecules (O_2) to produce one carbon dioxide molecule (CO_2) and two water molecules (H_2O). The chemical equation representing this process is provided in the upper half of **Figure 4.2**, with space-filling molecular models shown in the lower half of the figure.

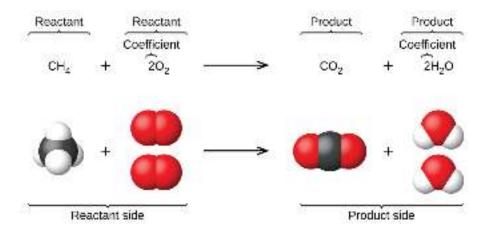


Figure 4.2 The reaction between methane and oxygen to yield carbon dioxide and water (shown at bottom) may be represented by a chemical equation using formulas (top).

This example illustrates the fundamental aspects of any chemical equation:

- 1. The substances undergoing reaction are called **reactants**, and their formulas are placed on the left side of the equation.
- 2. The substances generated by the reaction are called **products**, and their formulas are placed on the right side of the equation.
- 3. Plus signs (+) separate individual reactant and product formulas, and an arrow (→) separates the reactant and product (left and right) sides of the equation.
- 4. The relative numbers of reactant and product species are represented by **coefficients** (numbers placed immediately to the left of each formula). A coefficient of 1 is typically omitted.

It is common practice to use the smallest possible whole-number coefficients in a chemical equation, as is done in this example. Realize, however, that these coefficients represent the *relative* numbers of reactants and products, and, therefore, they may be correctly interpreted as ratios. Methane and oxygen react to yield carbon dioxide and water in a 1:2:1:2 ratio. This ratio is satisfied if the numbers of these molecules are, respectively, 1-2-1-2, or 2-4-2-4, or 3-6-3-6, and so on (**Figure 4.3**). Likewise, these coefficients may be interpreted with regard to any amount (number) unit, and so this equation may be correctly read in many ways, including:

• One methane molecule and two oxygen molecules react to yield one carbon dioxide molecule and two water

molecules.

- One dozen methane molecules and two dozen oxygen molecules react to yield one dozen carbon dioxide molecules and two dozen water molecules.
- One mole of methane molecules and 2 moles of oxygen molecules react to yield 1 mole of carbon dioxide
 molecules and 2 moles of water molecules.

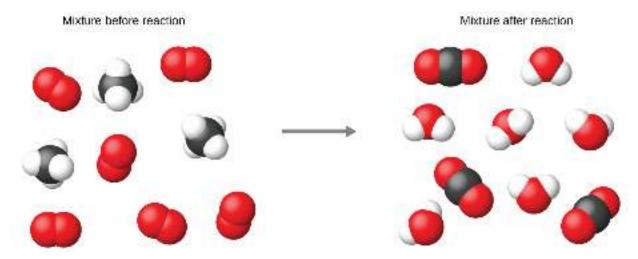


Figure 4.3 Regardless of the absolute numbers of molecules involved, the ratios between numbers of molecules of each species that react (the reactants) and molecules of each species that form (the products) are the same and are given by the chemical reaction equation.

Balancing Equations

The chemical equation described in section 4.1 is **balanced**, meaning that equal numbers of atoms for each element involved in the reaction are represented on the reactant and product sides. This is a requirement the equation must satisfy to be consistent with the law of conservation of matter. It may be confirmed by simply summing the numbers of atoms on either side of the arrow and comparing these sums to ensure they are equal. Note that the number of atoms for a given element is calculated by multiplying the coefficient of any formula containing that element by the element's subscript in the formula. If an element appears in more than one formula on a given side of the equation, the number of atoms represented in each must be computed and then added together. For example, both product species in the example reaction, CO_2 and H_2O , contain the element oxygen, and so the number of oxygen atoms on the product side of the equation is

$$\left(1 \text{ CO}_2 \text{ molecule} \times \frac{2 \text{ O atoms}}{\text{CO}_2 \text{ molecule}}\right) + \left(2 \text{ H}_2 \text{ O molecules} \times \frac{1 \text{ O atom}}{\text{H}_2 \text{ O molecule}}\right) = 4 \text{ O atoms}$$

The equation for the reaction between methane and oxygen to yield carbon dioxide and water is confirmed to be balanced per this approach, as shown here:

A balanced chemical equation often may be derived from a qualitative description of some chemical reaction by a

fairly simple approach known as balancing by inspection. Consider as an example the decomposition of water to yield molecular hydrogen and oxygen. This process is represented qualitatively by an unbalanced chemical equation:

$$H_2O \longrightarrow H_2 + O_2$$
 (unbalanced)

Comparing the number of H and O atoms on either side of this equation confirms its imbalance:

Element	Reactants	Products	Balanced?
Н	1 × 2 = 2	1 × 2 = 2	2 = 2, yes
0	1 × 1 = 1	1 × 2 = 2	1 ≠ 2, no

The numbers of H atoms on the reactant and product sides of the equation are equal, but the numbers of O atoms are not. To achieve balance, the coefficients of the equation may be changed as needed. Keep in mind, of course, that the formula subscripts define, in part, the identity of the substance, and so these cannot be changed without altering the qualitative meaning of the equation. For example, changing the reactant formula from H_2O to H_2O_2 would yield balance in the number of atoms, but doing so also changes the reactant's identity (it's now hydrogen peroxide and not water). The O atom balance may be achieved by changing the coefficient for H₂O to 2.

	2 H ₂	$O \longrightarrow H_2 + O$	2 (unba	lanced)
Eleme	ent	Reactants	Products	Balanced
Н		2 × 2 = 4	1 × 2 = 2	4 ≠ 2, no

 $2 \times 1 = 2$ $1 \times 2 = 2$ 2 = 2, yes

The H atom balance was upset by this change, but it is easily reestablished by changing the coefficient for the H₂ product to 2.

$2H_2O \longrightarrow 2H_2 + O_2$ (balanced)				
Element	Reactants	Products	Balanced?	
Н	2 × 2 = 4	2 × 2 = 4	4 = 4, yes	
0	2 × 1 = 2	1 × 2 = 2	2 = 2, yes	

These coefficients yield equal numbers of both H and O atoms on the reactant and product sides, and the balanced equation is, therefore:

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

Example 4.1

Balancing Chemical Equations

Write a balanced equation for the reaction of molecular nitrogen (N_2) and oxygen (O_2) to form dinitrogen pentoxide.

Solution

First, write the unbalanced equation.

$$N_2 + O_2 \longrightarrow N_2O_5$$
 (unbalanced)

Next, count the number of each type of atom present in the unbalanced equation.

Element	Reactants	Products	Balanced?
N	1 × 2 = 2	1 × 2 = 2	2 = 2, yes
0	1 × 2 = 2	1 × 5 = 5	2 ≠ 5, no

Though nitrogen is balanced, changes in coefficients are needed to balance the number of oxygen atoms. To balance the number of oxygen atoms, a reasonable first attempt would be to change the coefficients for the O_2 and N_2O_5 to integers that will yield 10 O atoms (the least common multiple for the O atom subscripts in these two formulas).

$N_2 + 5O_2$	\longrightarrow 2N ₂ O ₅	(unbalanced)
		(will distribute)

Element	Reactants	Products	Balanced?
N	1 × 2 = 2	2 × 2 = 4	2 ≠ 4, no
0	5 × 2 = 10	2 × 5 = 10	10 = 10, yes

The N atom balance has been upset by this change; it is restored by changing the coefficient for the reactant N_2 to 2.

$$2N_2 + 5O_2 \longrightarrow 2N_2O_5$$

Element	Reactants	Products	Balanced?
N	2 × 2 = 4	2 × 2 = 4	4 = 4, yes
0	5 × 2 = 10	2 × 5 = 10	10 = 10, yes

The numbers of N and O atoms on either side of the equation are now equal, and so the equation is balanced.

Check Your Learning

Write a balanced equation for the decomposition of ammonium nitrate to form molecular nitrogen, molecular oxygen, and water. (Hint: Balance oxygen last, since it is present in more than one molecule on the right side of the equation.)

Answer:
$$2NH_4NO_3 \longrightarrow 2N_2 + O_2 + 4H_2O$$

It is sometimes convenient to use fractions instead of integers as intermediate coefficients in the process of balancing a chemical equation. When balance is achieved, all the equation's coefficients may then be multiplied by a whole number to convert the fractional coefficients to integers without upsetting the atom balance. For example, consider the reaction of ethane (C_2H_6) with oxygen to yield H_2O and CO_2 , represented by the unbalanced equation:

$$C_2H_6 + O_2 \longrightarrow H_2O + CO_2$$
 (unbalanced)

Following the usual inspection approach, one might first balance C and H atoms by changing the coefficients for the two product species, as shown:

$$C_2H_6 + O_2 \longrightarrow 3H_2O + 2CO_2$$
 (unbalanced)

This results in seven O atoms on the product side of the equation, an odd number—no integer coefficient can be used with the O_2 reactant to yield an odd number, so a fractional coefficient, $\frac{7}{2}$, is used instead to yield a provisional balanced equation:

$$C_2H_6 + \frac{7}{2}O_2 \longrightarrow 3H_2O + 2CO_2$$

A conventional balanced equation with integer-only coefficients is derived by multiplying each coefficient by 2:

$$2C_2H_6 + 7O_2 \longrightarrow 6H_2O + 4CO_2$$

Finally with regard to balanced equations, recall that convention dictates use of the *smallest whole-number coefficients*. Although the equation for the reaction between molecular nitrogen and molecular hydrogen to produce ammonia is, indeed, balanced,

$$3N_2 + 9H_2 \longrightarrow 6NH_3$$

the coefficients are not the smallest possible integers representing the relative numbers of reactant and product molecules. Dividing each coefficient by the greatest common factor, 3, gives the preferred equation:

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

Link to Learning

Use this interactive tutorial (http://openstaxcollege.org/l/16BalanceEq) for additional practice balancing equations.

Additional Information in Chemical Equations

The physical states of reactants and products in chemical equations very often are indicated with a parenthetical abbreviation following the formulas. Common abbreviations include s for solids, l for liquids, g for gases, and aq for substances dissolved in water ($aqueous\ solutions$, as introduced in the preceding chapter). These notations are illustrated in the example equation here:

$$2\text{Na}(s) + 2\text{H}_2\text{O}(l) \longrightarrow 2\text{NaOH}(aq) + \text{H}_2(g)$$

This equation represents the reaction that takes place when sodium metal is placed in water. The solid sodium reacts with liquid water to produce molecular hydrogen gas and the ionic compound sodium hydroxide (a solid in pure form, but readily dissolved in water).

Special conditions necessary for a reaction are sometimes designated by writing a word or symbol above or below the equation's arrow. For example, a reaction carried out by heating may be indicated by the uppercase Greek letter delta (Δ) over the arrow.

