CHEMISTRY

Chapter 4 STOICHIOMETRY OF CHEMICAL REACTIONS

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HW problems: 3, 9, 11, 17, 20, 21, 23, 31, 41, 49, 53, 61, 67, 81, 87, 93

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CH. 4 OUTLINE

4.1: Writing and Balancing Chemical Equations

4.2: Classifying Chemical Reactions

4.3: Reaction Stoichiometry

4.4: Reaction Yields

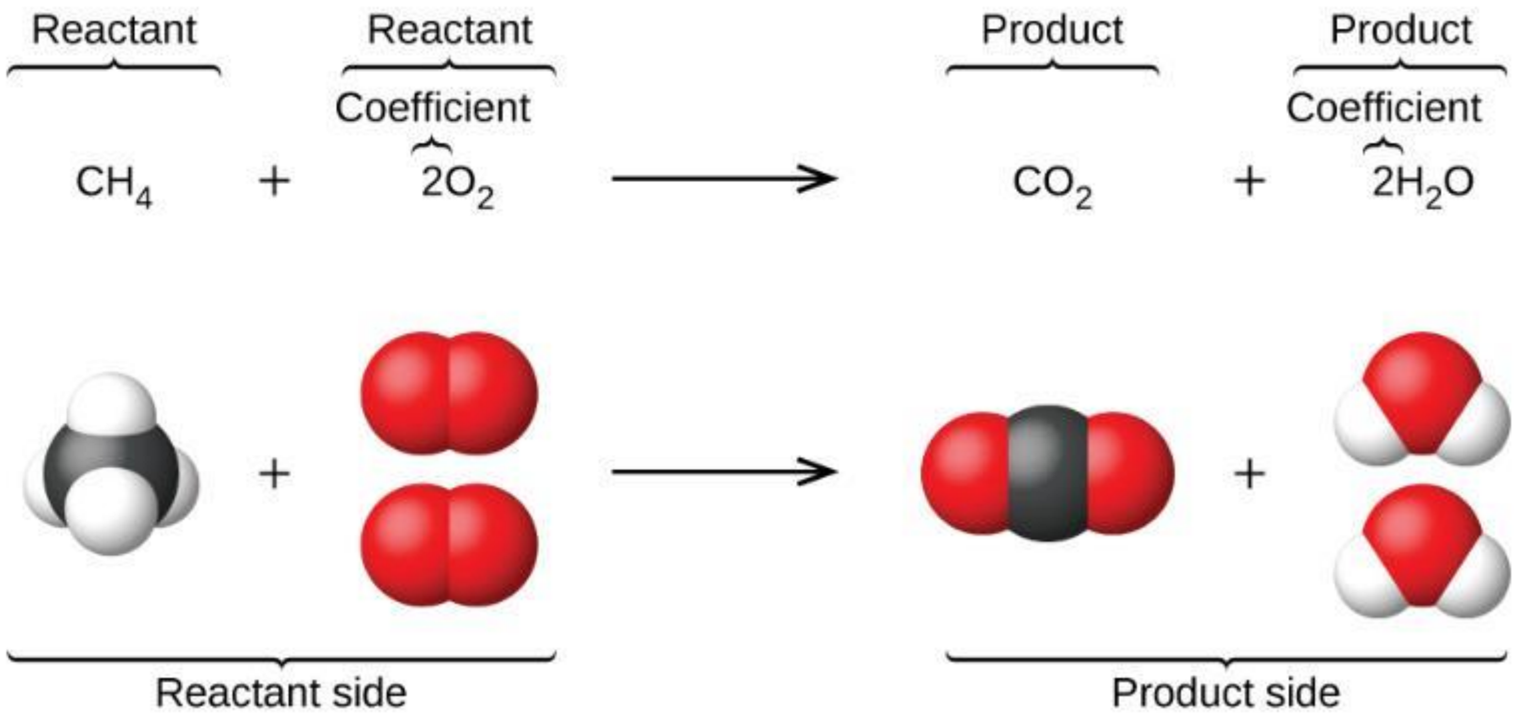
4.5: Quantitative Chemical Analysis

4.1 WRITING AND BALANCING CHEMICAL EQUATIONS

- Preceding chapters introduced the use of element symbols to represent individual atoms, molecules, and compounds.

- A ***Balanced Chemical Equation*** uses symbolism to represent both the ***identities and the relative quantities of substances*** undergoing a chemical (or physical) change.

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).

WRITING CHEMICAL EQUATIONS

- **This example illustrates the fundamental aspects of any chemical equation:**

1) The substances undergoing a 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.

WRITING CHEMICAL EQUATIONS

- **This example illustrates the fundamental aspects of any chemical 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.