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$$

Other examples of these special conditions will be encountered in more depth in later chapters.

Equations for Ionic Reactions

Given the abundance of water on earth, it stands to reason that a great many chemical reactions take place in aqueous media. When ions are involved in these reactions, the chemical equations may be written with various levels of detail appropriate to their intended use. To illustrate this, consider a reaction between ionic compounds taking place in an aqueous solution. When aqueous solutions of $CaCl_2$ and $AgNO_3$ are mixed, a reaction takes place producing aqueous

 $Ca(NO_3)_2$ and solid AgCl:

$$CaCl_2(aq) + 2AgNO_3(aq) \longrightarrow Ca(NO_3)_2(aq) + 2AgCl(s)$$

This balanced equation, derived in the usual fashion, is called a **molecular equation** because it doesn't explicitly represent the ionic species that are present in solution. When ionic compounds dissolve in water, they may *dissociate* into their constituent ions, which are subsequently dispersed homogenously throughout the resulting solution (a thorough discussion of this important process is provided in the chapter on solutions). Ionic compounds dissolved in water are, therefore, more realistically represented as dissociated ions, in this case:

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

 $2AgNO_3(aq) \longrightarrow 2Ag^+(aq) + 2NO_3^-(aq)$
 $Ca(NO_3)_2(aq) \longrightarrow Ca^{2+}(aq) + 2NO_3^-(aq)$

Unlike these three ionic compounds, AgCl does not dissolve in water to a significant extent, as signified by its physical state notation, *s*.

Explicitly representing all dissolved ions results in a **complete ionic equation**. In this particular case, the formulas for the dissolved ionic compounds are replaced by formulas for their dissociated ions:

$$\text{Ca}^{2+}(aq) + 2\text{Cl}^{-}(aq) + 2\text{Ag}^{+}(aq) + 2\text{NO}_{3}^{-}(aq) \longrightarrow \text{Ca}^{2+}(aq) + 2\text{NO}_{3}^{-}(aq) + 2\text{AgCl}(s)$$

Examining this equation shows that two chemical species are present in identical form on both sides of the arrow, $Ca^{2+}(aq)$ and $NO_3^-(aq)$. These **spectator ions**—ions whose presence is required to maintain charge neutrality—are neither chemically nor physically changed by the process, and so they may be eliminated from the equation to yield a more succinct representation called a **net ionic equation**:

$$\frac{\text{Ca}^{2+}(aq) + 2\text{Cl}^{-}(aq) + 2\text{Ag}^{+}(aq) + \frac{2\text{NO}_{3}^{-}(aq)}{3} \longrightarrow \frac{\text{Ca}^{2+}(aq)}{3} + \frac{2\text{NO}_{3}^{-}(aq)}{3} + 2\text{AgCl}(s)}{2\text{Cl}^{-}(aq) + 2\text{Ag}^{+}(aq) \longrightarrow 2\text{AgCl}(s)}$$

Following the convention of using the smallest possible integers as coefficients, this equation is then written:

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

This net ionic equation indicates that solid silver chloride may be produced from dissolved chloride and silver(I) ions, regardless of the source of these ions. These molecular and complete ionic equations provide additional information, namely, the ionic compounds used as sources of Cl^- and Ag^+ .

Example 4.2

Molecular and Ionic Equations

When carbon dioxide is dissolved in an aqueous solution of sodium hydroxide, the mixture reacts to yield aqueous sodium carbonate and liquid water. Write balanced molecular, complete ionic, and net ionic equations for this process.

Solution

Begin by identifying formulas for the reactants and products and arranging them properly in chemical equation form:

$$CO_2(aq) + NaOH(aq) \longrightarrow Na_2CO_3(aq) + H_2O(l)$$
 (unbalanced)

Balance is achieved easily in this case by changing the coefficient for NaOH to 2, resulting in the molecular equation for this reaction:

$$CO_2(aq) + 2NaOH(aq) \longrightarrow Na_2CO_3(aq) + H_2O(l)$$

The two dissolved ionic compounds, NaOH and Na₂CO₃, can be represented as dissociated ions to yield the

complete ionic equation:

$$CO_2(aq) + 2Na^+(aq) + 2OH^-(aq) \longrightarrow 2Na^+(aq) + CO_3^{2-}(aq) + H_2O(l)$$

Finally, identify the spectator ion(s), in this case $Na^+(aq)$, and remove it from each side of the equation to generate the net ionic equation:

$$CO_2(aq) + \frac{2Na^+(aq)}{2Na^+(aq)} + 2OH^-(aq) \longrightarrow \frac{2Na^+(aq)}{2Na^+(aq)} + CO_3^{2-}(aq) + H_2O(l)$$

 $CO_2(aq) + 2OH^-(aq) \longrightarrow CO_3^{2-}(aq) + H_2O(l)$

Check Your Learning

Diatomic chlorine and sodium hydroxide (lye) are commodity chemicals produced in large quantities, along with diatomic hydrogen, via the electrolysis of brine, according to the following unbalanced equation:

$$NaCl(aq) + H_2O(l) \xrightarrow{\text{electricity}} NaOH(aq) + H_2(g) + Cl_2(g)$$

Write balanced molecular, complete ionic, and net ionic equations for this process.

Answer:
$$2\text{NaCl}(aq) + 2\text{H}_2\text{O}(l) \longrightarrow 2\text{NaOH}(aq) + \text{H}_2(g) + \text{Cl}_2(g)$$
 (molecular) $2\text{Na}^+(aq) + 2\text{Cl}^-(aq) + 2\text{H}_2\text{O}(l) \longrightarrow 2\text{Na}^+(aq) + 2\text{OH}^-(aq) + \text{H}_2(g) + \text{Cl}_2(g)$ (complete ionic) $2\text{Cl}^-(aq) + 2\text{H}_2\text{O}(l) \longrightarrow 2\text{OH}^-(aq) + \text{H}_2(g) + \text{Cl}_2(g)$ (net ionic)

4.2 Classifying Chemical Reactions

By the end of this section, you will be able to:

- Define three common types of chemical reactions (precipitation, acid-base, and oxidation-reduction)
- Classify chemical reactions as one of these three types given appropriate descriptions or chemical equations
- Identify common acids and bases
- Predict the solubility of common inorganic compounds by using solubility rules
- · Compute the oxidation states for elements in compounds

Humans interact with one another in various and complex ways, and we classify these interactions according to common patterns of behavior. When two humans exchange information, we say they are communicating. When they exchange blows with their fists or feet, we say they are fighting. Faced with a wide range of varied interactions between chemical substances, scientists have likewise found it convenient (or even necessary) to classify chemical interactions by identifying common patterns of reactivity. This module will provide an introduction to three of the most prevalent types of chemical reactions: precipitation, acid-base, and oxidation-reduction.

Precipitation Reactions and Solubility Rules

A **precipitation reaction** is one in which dissolved substances react to form one (or more) solid products. Many reactions of this type involve the exchange of ions between ionic compounds in aqueous solution and are sometimes referred to as *double displacement*, *double replacement*, or *metathesis* reactions. These reactions are common in nature and are responsible for the formation of coral reefs in ocean waters and kidney stones in animals. They are used widely in industry for production of a number of commodity and specialty chemicals. Precipitation reactions also play a central role in many chemical analysis techniques, including spot tests used to identify metal ions and *gravimetric methods* for determining the composition of matter (see the last module of this chapter).

The extent to which a substance may be dissolved in water, or any solvent, is quantitatively expressed as its solubility,

defined as the maximum concentration of a substance that can be achieved under specified conditions. Substances with relatively large solubilities are said to be **soluble**. A substance will **precipitate** when solution conditions are such that its concentration exceeds its solubility. Substances with relatively low solubilities are said to be **insoluble**, and these are the substances that readily precipitate from solution. More information on these important concepts is provided in a later chapter on solutions. For purposes of predicting the identities of solids formed by precipitation reactions, one may simply refer to patterns of solubility that have been observed for many ionic compounds (**Table 4.1**).

Soluble Ionic Compounds	contain these ions	exceptions
	group I cations:	
	Li ⁺	
	Na ⁺	
	\mathbf{K}^{+}	none
	Rb ⁺	
	Cs ⁺	
	Cl ⁻	
	Br⁻	compounds with $\mathrm{Ag^+}$, $\mathrm{Hg_2^{2^+}}$, and $\mathrm{Pb^{2^+}}$
	I-	
	F ⁻	compounds with group 2 metal cations, Pb ²⁺ and Fe ³⁺
	C ₂ H ₃ O ₂ -	
	HCO ₃ -	none
	NO ₃ -	none
	ClO ₃ -	
	SO ₄ ²⁻	compounds with Ag ⁺ , Ba ²⁺ , Ca ²⁺ , Hg ₂ ²⁺ , Pb ²⁺ and Sr ²⁺
Insoluble Ionic Compounds	contain these ions	exceptions
	CO ₃ ²⁻	
	CrO ₄ ²⁻	
	PO ₄ ³⁻	compounds with group 1 cations and $\mathrm{NH_4}^+$
	S ²⁻	
	OH ⁻	compounds with group 1 cations and Ba ²⁺

Table 4.1

A vivid example of precipitation is observed when solutions of potassium iodide and lead nitrate are mixed, resulting in the formation of solid lead iodide:

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

This observation is consistent with the solubility guidelines: The only insoluble compound among all those involved is lead iodide, one of the exceptions to the general solubility of iodide salts.

The net ionic equation representing this reaction is:

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

Lead iodide is a bright yellow solid that was formerly used as an artist's pigment known as iodine yellow (**Figure 4.4**). The properties of pure PbI₂ crystals make them useful for fabrication of X-ray and gamma ray detectors.



Figure 4.4 A precipitate of PbI₂ forms when solutions containing Pb²⁺ and I⁻ are mixed. (credit: Der Kreole/ Wikimedia Commons)

The solubility guidelines in **Table 4.1** may be used to predict whether a precipitation reaction will occur when solutions of soluble ionic compounds are mixed together. One merely needs to identify all the ions present in the solution and then consider if possible cation/anion pairing could result in an insoluble compound. For example, mixing solutions of silver nitrate and sodium fluoride will yield a solution containing Ag⁺, NO₃⁻, Na⁺, and F⁻ ions. Aside from the two ionic compounds originally present in the solutions, AgNO₃ and NaF, two additional ionic compounds may be derived from this collection of ions: NaNO₃ and AgF. The solubility guidelines indicate all nitrate salts are soluble but that AgF is one of the exceptions to the general solubility of fluoride salts. A precipitation reaction, therefore, is predicted to occur, as described by the following equations:

$$NaF(aq) + AgNO_3(aq) \longrightarrow AgF(s) + NaNO_3(aq)$$
 (molecular)
 $Ag^+(aq) + F^-(aq) \longrightarrow AgF(s)$ (net ionic)

Example 4.3

Predicting Precipitation Reactions

Predict the result of mixing reasonably concentrated solutions of the following ionic compounds. If precipitation is expected, write a balanced net ionic equation for the reaction.

- (a) potassium sulfate and barium nitrate
- (b) lithium chloride and silver acetate

(c) lead nitrate and ammonium carbonate

Solution

(a) The two possible products for this combination are KNO_3 and $BaSO_4$. The solubility guidelines indicate $BaSO_4$ is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

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

(b) The two possible products for this combination are $LiC_2H_3O_2$ and AgCl. The solubility guidelines indicate AgCl is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

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

(c) The two possible products for this combination are $PbCO_3$ and NH_4NO_3 . The solubility guidelines indicate $PbCO_3$ is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

$$Pb^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow PbCO_3(s)$$

Check Your Learning

Which solution could be used to precipitate the barium ion, Ba²⁺, in a water sample: sodium chloride, sodium hydroxide, or sodium sulfate? What is the formula for the expected precipitate?

Answer: sodium sulfate, BaSO₄

Acid-Base Reactions

An **acid-base reaction** is one in which a hydrogen ion, H⁺, is transferred from one chemical species to another. Such reactions are of central importance to numerous natural and technological processes, ranging from the chemical transformations that take place within cells and the lakes and oceans, to the industrial-scale production of fertilizers, pharmaceuticals, and other substances essential to society. The subject of acid-base chemistry, therefore, is worthy of thorough discussion, and a full chapter is devoted to this topic later in the text.

For purposes of this brief introduction, we will consider only the more common types of acid-base reactions that take place in aqueous solutions. In this context, an **acid** is a substance that will dissolve in water to yield hydronium ions, H_3O^+ . As an example, consider the equation shown here:

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

The process represented by this equation confirms that hydrogen chloride is an acid. When dissolved in water, H_3O^+ ions are produced by a chemical reaction in which H^+ ions are transferred from HCl molecules to H_2O molecules (**Figure 4.5**).

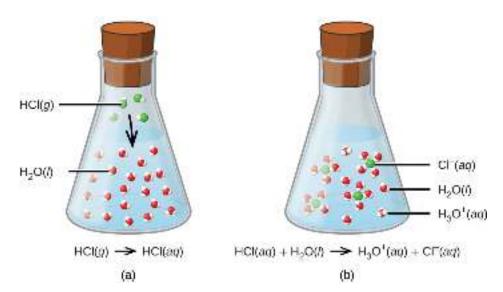


Figure 4.5 When hydrogen chloride gas dissolves in water, (a) it reacts as an acid, transferring protons to water molecules to yield (b) hydronium ions (and solvated chloride ions).

The nature of HCl is such that its reaction with water as just described is essentially 100% efficient: Virtually every HCl molecule that dissolves in water will undergo this reaction. Acids that completely react in this fashion are called **strong acids**, and HCl is one among just a handful of common acid compounds that are classified as strong (**Table 4.2**). A far greater number of compounds behave as **weak acids** and only partially react with water, leaving a large majority of dissolved molecules in their original form and generating a relatively small amount of hydronium ions. Weak acids are commonly encountered in nature, being the substances partly responsible for the tangy taste of citrus fruits, the stinging sensation of insect bites, and the unpleasant smells associated with body odor. A familiar example of a weak acid is acetic acid, the main ingredient in food vinegars:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons CH_3CO_2^-(aq) + H_3O^+(aq)$$

When dissolved in water under typical conditions, only about 1% of acetic acid molecules are present in the ionized form, $CH_3CO_2^-$ (**Figure 4.6**). (The use of a double-arrow in the equation above denotes the partial reaction aspect of this process, a concept addressed fully in the chapters on chemical equilibrium.)

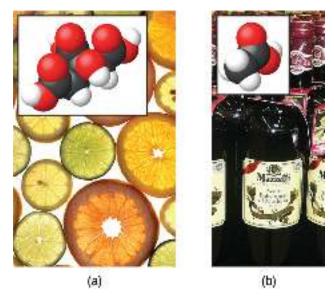


Figure 4.6 (a) Fruits such as oranges, lemons, and grapefruit contain the weak acid citric acid. (b) Vinegars contain the weak acid acetic acid. (credit a: modification of work by Scott Bauer; credit b: modification of work by Brücke-Osteuropa/Wikimedia Commons)

Common Strong Acids Formula Name in Aqueo

Compound Formula	Name in Aqueous Solution
HBr	hydrobromic acid
HCI	hydrochloric acid
HI	hydroiodic acid
HNO ₃	nitric acid
HClO ₄	perchloric acid
H ₂ SO ₄	sulfuric acid

Table 4.2

A **base** is a substance that will dissolve in water to yield hydroxide ions, OH⁻. The most common bases are ionic compounds composed of alkali or alkaline earth metal cations (groups 1 and 2) combined with the hydroxide ion—for example, NaOH and Ca(OH)₂. Unlike the acid compounds discussed previously, these compounds do not react chemically with water; instead they dissolve and dissociate, releasing hydroxide ions directly into the solution. For example, KOH and Ba(OH)₂ dissolve in water and dissociate completely to produce cations (K⁺ and Ba²⁺, respectively) and hydroxide ions, OH⁻. These bases, along with other hydroxides that completely dissociate in water, are considered **strong bases**.

Consider as an example the dissolution of lye (sodium hydroxide) in water:

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

This equation confirms that sodium hydroxide is a base. When dissolved in water, NaOH dissociates to yield Na⁺ and OH⁻ ions. This is also true for any other ionic compound containing hydroxide ions. Since the dissociation process is essentially complete when ionic compounds dissolve in water under typical conditions, NaOH and other ionic hydroxides are all classified as strong bases.

Unlike ionic hydroxides, some compounds produce hydroxide ions when dissolved by chemically reacting with water

molecules. In all cases, these compounds react only partially and so are classified as **weak bases**. These types of compounds are also abundant in nature and important commodities in various technologies. For example, global production of the weak base ammonia is typically well over 100 metric tons annually, being widely used as an agricultural fertilizer, a raw material for chemical synthesis of other compounds, and an active ingredient in household cleaners (**Figure 4.7**). When dissolved in water, ammonia reacts partially to yield hydroxide ions, as shown here:

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

This is, by definition, an acid-base reaction, in this case involving the transfer of H^+ ions from water molecules to ammonia molecules. Under typical conditions, only about 1% of the dissolved ammonia is present as NH_4^+ ions.





Figure 4.7 Ammonia is a weak base used in a variety of applications. (a) Pure ammonia is commonly applied as an agricultural fertilizer. (b) Dilute solutions of ammonia are effective household cleansers. (credit a: modification of work by National Resources Conservation Service; credit b: modification of work by pat00139)

A **neutralization reaction** is a specific type of acid-base reaction in which the reactants are an acid and a base (but not water), and the products are often a **salt** and water

$$acid + base \longrightarrow salt + water$$

To illustrate a neutralization reaction, consider what happens when a typical antacid such as milk of magnesia (an aqueous suspension of solid $Mg(OH)_2$) is ingested to ease symptoms associated with excess stomach acid (HCl):

$$Mg(OH)_2(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + 2H_2O(l).$$

Note that in addition to water, this reaction produces a salt, magnesium chloride.

Example 4.4

Writing Equations for Acid-Base Reactions

Write balanced chemical equations for the acid-base reactions described here:

- (a) the weak acid hydrogen hypochlorite reacts with water
- (b) a solution of barium hydroxide is neutralized with a solution of nitric acid

Solution

(a) The two reactants are provided, HOCl and H_2O . Since the substance is reported to be an acid, its reaction with water will involve the transfer of H^+ from HOCl to H_2O to generate hydronium ions, H_3O^+ and hypochlorite ions, OCl^- .

$$HOCl(aq) + H_2O(l) \rightleftharpoons OCl^-(aq) + H_3O^+(aq)$$

A double-arrow is appropriate in this equation because it indicates the HOCl is a weak acid that has not reacted completely.

(b) The two reactants are provided, $Ba(OH)_2$ and HNO_3 . Since this is a neutralization reaction, the two products will be water and a salt composed of the cation of the ionic hydroxide (Ba^{2+}) and the anion generated when the acid transfers its hydrogen ion (NO_3 ⁻).

$$Ba(OH)_2(aq) + 2HNO_3(aq) \longrightarrow Ba(NO_3)_2(aq) + 2H_2O(l)$$

Check Your Learning

Write the net ionic equation representing the neutralization of any strong acid with an ionic hydroxide. (Hint: Consider the ions produced when a strong acid is dissolved in water.)

Answer:
$$H_3O^+(aq) + OH^-(aq) \longrightarrow 2H_2O(l)$$

Chemistry in Everyday Life

Stomach Antacids

Our stomachs contain a solution of roughly 0.03~M HCl, which helps us digest the food we eat. The burning sensation associated with heartburn is a result of the acid of the stomach leaking through the muscular valve at the top of the stomach into the lower reaches of the esophagus. The lining of the esophagus is not protected from the corrosive effects of stomach acid the way the lining of the stomach is, and the results can be very painful. When we have heartburn, it feels better if we reduce the excess acid in the esophagus by taking an antacid. As you may have guessed, antacids are bases. One of the most common antacids is calcium carbonate, $CaCO_3$. The reaction,

$$CaCO_3(s) + 2HCl(aq) \Rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

not only neutralizes stomach acid, it also produces $CO_2(q)$, which may result in a satisfying belch.

Milk of Magnesia is a suspension of the sparingly soluble base magnesium hydroxide, $Mg(OH)_2$. It works according to the reaction:

$$Mg(OH)_2(s) \Rightarrow Mg^{2+}(aq) + 2OH^{-}(aq)$$

The hydroxide ions generated in this equilibrium then go on to react with the hydronium ions from the stomach acid, so that:

$$H_3O^+ + OH^- \rightleftharpoons 2H_2O(l)$$

This reaction does not produce carbon dioxide, but magnesium-containing antacids can have a laxative effect. Several antacids have aluminum hydroxide, Al(OH)₃, as an active ingredient. The aluminum hydroxide tends to cause constipation, and some antacids use aluminum hydroxide in concert with magnesium hydroxide to balance the side effects of the two substances.

Chemistry in Everyday Life

Culinary Aspects of Chemistry

Examples of acid-base chemistry are abundant in the culinary world. One example is the use of baking soda, or sodium bicarbonate in baking. NaHCO₃ is a base. When it reacts with an acid such as lemon juice, buttermilk, or sour cream in a batter, bubbles of carbon dioxide gas are formed from decomposition of the resulting carbonic acid, and the batter "rises." Baking powder is a combination of sodium bicarbonate, and one or more acid salts that react when the two chemicals come in contact with water in the batter.

Many people like to put lemon juice or vinegar, both of which are acids, on cooked fish (Figure 4.8). It turns

out that fish have volatile amines (bases) in their systems, which are neutralized by the acids to yield involatile ammonium salts. This reduces the odor of the fish, and also adds a "sour" taste that we seem to enjoy.