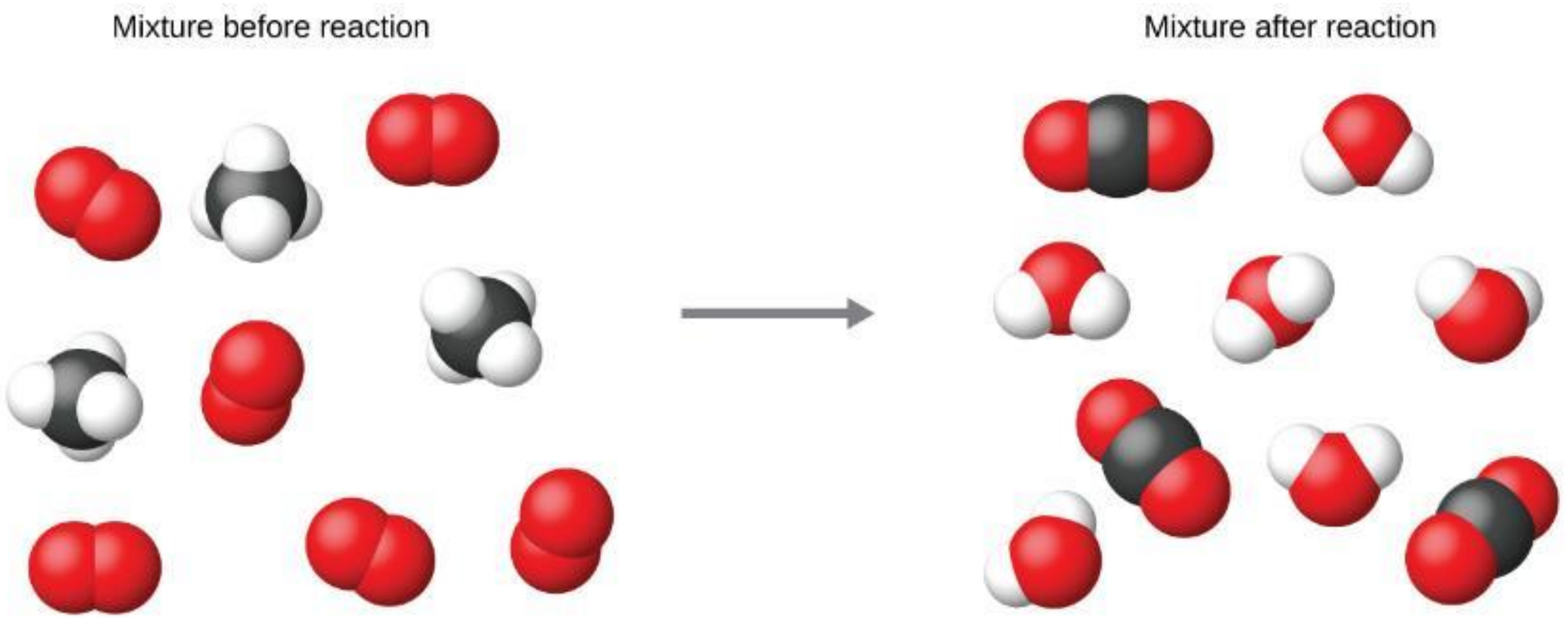
COEFFICIENTS

- It is common practice to use the smallest possible whole-number coefficients in a chemical equation.

- These ***coefficients represent the relative numbers of reactants and products***, and, therefore, they may be correctly interpreted as ratios.

- **Previous example:** Methane and oxygen react to yield carbon dioxide and water in a 1:2:1:2 ratio.

FIGURE 4.3



Regardless of the absolute number of molecules involved, the ratios between numbers of molecules are the same as that given in the chemical equation.

BALANCING EQUATIONS

- The chemical equation described previously is ***balanced***.
  - Equal numbers of atoms for each element are represented on the reactant and product sides.

- 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.

BALANCING EQUATIONS

- 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.

$$\left(1\,CO_2\ molecule \times \frac{2\ O\ atoms}{CO_2\ molecule}\right) + \left(2\ H_2O\ molecules \times \frac{1\ O\ atom}{H_2O\ molecule}\right)$$

$$= 4\ O\ atoms$$

BALANCING EQUATIONS

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

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

Element	Reactants	Products	Balanced?
C	$1 \times 1 = 1$	$1 \times 1 = 1$	1 = 1, yes
H	$1 \times 4 = 4$	$2 \times 2 = 4$	4 = 4, yes
O	$2 \times 2 = 4$	$(1 \times 2) + (2 \times 1) = 4$	4 = 4, yes

BALANCING EQUATIONS

- An unbalanced chemical reaction can be balanced by a fairly simple approach known as balancing by inspection.

$$H_2O \longrightarrow H_2 + O_2 \qquad \textit{(unbalanced)}$$

Element	Reactants	Products	Balanced?
H	$1 \times 2 = 2$	$1 \times 2 = 2$	$2 = 2$, yes
O	$1 \times 1 = 1$	$1 \times 2 = 2$	$1 \neq 2$, no

- The numbers of H atoms are balanced, but the numbers of O atoms are not.

BALANCING EQUATIONS

- To achieve balance, the coefficients of the equation must be changed as needed.

- Subscripts define the identity of the substance, and so these ***cannot be changed*** without altering the qualitative meaning of the equation.