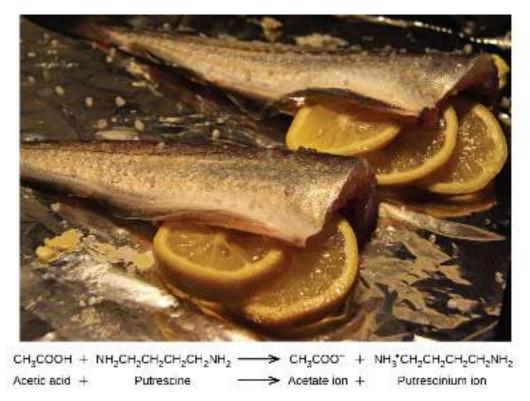


Figure 4.8 A neutralization reaction takes place between citric acid in lemons or acetic acid in vinegar, and the bases in the flesh of fish.

Pickling is a method used to preserve vegetables using a naturally produced acidic environment. The vegetable, such as a cucumber, is placed in a sealed jar submerged in a brine solution. The brine solution favors the growth of beneficial bacteria and suppresses the growth of harmful bacteria. The beneficial bacteria feed on starches in the cucumber and produce lactic acid as a waste product in a process called fermentation. The lactic acid eventually increases the acidity of the brine to a level that kills any harmful bacteria, which require a basic environment. Without the harmful bacteria consuming the cucumbers they are able to last much longer than if they were unprotected. A byproduct of the pickling process changes the flavor of the vegetables with the acid making them taste sour.

Link to Learning

Explore the microscopic view (http://openstaxcollege.org/II/16AcidsBases) of strong and weak acids and bases.

Oxidation-Reduction Reactions

Earth's atmosphere contains about 20% molecular oxygen, O_2 , a chemically reactive gas that plays an essential role in the metabolism of aerobic organisms and in many environmental processes that shape the world. The term **oxidation**

was originally used to describe chemical reactions involving O_2 , but its meaning has evolved to refer to a broad and important reaction class known as *oxidation-reduction* (*redox*) *reactions*. A few examples of such reactions will be used to develop a clear picture of this classification.

Some redox reactions involve the transfer of electrons between reactant species to yield ionic products, such as the reaction between sodium and chlorine to yield sodium chloride:

$$2\text{Na}(s) + \text{Cl}_2(g) \longrightarrow 2\text{NaCl}(s)$$

It is helpful to view the process with regard to each individual reactant, that is, to represent the fate of each reactant in the form of an equation called a **half-reaction**:

$$2\text{Na}(s) \longrightarrow 2\text{Na}^+(s) + 2\text{e}^-$$

 $\text{Cl}_2(g) + 2\text{e}^- \longrightarrow 2\text{Cl}^-(s)$

These equations show that Na atoms *lose electrons* while Cl atoms (in the Cl_2 molecule) *gain electrons*, the "s" subscripts for the resulting ions signifying they are present in the form of a solid ionic compound. For redox reactions of this sort, the loss and gain of electrons define the complementary processes that occur:

oxidation = loss of electrons
reduction = gain of electrons

In this reaction, then, sodium is *oxidized* and chlorine undergoes **reduction**. Viewed from a more active perspective, sodium functions as a **reducing agent (reductant)**, since it provides electrons to (or reduces) chlorine. Likewise, chlorine functions as an **oxidizing agent (oxidiant)**, as it effectively removes electrons from (oxidizes) sodium.

reducing agent = species that is oxidized oxidizing agent = species that is reduced

Some redox processes, however, do not involve the transfer of electrons. Consider, for example, a reaction similar to the one yielding NaCl:

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

The product of this reaction is a covalent compound, so transfer of electrons in the explicit sense is not involved. To clarify the similarity of this reaction to the previous one and permit an unambiguous definition of redox reactions, a property called *oxidation number* has been defined. The **oxidation number** (or **oxidation state**) of an element in a compound is the charge its atoms would possess *if the compound was ionic*. The following guidelines are used to assign oxidation numbers to each element in a molecule or ion.

- 1. The oxidation number of an atom in an elemental substance is zero.
- 2. The oxidation number of a monatomic ion is equal to the ion's charge.
- 3. Oxidation numbers for common nonmetals are usually assigned as follows:
 - Hydrogen: +1 when combined with nonmetals, -1 when combined with metals
 - Oxygen: -2 in most compounds, sometimes -1 (so-called peroxides, O_2^{2-}), very rarely $-\frac{1}{2}$ (so-called superoxides, O_2^{-}), positive values when combined with F (values vary)
 - Halogens: -1 for F always, -1 for other halogens except when combined with oxygen or other halogens (positive oxidation numbers in these cases, varying values)
- 4. The sum of oxidation numbers for all atoms in a molecule or polyatomic ion equals the charge on the molecule or ion.

Note: The proper convention for reporting charge is to write the number first, followed by the sign (e.g., 2+), while oxidation number is written with the reversed sequence, sign followed by number (e.g., +2). This convention aims to emphasize the distinction between these two related properties.

Example 4.5

Assigning Oxidation Numbers

Follow the guidelines in this section of the text to assign oxidation numbers to all the elements in the following species:

- (a) H_2S
- (b) SO_3^{2-}
- (c) Na₂SO₄

Solution

(a) According to guideline 1, the oxidation number for H is +1.

Using this oxidation number and the compound's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:

charge on
$$H_2 S = 0 = (2 \times +1) + (1 \times x)$$

 $x = 0 - (2 \times +1) = -2$

(b) Guideline 3 suggests the oxidation number for oxygen is −2.

Using this oxidation number and the ion's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:

charge on
$$SO_3^{2-} = -2 = (3 \times -2) + (1 \times x)$$

 $x = -2 - (3 \times -2) = +4$

(c) For ionic compounds, it's convenient to assign oxidation numbers for the cation and anion separately.

According to guideline 2, the oxidation number for sodium is +1.

Assuming the usual oxidation number for oxygen (–2 per guideline 3), the oxidation number for sulfur is calculated as directed by guideline 4:

charge on
$$SO_4^{2-} = -2 = (4 \times -2) + (1 \times x)$$

 $x = -2 - (4 \times -2) = +6$

Check Your Learning

Assign oxidation states to the elements whose atoms are underlined in each of the following compounds or ions:

- (a) KNO₃
- (b) <u>Al</u>H₃
- (c) $\underline{N}H_4^+$
- (d) $H_2 \underline{PO_4}^-$

Using the oxidation number concept, an all-inclusive definition of redox reaction has been established. **Oxidation-reduction (redox) reactions** are those in which one or more elements involved undergo a change in oxidation number. (While the vast majority of redox reactions involve changes in oxidation number for two or more elements,

a few interesting exceptions to this rule do exist **Example 4.6.**) Definitions for the complementary processes of this reaction class are correspondingly revised as shown here:

oxidation = increase in oxidation numberreduction = decrease in oxidation number

Returning to the reactions used to introduce this topic, they may now both be identified as redox processes. In the reaction between sodium and chlorine to yield sodium chloride, sodium is oxidized (its oxidation number increases from 0 in Na to +1 in NaCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to Cl_2 to Cl_3 in NaCl). In the reaction between molecular hydrogen and chlorine, hydrogen is oxidized (its oxidation number increases from 0 in Cl_3 to Cl_3 in HCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_3 to Cl_3 in HCl).

Several subclasses of redox reactions are recognized, including **combustion reactions** in which the reductant (also called a *fuel*) and oxidant (often, but not necessarily, molecular oxygen) react vigorously and produce significant amounts of heat, and often light, in the form of a flame. Solid rocket-fuel reactions such as the one depicted in **Figure 4.1** are combustion processes. A typical propellant reaction in which solid aluminum is oxidized by ammonium perchlorate is represented by this equation:

$$10\text{Al}(s) + 6\text{NH}_4\text{ClO}_4(s) \longrightarrow 4\text{Al}_2\text{O}_3(s) + 2\text{AlCl}_3(s) + 12\text{H}_2\text{O}(g) + 3\text{N}_2(g)$$

Link to Learning

Watch a brief video (http://openstaxcollege.org/l/16hybridrocket) showing the test firing of a small-scale, prototype, hybrid rocket engine planned for use in the new Space Launch System being developed by NASA. The first engines firing at

3 s (green flame) use a liquid fuel/oxidant mixture, and the second, more powerful engines firing at 4 s (yellow flame) use a solid mixture.

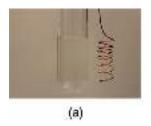
Single-displacement (replacement) reactions are redox reactions in which an ion in solution is displaced (or replaced) via the oxidation of a metallic element. One common example of this type of reaction is the acid oxidation of certain metals:

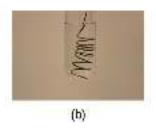
$$Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$$

Metallic elements may also be oxidized by solutions of other metal salts; for example:

$$Cu(s) + 2AgNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2Ag(s)$$

This reaction may be observed by placing copper wire in a solution containing a dissolved silver salt. Silver ions in solution are reduced to elemental silver at the surface of the copper wire, and the resulting Cu²⁺ ions dissolve in the solution to yield a characteristic blue color (**Figure 4.9**).





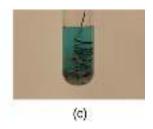


Figure 4.9 (a) A copper wire is shown next to a solution containing silver(I) ions. (b) Displacement of dissolved silver ions by copper ions results in (c) accumulation of gray-colored silver metal on the wire and development of a blue color in the solution, due to dissolved copper ions. (credit: modification of work by Mark Ott)

Example 4.6

Describing Redox Reactions

Identify which equations represent redox reactions, providing a name for the reaction if appropriate. For those reactions identified as redox, name the oxidant and reductant.

(a)
$$ZnCO_3(s) \longrightarrow ZnO(s) + CO_2(g)$$

(b)
$$2Ga(l) + 3Br_2(l) \longrightarrow 2GaBr_3(s)$$

(c)
$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

(d)
$$BaCl_2(aq) + K_2SO_4(aq) \longrightarrow BaSO_4(s) + 2KCl(aq)$$

(e)
$$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$$

Solution

Redox reactions are identified per definition if one or more elements undergo a change in oxidation number.

- (a) This is not a redox reaction, since oxidation numbers remain unchanged for all elements.
- (b) This is a redox reaction. Gallium is oxidized, its oxidation number increasing from 0 in Ga(l) to +3 in $GaBr_3(s)$. The reducing agent is Ga(l). Bromine is reduced, its oxidation number decreasing from 0 in $Br_2(l)$ to -1 in $GaBr_3(s)$. The oxidizing agent is $Br_2(l)$.
- (c) This is a redox reaction. It is a particularly interesting process, as it involves the same element, oxygen, undergoing both oxidation and reduction (a so-called *disproportionation reaction*). Oxygen is oxidized, its oxidation number increasing from -1 in $H_2O_2(aq)$ to 0 in $O_2(g)$. Oxygen is also reduced, its oxidation number decreasing from -1 in $H_2O_2(aq)$ to -2 in $H_2O(l)$. For disproportionation reactions, the same substance functions as an oxidant and a reductant.
- (d) This is not a redox reaction, since oxidation numbers remain unchanged for all elements.
- (e) This is a redox reaction (combustion). Carbon is oxidized, its oxidation number increasing from -2 in $C_2H_4(g)$ to +4 in $CO_2(g)$. The reducing agent (fuel) is $C_2H_4(g)$. Oxygen is reduced, its oxidation number decreasing from 0 in $O_2(g)$ to -2 in $H_2O(l)$. The oxidizing agent is $O_2(g)$.

Check Your Learning

This equation describes the production of tin(II) chloride:

$$Sn(s) + 2HCl(g) \longrightarrow SnCl_2(s) + H_2(g)$$

Is this a redox reaction? If so, provide a more specific name for the reaction if appropriate, and identify the oxidant and reductant.

Answer: Yes, a single-replacement reaction. Sn(s) is the reductant, HCl(q) is the oxidant.

Balancing Redox Reactions via the Half-Reaction Method

Redox reactions that take place in aqueous media often involve water, hydronium ions, and hydroxide ions as reactants or products. Although these species are not oxidized or reduced, they do participate in chemical change in other ways (e.g., by providing the elements required to form oxyanions). Equations representing these reactions are sometimes very difficult to balance by inspection, so systematic approaches have been developed to assist in the process. One very useful approach is to use the method of half-reactions, which involves the following steps:

- 1. Write the two half-reactions representing the redox process.
- 2. Balance all elements except oxygen and hydrogen.
- 3. Balance oxygen atoms by adding H₂O molecules.
- 4. Balance hydrogen atoms by adding H⁺ ions.
- 5. Balance charge by adding electrons.
- 6. If necessary, multiply each half-reaction's coefficients by the smallest possible integers to yield equal numbers of electrons in each.
- 7. Add the balanced half-reactions together and simplify by removing species that appear on both sides of the equation.
- 8. For reactions occurring in basic media (excess hydroxide ions), carry out these additional steps:
 - a. Add OH⁻ ions to both sides of the equation in numbers equal to the number of H⁺ ions.
 - b. On the side of the equation containing both H⁺ and OH⁻ ions, combine these ions to yield water molecules.
 - c. Simplify the equation by removing any redundant water molecules.
- 9. Finally, check to see that both the number of atoms and the total charges^[1] are balanced.

Example 4.7

Balancing Redox Reactions in Acidic Solution

Write a balanced equation for the reaction between dichromate ion and iron(II) to yield iron(III) and chromium(III) in acidic solution.

$$\operatorname{Cr}_2 \operatorname{O}_7^{2-} + \operatorname{Fe}^{2+} \longrightarrow \operatorname{Cr}^{3+} + \operatorname{Fe}^{3+}$$

Solution

Step 1. Write the two half-reactions.

Each half-reaction will contain one reactant and one product with one element in common.

$$Fe^{2+} \longrightarrow Fe^{3+}$$
 $Cr_2 O_7^{2-} \longrightarrow Cr^{3+}$

Step 2. Balance all elements except oxygen and hydrogen. The iron half-reaction is already balanced, but the chromium half-reaction shows two Cr atoms on the left and one Cr atom on the right. Changing the coefficient on the right side of the equation to 2 achieves balance with regard to Cr atoms.

$$Fe^{2+} \longrightarrow Fe^{3+}$$
 $Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$

Step 3. Balance oxygen atoms by adding H₂O molecules. The iron half-reaction does not contain O atoms. The chromium half-reaction shows seven O atoms on the left and none on the right, so

^{1.} The requirement of "charge balance" is just a specific type of "mass balance" in which the species in question are electrons. An equation must represent equal numbers of electrons on the reactant and product sides, and so both atoms and charges must be balanced.

seven water molecules are added to the right side.

$$Fe^{2+} \longrightarrow Fe^{3+}$$

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

Step 4. Balance hydrogen atoms by adding H⁺ions. The iron half-reaction does not contain H atoms. The chromium half-reaction shows 14 H atoms on the right and none on the left, so 14 hydrogen ions are added to the left side.

$$Fe^{2+} \longrightarrow Fe^{3+}$$

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

Step 5. Balance charge by adding electrons. The iron half-reaction shows a total charge of 2+ on the left side (1 Fe²⁺ ion) and 3+ on the right side (1 Fe³⁺ ion). Adding one electron to the right side brings that side's total charge to (3+) + (1-) = 2+, and charge balance is achieved.

The chromium half-reaction shows a total charge of $(1 \times 2^-) + (14 \times 1^+) = 12^+$ on the left side $(1 \text{ Cr}_2 \text{ O}_7)^{2^-}$ ion and 14 H^+ ions). The total charge on the right side is $(2 \times 3^+) = 6 + (2 \text{ Cr}^{3^+} \text{ ions})$.

Adding six electrons to the left side will bring that side's total charge to (12++6-)=6+, and charge balance is achieved.

$$Fe^{2+} \longrightarrow Fe^{3+} + e^{-}$$

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

Step 6. Multiply the two half-reactions so the number of electrons in one reaction equals the number of electrons in the other reaction. To be consistent with mass conservation, and the idea that redox reactions involve the transfer (not creation or destruction) of electrons, the iron half-reaction's coefficient must be multiplied by 6.

$$6Fe^{2+} \longrightarrow 6Fe^{3+} + 6e^{-}$$

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

Step 7. Add the balanced half-reactions and cancel species that appear on both sides of the equation.

$$6Fe^{2+} + Cr_2O_7^{2-} + 6e^- + 14H^+ \longrightarrow 6Fe^{3+} + 6e^- + 2Cr^{3+} + 7H_2O_7^{2-}$$

Only the six electrons are redundant species. Removing them from each side of the equation yields the simplified, balanced equation here:

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O_7^{2-}$$

A final check of atom and charge balance confirms the equation is balanced.

	Reactants	Products
Fe	6	6
Cr	2	2
0	7	7
Н	14	14
charge	24+	24+

Check Your Learning

In basic solution, molecular chlorine, Cl₂, reacts with hydroxide ions, OH⁻, to yield chloride ions, Cl⁻. and

chlorate ions, ClO_4^- . HINT: This is a *disproportionation reaction* in which the element chlorine is both oxidized and reduced. Write a balanced equation for this reaction.

Answer:
$$3\text{Cl}_2(aq) + 6\text{OH}^-(aq) \longrightarrow 5\text{Cl}^-(aq) + \text{ClO}_3^-(aq) + 3\text{H}_2\text{O}(l)$$

4.3 Reaction Stoichiometry

By the end of this section, you will be able to:

- · Explain the concept of stoichiometry as it pertains to chemical reactions
- Use balanced chemical equations to derive stoichiometric factors relating amounts of reactants and products
- · Perform stoichiometric calculations involving mass, moles, and solution molarity

A balanced chemical equation provides a great deal of information in a very succinct format. Chemical formulas provide the identities of the reactants and products involved in the chemical change, allowing classification of the reaction. Coefficients provide the relative numbers of these chemical species, allowing a quantitative assessment of the relationships between the amounts of substances consumed and produced by the reaction. These quantitative relationships are known as the reaction's **stoichiometry**, a term derived from the Greek words *stoicheion* (meaning "element") and *metron* (meaning "measure"). In this module, the use of balanced chemical equations for various stoichiometric applications is explored.

The general approach to using stoichiometric relationships is similar in concept to the way people go about many common activities. Food preparation, for example, offers an appropriate comparison. A recipe for making eight pancakes calls for 1 cup pancake mix, $\frac{3}{4}$ cup milk, and one egg. The "equation" representing the preparation of pancakes per this recipe is

1 cup mix +
$$\frac{3}{4}$$
 cup milk + 1 egg \longrightarrow 8 pancakes

If two dozen pancakes are needed for a big family breakfast, the ingredient amounts must be increased proportionally according to the amounts given in the recipe. For example, the number of eggs required to make 24 pancakes is

$$24 \frac{\text{pancakes}}{8 \frac{\text{pancakes}}{\text{pancakes}}} = 3 \text{ eggs}$$

Balanced chemical equations are used in much the same fashion to determine the amount of one reactant required to react with a given amount of another reactant, or to yield a given amount of product, and so forth. The coefficients in the balanced equation are used to derive **stoichiometric factors** that permit computation of the desired quantity. To illustrate this idea, consider the production of ammonia by reaction of hydrogen and nitrogen:

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

This equation shows ammonia molecules are produced from hydrogen molecules in a 2:3 ratio, and stoichiometric factors may be derived using any amount (number) unit:

$$\frac{2\,\text{NH}_3\text{ molecules}}{3\,\text{H}_2\text{ molecules}}\text{ or }\frac{2\,\text{doz}\,\text{NH}_3\text{ molecules}}{3\,\text{doz}\,\text{H}_2\text{ molecules}}\text{ or }\frac{2\,\text{mol}\,\text{NH}_3\text{ molecules}}{3\,\text{mol}\,\text{H}_2\text{ molecules}}$$

These stoichiometric factors can be used to compute the number of ammonia molecules produced from a given number of hydrogen molecules, or the number of hydrogen molecules required to produce a given number of ammonia molecules. Similar factors may be derived for any pair of substances in any chemical equation.

Example 4.8

Moles of Reactant Required in a Reaction

How many moles of I_2 are required to react with 0.429 mol of Al according to the following equation (see **Figure 4.10**)?

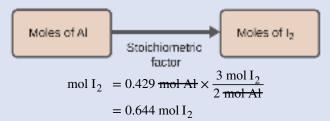
$$2Al + 3I_2 \longrightarrow 2AlI_3$$



Figure 4.10 Aluminum and iodine react to produce aluminum iodide. The heat of the reaction vaporizes some of the solid iodine as a purple vapor. (credit: modification of work by Mark Ott)

Solution

Referring to the balanced chemical equation, the stoichiometric factor relating the two substances of interest is $\frac{3 \text{ mol } I_2}{2 \text{ mol } Al}$. The molar amount of iodine is derived by multiplying the provided molar amount of aluminum by this factor:



Check Your Learning

How many moles of Ca(OH)₂ are required to react with 1.36 mol of H_3PO_4 to produce $Ca_3(PO_4)_2$ according to the equation $3Ca(OH)_2 + 2H_3PO_4 \longrightarrow Ca_3(PO_4)_2 + 6H_2O$?

Answer: 2.04 mol

Example 4.9

Number of Product Molecules Generated by a Reaction

How many carbon dioxide molecules are produced when 0.75 mol of propane is combusted according to this equation?

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

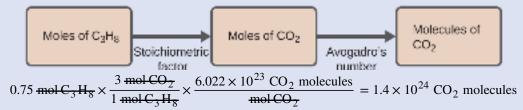
Solution

The approach here is the same as for **Example 4.8**, though the absolute number of molecules is requested, not the number of moles of molecules. This will simply require use of the moles-to-numbers conversion factor, Avogadro's number.

The balanced equation shows that carbon dioxide is produced from propane in a 3:1 ratio:

$$\frac{3 \bmod CO_2}{1 \bmod C_3H_8}$$

Using this stoichiometric factor, the provided molar amount of propane, and Avogadro's number,



Check Your Learning

How many NH_3 molecules are produced by the reaction of 4.0 mol of $Ca(OH)_2$ according to the following equation:

$$({\rm NH_4})_2\,{\rm SO_4} + {\rm Ca(OH)}_2\, \longrightarrow 2{\rm NH_3} + {\rm CaSO_4} + 2{\rm H_2\,O}$$

$${\bf Answer:} \ \ 4.8\,\times\,10^{24}\,{\rm NH_3\,molecules}$$

These examples illustrate the ease with which the amounts of substances involved in a chemical reaction of known stoichiometry may be related. Directly measuring numbers of atoms and molecules is, however, not an easy task, and the practical application of stoichiometry requires that we use the more readily measured property of mass.

Example 4.10

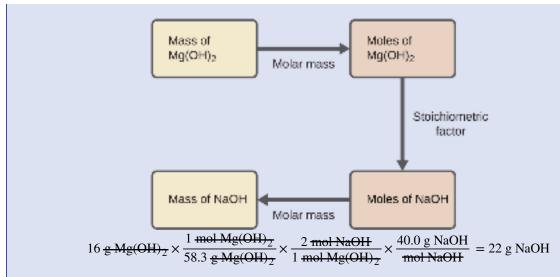
Relating Masses of Reactants and Products

What mass of sodium hydroxide, NaOH, would be required to produce 16 g of the antacid milk of magnesia [magnesium hydroxide, Mg(OH)₂] by the following reaction?

$$MgCl_2(aq) + 2NaOH(aq) \longrightarrow Mg(OH)_2(s) + 2NaCl(aq)$$

Solution

The approach used previously in **Example 4.8** and **Example 4.9** is likewise used here; that is, we must derive an appropriate stoichiometric factor from the balanced chemical equation and use it to relate the amounts of the two substances of interest. In this case, however, masses (not molar amounts) are provided and requested, so additional steps of the sort learned in the previous chapter are required. The calculations required are outlined in this flowchart:



Check Your Learning

What mass of gallium oxide, Ga_2O_3 , can be prepared from 29.0 g of gallium metal? The equation for the reaction is $4Ga + 3O_2 \longrightarrow 2Ga_2O_3$.

Answer: 39.0 g

Example 4.11

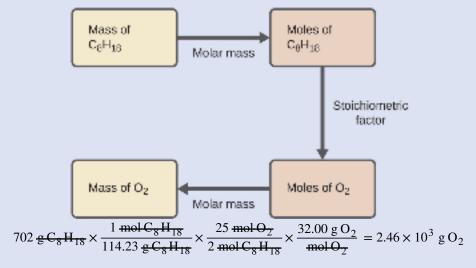
Relating Masses of Reactants

What mass of oxygen gas, O_2 , from the air is consumed in the combustion of 702 g of octane, C_8H_{18} , one of the principal components of gasoline?

$$2C_8H_{18} + 25O_2 \longrightarrow 16CO_2 + 18H_2O$$

Solution

The approach required here is the same as for the **Example 4.10**, differing only in that the provided and requested masses are both for reactant species.



Check Your Learning

What mass of CO is required to react with 25.13 g of Fe₂O₃ according to the equation

$$\text{Fe}_2\text{O}_3 + 3\text{CO} \longrightarrow 2\text{Fe} + 3\text{CO}_2?$$

Answer: 13.22 g

These examples illustrate just a few instances of reaction stoichiometry calculations. Numerous variations on the beginning and ending computational steps are possible depending upon what particular quantities are provided and sought (volumes, solution concentrations, and so forth). Regardless of the details, all these calculations share a common essential component: the use of stoichiometric factors derived from balanced chemical equations. **Figure 4.11** provides a general outline of the various computational steps associated with many reaction stoichiometry calculations.

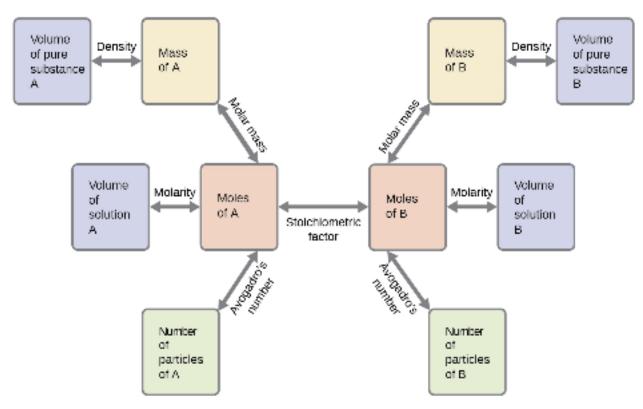


Figure 4.11 The flowchart depicts the various computational steps involved in most reaction stoichiometry calculations.

Chemistry in Everyday Life

Airbags

Airbags (Figure 4.12) are a safety feature provided in most automobiles since the 1990s. The effective operation of an airbag requires that it be rapidly inflated with an appropriate amount (volume) of gas when the vehicle is involved in a collision. This requirement is satisfied in many automotive airbag systems through use of explosive chemical reactions, one common choice being the decomposition of sodium azide, NaN_3 . When sensors in the vehicle detect a collision, an electrical current is passed through a carefully measured amount of NaN_3 to initiate its decomposition:

$$2\text{NaN}_3(s) \longrightarrow 3\text{N}_2(g) + 2\text{Na}(s)$$

This reaction is very rapid, generating gaseous nitrogen that can deploy and fully inflate a typical airbag in a fraction of a second (\sim 0.03-0.1 s). Among many engineering considerations, the amount of sodium azide used must be appropriate for generating enough nitrogen gas to fully inflate the air bag and ensure its proper function. For example, a small mass (\sim 100 g) of NaN₃ will generate approximately 50 L of N₂.



Figure 4.12 Airbags deploy upon impact to minimize serious injuries to passengers. (credit: Jon Seidman)

4.4 Reaction Yields

By the end of this section, you will be able to:

- Explain the concepts of theoretical yield and limiting reactants/reagents.
- Derive the theoretical yield for a reaction under specified conditions.
- Calculate the percent yield for a reaction.

The relative amounts of reactants and products represented in a balanced chemical equation are often referred to as *stoichiometric amounts*. All the exercises of the preceding module involved stoichiometric amounts of reactants. For example, when calculating the amount of product generated from a given amount of reactant, it was assumed that any other reactants required were available in stoichiometric amounts (or greater). In this module, more realistic situations are considered, in which reactants are not present in stoichiometric amounts.

Limiting Reactant

Consider another food analogy, making grilled cheese sandwiches (Figure 4.13):

1 slice of cheese + 2 slices of bread \longrightarrow 1 sandwich

Stoichiometric amounts of sandwich ingredients for this recipe are bread and cheese slices in a 2:1 ratio. Provided with 28 slices of bread and 11 slices of cheese, one may prepare 11 sandwiches per the provided recipe, using all the provided cheese and having six slices of bread left over. In this scenario, the number of sandwiches prepared has been *limited* by the number of cheese slices, and the bread slices have been provided in *excess*.

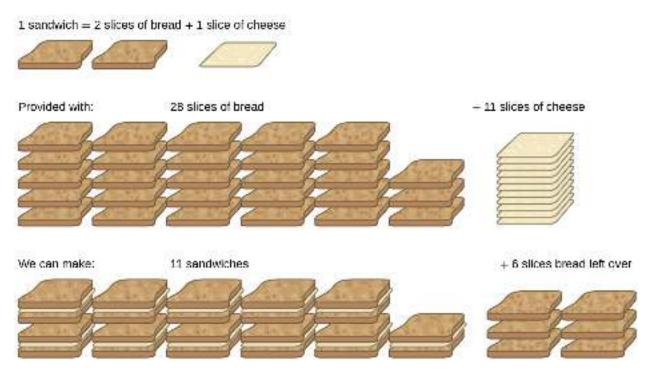


Figure 4.13 Sandwich making can illustrate the concepts of limiting and excess reactants.

Consider this concept now with regard to a chemical process, the reaction of hydrogen with chlorine to yield hydrogen chloride:

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

The balanced equation shows the hydrogen and chlorine react in a 1:1 stoichiometric ratio. If these reactants are provided in any other amounts, one of the reactants will nearly always be entirely consumed, thus limiting the amount of product that may be generated. This substance is the **limiting reactant**, and the other substance is the **excess reactant**. Identifying the limiting and excess reactants for a given situation requires computing the molar amounts of each reactant provided and comparing them to the stoichiometric amounts represented in the balanced chemical equation. For example, imagine combining 3 moles of H₂ and 2 moles of Cl₂. This represents a 3:2 (or 1.5:1) ratio of hydrogen to chlorine present for reaction, which is greater than the stoichiometric ratio of 1:1. Hydrogen, therefore, is present in excess, and chlorine is the limiting reactant. Reaction of all the provided chlorine (2 mol) will consume 2 mol of the 3 mol of hydrogen provided, leaving 1 mol of hydrogen unreacted.

An alternative approach to identifying the limiting reactant involves comparing the amount of product expected for the complete reaction of each reactant. Each reactant amount is used to separately calculate the amount of product that would be formed per the reaction's stoichiometry. The reactant yielding the lesser amount of product is the limiting reactant. For the example in the previous paragraph, complete reaction of the hydrogen would yield

mol HCl produced = 3 mol H₂
$$\times \frac{2 \text{ mol HCl}}{1 \text{ mol H}_2}$$
 = 6 mol HCl

Complete reaction of the provided chlorine would produce

mol HCl produced =
$$2 \text{ mol Cl}_2 \times \frac{2 \text{ mol HCl}}{1 \text{ mol Cl}_2} = 4 \text{ mol HCl}$$

The chlorine will be completely consumed once 4 moles of HCl have been produced. Since enough hydrogen was provided to yield 6 moles of HCl, there will be unreacted hydrogen remaining once this reaction is complete. Chlorine, therefore, is the limiting reactant and hydrogen is the excess reactant (**Figure 4.14**).

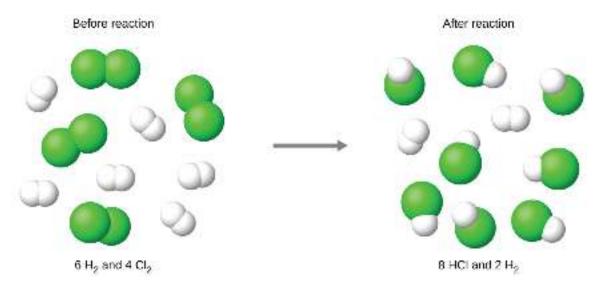


Figure 4.14 When H_2 and Cl_2 are combined in nonstoichiometric amounts, one of these reactants will limit the amount of HCl that can be produced. This illustration shows a reaction in which hydrogen is present in excess and chlorine is the limiting reactant.

Link to Learning

View this interactive simulation (http://openstaxcollege.org/l/16reactantprod) illustrating the concepts of limiting and excess reactants.

Example 4.12

Identifying the Limiting Reactant

Silicon nitride is a very hard, high-temperature-resistant ceramic used as a component of turbine blades in jet engines. It is prepared according to the following equation:

$$3Si(s) + 2N_2(g) \longrightarrow Si_3 N_4(s)$$

Which is the limiting reactant when 2.00 g of Si and 1.50 g of N₂ react?

Solution

Compute the provided molar amounts of reactants, and then compare these amounts to the balanced equation to identify the limiting reactant.

$$\begin{aligned} &\text{mol Si} = 2.00 \ \tfrac{\text{g Si}}{\text{g Si}} \times \frac{1 \ \text{mol Si}}{28.09 \ \tfrac{\text{g Si}}{\text{g Si}}} = 0.0712 \ \text{mol Si} \\ &\text{mol N}_2 = 1.50 \ \tfrac{\text{g N}_2}{\text{g N}_2} \times \frac{1 \ \text{mol N}_2}{28.02 \ \tfrac{\text{g N}_2}{\text{g N}_2}} = 0.0535 \ \text{mol N}_2 \end{aligned}$$

The provided Si:N₂ molar ratio is:

$$\frac{0.0712 \text{ mol Si}}{0.0535 \text{ mol N}_2} = \frac{1.33 \text{ mol Si}}{1 \text{ mol N}_2}$$

The stoichiometric Si:N₂ ratio is:

$$\frac{3 \text{ mol Si}}{2 \text{ mol N}_2} = \frac{1.5 \text{ mol Si}}{1 \text{ mol N}_2}$$

Comparing these ratios shows that Si is provided in a less-than-stoichiometric amount, and so is the limiting reactant.

Alternatively, compute the amount of product expected for complete reaction of each of the provided reactants. The 0.0712 moles of silicon would yield

mol Si₃ N₄ produced = 0.0712 mol Si
$$\times \frac{1 \text{ mol Si}_3 \text{ N}_4}{3 \text{ mol Si}} = 0.0237 \text{ mol Si}_3 \text{ N}_4$$

while the 0.0535 moles of nitrogen would produce

$$\mathsf{mol}\,\mathsf{Si}_3\,\mathsf{N}_4\,\,\mathsf{produced} = 0.0535\,\,\mathsf{mol}\,\mathsf{N}_2 \times \frac{1\,\,\mathsf{mol}\,\mathsf{Si}_3\,\mathsf{N}_4}{2\,\,\mathsf{mol}\,\mathsf{N}_2} = 0.0268\,\,\mathsf{mol}\,\mathsf{Si}_3\,\mathsf{N}_4$$

Since silicon yields the lesser amount of product, it is the limiting reactant.

Check Your Learning

Which is the limiting reactant when 5.00 g of H₂ and 10.0 g of O₂ react and form water?

Answer: O₂

Percent Yield

The amount of product that *may be* produced by a reaction under specified conditions, as calculated per the stoichiometry of an appropriate balanced chemical equation, is called the **theoretical yield** of the reaction. In practice, the amount of product obtained is called the **actual yield**, and it is often less than the theoretical yield for a number of reasons. Some reactions are inherently inefficient, being accompanied by *side reactions* that generate other products. Others are, by nature, incomplete (consider the partial reactions of weak acids and bases discussed earlier in this chapter). Some products are difficult to collect without some loss, and so less than perfect recovery will reduce the actual yield. The extent to which a reaction's theoretical yield is achieved is commonly expressed as its **percent yield**:

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

Actual and theoretical yields may be expressed as masses or molar amounts (or any other appropriate property; e.g., volume, if the product is a gas). As long as both yields are expressed using the same units, these units will cancel when percent yield is calculated.

Example 4.13

Calculation of Percent Yield

Upon reaction of 1.274 g of copper sulfate with excess zinc metal, 0.392 g copper metal was obtained according to the equation:

$$CuSO_4(aq) + Zn(s) \longrightarrow Cu(s) + ZnSO_4(aq)$$

What is the percent yield?

Solution

The provided information identifies copper sulfate as the limiting reactant, and so the theoretical yield is found by the approach illustrated in the previous module, as shown here:

$$1.274 \frac{\text{g CuSO}_4}{\text{g CuSO}_4} \times \frac{1 \frac{\text{mol CuSO}_4}{159.62 \frac{\text{g CuSO}_4}{\text{g CuSO}_4}} \times \frac{1 \frac{\text{mol Cu}}{1 \frac{\text{mol CuSO}_4}{\text{mol CuSO}_4}} \times \frac{63.55 \text{ g Cu}}{1 \frac{\text{mol Cu}}{\text{mol CuSO}_4}} = 0.5072 \text{ g Cu}$$

Using this theoretical yield and the provided value for actual yield, the percent yield is calculated to be

percent yield =
$$\left(\frac{\text{actual yield}}{\text{theoretical yield}}\right) \times 100$$

percent yield = $\left(\frac{0.392 \text{ g Cu}}{0.5072 \text{ g Cu}}\right) \times 100$
= 77.3%

Check Your Learning

What is the percent yield of a reaction that produces 12.5 g of the gas Freon CF₂Cl₂ from 32.9 g of CCl₄ and excess HF?

$$CCl_4 + 2HF \longrightarrow CF_2Cl_2 + 2HCl$$

Answer: 48.3%

How Sciences Interconnect

Green Chemistry and Atom Economy

The purposeful design of chemical products and processes that minimize the use of environmentally hazardous substances and the generation of waste is known as *green chemistry*. Green chemistry is a philosophical approach that is being applied to many areas of science and technology, and its practice is summarized by guidelines known as the "Twelve Principles of Green Chemistry" (see details at this **website** (http://openstaxcollege.org/l/16greenchem)). One of the 12 principles is aimed specifically at maximizing the efficiency of processes for synthesizing chemical products. The *atom economy* of a process is a measure of this efficiency, defined as the percentage by mass of the final product of a synthesis relative to the masses of *all* the reactants used:

atom economy =
$$\frac{\text{mass of product}}{\text{mass of reactants}} \times 100\%$$

Though the definition of atom economy at first glance appears very similar to that for percent yield, be aware that this property represents a difference in the *theoretical* efficiencies of *different* chemical processes. The percent yield of a given chemical process, on the other hand, evaluates the efficiency of a process by comparing the yield of product actually obtained to the maximum yield predicted by stoichiometry.

The synthesis of the common nonprescription pain medication, ibuprofen, nicely illustrates the success of a green chemistry approach (Figure 4.15). First marketed in the early 1960s, ibuprofen was produced using a six-step synthesis that required 514 g of reactants to generate each mole (206 g) of ibuprofen, an atom economy of 40%. In the 1990s, an alternative process was developed by the BHC Company (now BASF Corporation) that requires only three steps and has an atom economy of ~80%, nearly twice that of the original process. The BHC process generates significantly less chemical waste; uses less-hazardous and recyclable materials; and provides significant cost-savings to the manufacturer (and, subsequently, the consumer). In recognition of the positive environmental impact of the BHC process, the company received the Environmental Protection Agency's Greener Synthetic Pathways Award in 1997.



Figure 4.15 (a) Ibuprofen is a popular nonprescription pain medication commonly sold as 200 mg tablets. (b) The BHC process for synthesizing ibuprofen requires only three steps and exhibits an impressive atom economy. (credit a: modification of work by Derrick Coetzee)

4.5 Quantitative Chemical Analysis

By the end of this section, you will be able to:

- Describe the fundamental aspects of titrations and gravimetric analysis.
- Perform stoichiometric calculations using typical titration and gravimetric data.

In the 18th century, the strength (actually the concentration) of vinegar samples was determined by noting the amount of potassium carbonate, K_2CO_3 , which had to be added, a little at a time, before bubbling ceased. The greater the weight of potassium carbonate added to reach the point where the bubbling ended, the more concentrated the vinegar.

We now know that the effervescence that occurred during this process was due to reaction with acetic acid, CH₃CO₂H, the compound primarily responsible for the odor and taste of vinegar. Acetic acid reacts with potassium carbonate according to the following equation:

$$2CH_3CO_2H(aq) + K_2CO_3(s) \longrightarrow 2CH_3CO_2K(aq) + CO_2(g) + H_2O(l)$$

The bubbling was due to the production of CO_2 .

The test of vinegar with potassium carbonate is one type of **quantitative analysis**—the determination of the amount or concentration of a substance in a sample. In the analysis of vinegar, the concentration of the solute (acetic acid) was determined from the amount of reactant that combined with the solute present in a known volume of the solution. In other types of chemical analyses, the amount of a substance present in a sample is determined by measuring the amount of product that results.

Titration

The described approach to measuring vinegar strength was an early version of the analytical technique known as titration analysis. A typical titration analysis involves the use of a buret (Figure 4.16) to make incremental additions of a solution containing a known concentration of some substance (the titrant) to a sample solution containing the substance whose concentration is to be measured (the analyte). The titrant and analyte undergo a chemical reaction of known stoichiometry, and so measuring the volume of titrant solution required for complete reaction with the analyte (the **equivalence point** of the titration) allows calculation of the analyte concentration. The equivalence point of a titration may be detected visually if a distinct change in the appearance of the sample solution accompanies the completion of the reaction. The halt of bubble formation in the classic vinegar analysis is one such example, though, more commonly, special dyes called **indicators** are added to the sample solutions to impart a change in color at or very near the equivalence point of the titration. Equivalence points may also be detected by measuring some solution property that changes in a predictable way during the course of the titration. Regardless of the approach taken to detect a titration's equivalence point, the volume of titrant actually measured is called the **end point**. Properly designed titration methods typically ensure that the difference between the equivalence and end points is negligible. Though any type of chemical reaction may serve as the basis for a titration analysis, the three described in this chapter (precipitation, acid-base, and redox) are most common. Additional details regarding titration analysis are provided in the chapter on acid-base equilibria.

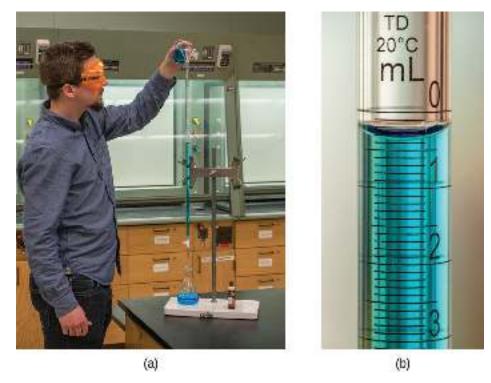


Figure 4.16 (a) A student fills a buret in preparation for a titration analysis. (b) A typical buret permits volume measurements to the nearest 0.01 mL. (credit a: modification of work by Mark Blaser and Matt Evans; credit b: modification of work by Mark Blaser and Matt Evans)

Example 4.14

Titration Analysis

The end point in a titration of a 50.00-mL sample of aqueous HCl was reached by addition of 35.23 mL of 0.250 M NaOH titrant. The titration reaction is:

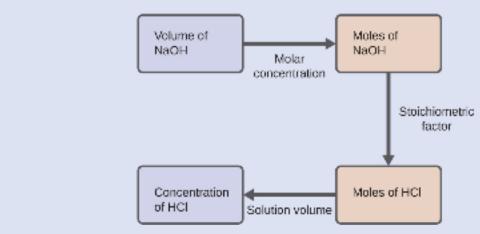
$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

What is the molarity of the HCl?

Solution

As for all reaction stoichiometry calculations, the key issue is the relation between the molar amounts of the chemical species of interest as depicted in the balanced chemical equation. The approach outlined in previous modules of this chapter is followed, with additional considerations required, since the amounts of reactants provided and requested are expressed as solution concentrations.

For this exercise, the calculation will follow the following outlined steps:



The molar amount of HCl is calculated to be:

$$35.23~\textrm{mL NaOH} \times \frac{1~\textrm{L}}{1000~\textrm{mL}} \times \frac{0.250~\textrm{mol NaOH}}{1~\textrm{L}} \times \frac{1~\textrm{mol HCl}}{1~\textrm{mol NaOH}} = 8.81 \times 10^{-3}~\textrm{mol HCl}$$

Using the provided volume of HCl solution and the definition of molarity, the HCl concentration is:

$$M = \frac{\text{mol HCl}}{\text{L solution}}$$

$$M = \frac{8.81 \times 10^{-3} \text{ mol HCl}}{50.00 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}}$$

$$M = 0.176 M$$

Note: For these types of titration calculations, it is convenient to recognize that solution molarity is also equal to the number of *milli*moles of solute per *milli*liter of solution:

$$M = \frac{\text{mol solute}}{\text{L solution}} \times \frac{\frac{10^3 \text{ mmol}}{\text{mol}}}{\frac{10^3 \text{ mL}}{\text{L}}} = \frac{\text{mmol solute}}{\text{mL solution}}$$

Using this version of the molarity unit will shorten the calculation by eliminating two conversion factors:

$$\frac{35.23 \text{ mL NaOH} \times \frac{0.250 \text{ mmol NaOH}}{\text{mL NaOH}} \times \frac{1 \text{ mmol HCl}}{1 \text{ mmol NaOH}}}{50.00 \text{ mL solution}} = 0.176 \text{ M HCl}$$

Check Your Learning

A 20.00-mL sample of aqueous oxalic acid, $H_2C_2O_4$, was titrated with a 0.09113-M solution of potassium permanganate, KMnO₄.

$$2 \text{MnO}_4^{-}(aq) + 5 \text{H}_2 \text{C}_2 \text{O}_4(aq) + 6 \text{H}^+(aq) \longrightarrow 10 \text{CO}_2(g) + 2 \text{Mn}^{2+}(aq) + 8 \text{H}_2 \text{O}(l)$$

A volume of 23.24 mL was required to reach the end point. What is the oxalic acid molarity?

Answer: 0.2648 *M*

Gravimetric Analysis

A **gravimetric analysis** is one in which a sample is subjected to some treatment that causes a change in the physical state of the analyte that permits its separation from the other components of the sample. Mass measurements of the sample, the isolated analyte, or some other component of the analysis system, used along with the known stoichiometry of the compounds involved, permit calculation of the analyte concentration. Gravimetric methods were the first techniques used for quantitative chemical analysis, and they remain important tools in the modern chemistry laboratory.

The required change of state in a gravimetric analysis may be achieved by various physical and chemical processes. For example, the moisture (water) content of a sample is routinely determined by measuring the mass of a sample before and after it is subjected to a controlled heating process that evaporates the water. Also common are gravimetric techniques in which the analyte is subjected to a precipitation reaction of the sort described earlier in this chapter. The precipitate is typically isolated from the reaction mixture by filtration, carefully dried, and then weighed (**Figure 4.17**). The mass of the precipitate may then be used, along with relevant stoichiometric relationships, to calculate analyte concentration.

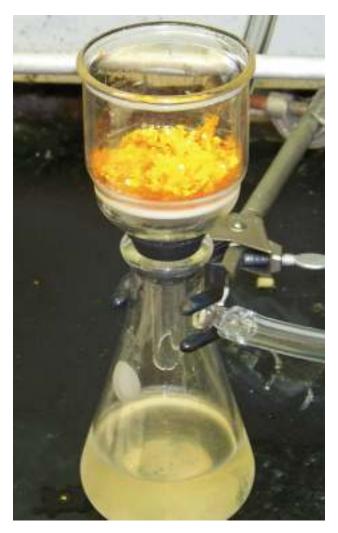


Figure 4.17 Precipitate may be removed from a reaction mixture by filtration.

Example 4.15

Gravimetric Analysis

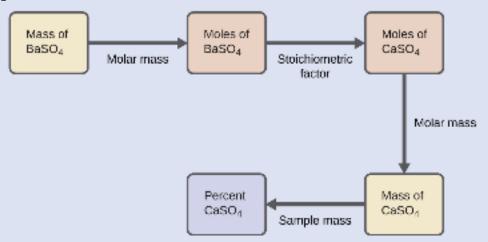
A 0.4550-g solid mixture containing $MgSO_4$ is dissolved in water and treated with an excess of $Ba(NO_3)_2$, resulting in the precipitation of 0.6168 g of $BaSO_4$.

$$MgSO_4(aq) + Ba(NO_3)_2(aq) \longrightarrow BaSO_4(s) + Mg(NO_3)_2(aq)$$

What is the concentration (mass percent) of MgSO₄ in the mixture?

Solution

The plan for this calculation is similar to others used in stoichiometric calculations, the central step being the connection between the moles of BaSO₄ and MgSO₄ through their stoichiometric factor. Once the mass of MgSO₄ is computed, it may be used along with the mass of the sample mixture to calculate the requested percentage concentration.



The mass of MgSO₄ that would yield the provided precipitate mass is

The concentration of MgSO₄ in the sample mixture is then calculated to be

percent MgSO₄ =
$$\frac{\text{mass MgSO}_4}{\text{mass sample}} \times 100\%$$

$$\frac{0.3181 \text{ g}}{0.4550 \text{ g}} \times 100\% = 69.91\%$$

Check Your Learning

What is the percent of chloride ion in a sample if 1.1324 g of the sample produces 1.0881 g of AgCl when treated with excess Ag⁺?

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

Answer: 23.76%

The elemental composition of hydrocarbons and related compounds may be determined via a gravimetric method known as **combustion analysis**. In a combustion analysis, a weighed sample of the compound is heated to a high temperature under a stream of oxygen gas, resulting in its complete combustion to yield gaseous products of known identities. The complete combustion of hydrocarbons, for example, will yield carbon dioxide and water as the only products. The gaseous combustion products are swept through separate, preweighed collection devices containing compounds that selectively absorb each product (**Figure 4.18**). The mass increase of each device corresponds to the mass of the absorbed product and may be used in an appropriate stoichiometric calculation to derive the mass of the relevant element.

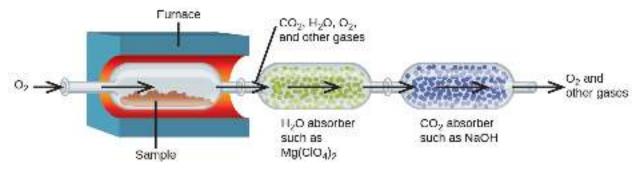


Figure 4.18 This schematic diagram illustrates the basic components of a combustion analysis device for determining the carbon and hydrogen content of a sample.

Example 4.16

Combustion Analysis

Polyethylene is a hydrocarbon polymer used to produce food-storage bags and many other flexible plastic items. A combustion analysis of a 0.00126-g sample of polyethylene yields 0.00394 g of CO_2 and 0.00161 g of H_2O . What is the empirical formula of polyethylene?

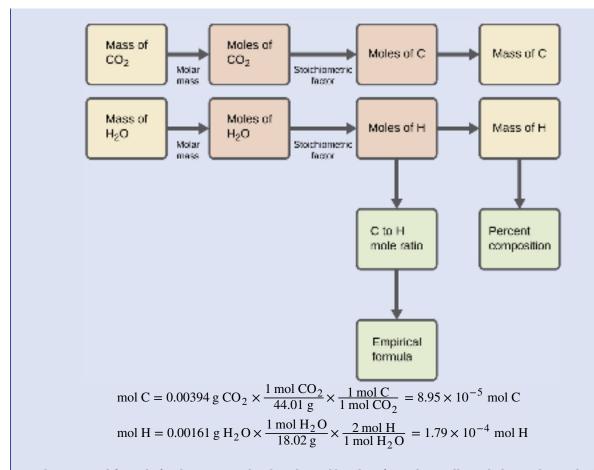
Solution

The primary assumption in this exercise is that all the carbon in the sample combusted is converted to carbon dioxide, and all the hydrogen in the sample is converted to water:

$$C_x H_y(s) + \text{ excess } O_2(g) \longrightarrow xCO_2(g) + \frac{y}{2}H_2 O(g)$$

Note that a balanced equation is not necessary for the task at hand. To derive the empirical formula of the compound, only the subscripts *x* and *y* are needed.

First, calculate the molar amounts of carbon and hydrogen in the sample, using the provided masses of the carbon dioxide and water, respectively. With these molar amounts, the empirical formula for the compound may be written as described in the previous chapter of this text. An outline of this approach is given in the following flow chart:



The empirical formula for the compound is then derived by identifying the smallest whole-number multiples for these molar amounts. The H-to-C molar ratio is

$$\frac{\text{mol H}}{\text{mol C}} = \frac{1.79 \times 10^{-4} \text{ mol H}}{8.95 \times 10^{-5} \text{ mol C}} = \frac{2 \text{ mol H}}{1 \text{ mol C}}$$

and the empirical formula for polyethylene is CH₂.

Check Your Learning

A 0.00215-g sample of polystyrene, a polymer composed of carbon and hydrogen, produced 0.00726 g of CO_2 and 0.00148 g of H_2O in a combustion analysis. What is the empirical formula for polystyrene?

Answer: CH