BALANCING EQUATIONS

- The O atom balance may be achieved by changing the coefficient for H_2O to 2.

$$2H_2O \longrightarrow H_2 + O_2 \qquad \textit{(unbalanced)}$$

Element	**Reactants**	**Products**	**Balanced?**
H	$2 \times 2 = 4$	$1 \times 2 = 2$	$4 \neq 2$, no
O	$2 \times 1 = 2$	$1 \times 2 = 2$	$2 = 2$, yes

BALANCING EQUATIONS

- The H atom balance was upset by this change, but it is easily reestablished by changing the coefficient for H_2 to 2.

$$2H_2O \longrightarrow 2H_2 + O_2 \qquad \textit{(balanced)}$$

Element	Reactants	Products	Balanced?
H	2 × 2 = 4	2 × 2 = 4	4 = 4, yes
O	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 equation is therefore balanced!

BALANCING EQUATIONS

- It is sometimes convenient to use fractions instead of integers as intermediate coefficients.

$$C_2H_6 + \frac{7}{2}O_2 \longrightarrow 3H_2O + 2CO_2 \qquad \textit{(balanced)}$$

- When balance is achieved, all the equation's coefficients may then be multiplied by a whole number to convert the fractional coefficients to integers.

- Multiplying each coefficient by 2:

$$2C_2H_6 + 7O_2 \longrightarrow 6H_2O + 4CO_2 \qquad \textit{(balanced)}$$

HOW TO "READ" CHEMICAL EQUATIONS

$2\ Mg + O_2 \longrightarrow 2\ MgO$ can mean any of the following:

- 2 atoms Mg + 1 molecule O_2 makes 2 formula units MgO
- 2 moles Mg + 1 mole O_2 makes 2 moles MgO
- 48.6 grams Mg + 32.0 grams O_2 makes 80.6 g MgO

BUT NOT

- 2 grams Mg + 1 gram O_2 makes 2 g MgO

This 2:1:2 relationship is known as STOICHIOMETRY, and the numbers themselves are the stoichiometric coefficients.

BALANCING CHEMICAL EQUATIONS

1. Write the **correct** formula(s) for the reactant(s) on the left side and the **correct** formula(s) for the product(s) on the right side of the equation.

Ethane reacts with oxygen to form carbon dioxide and water

$C_2H_6 + O_2 \longrightarrow CO_2 + H_2O$

2. Goal: comply with the law of conservation of matter. Change the big numbers in *front* of the formulas (***coefficients***) to make the number of atoms of each element the same on both sides of the equation. Do *not* change the subscripts.

$2C_2H_6$ **NOT** C_4H_{12}

BALANCING CHEMICAL EQ- STRATEGY

Start with the heaviest element that is not "alone" in a compound.

2 carbons on left

$C_2H_6 + O_2 \longrightarrow CO_2 + H_2O$

1 carbon on right

multiply CO_2 by 2

6 hydrogen on left

$C_2H_6 + O_2 \longrightarrow 2CO_2 + H_2O$

2 hydrogen on right

multiply H_2O by 3

$C_2H_6 + O_2 \longrightarrow 2CO_2 + 3H_2O$

either start over with a 2 in front, or multiply O_2 by $\frac{7}{2}$

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

remove fraction
multiply both sides by 2

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

ADDITIONAL INFORMATION IN CHEMICAL EQUATIONS

- The physical states of reactants and products are often indicated with a parenthetical abbreviation following the formulas.

(*g*) gas

(*l*) liquid

(*s*) solid

(*aq*) *aqueous*

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

ADDITIONAL INFORMATION IN CHEMICAL EQUATIONS

- 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.

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

EQUATIONS FOR IONIC REACTIONS

- Many chemical reactions take place in aqueous media.

- When ions are involved, the chemical equations may be written with various levels of detail.

- ***Molecular equation:***

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

- Molecular equations don’t explicitly represent the ionic species that are present in solution.

EQUATIONS FOR IONIC REACTIONS

- When ionic compounds dissolve in water, they may ***dissociate*** into their constituent ions

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

$$2AgNO_3(aq) \longrightarrow 2Ag^+(aq) + 2NO_3^-(aq)$$

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

- Unlike these three ionic compounds, AgCl does not dissolve in water to a significant extent.

COMPLETE IONIC EQUATION

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- Ionic compounds dissolved in water are more realistically represented as dissociated ions.

- Explicitly representing all dissolved ions results in a ***complete ionic equation***:

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

NET IONIC EQUATION

- Two chemical species are present in identical form on both sides of the arrow, Ca^{2+}(aq) and NO_3^-(*aq*).

- These ions are ***spectator ions*** - ions whose presence is required to maintain charge neutrality and are neither chemically nor physically changed by the process.

- Elimination of the spectator ions results in a ***net ionic equation***:

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

4.2 CLASSIFYING CHEMICAL REACTIONS

- A ***precipitation reaction*** is one in which dissolved substances react to form one (or more) solid products.
  - Also known as a double displacement, double replacement, or metathesis reaction.

- Many reactions of this type involve the exchange of ions between ionic compounds in aqueous solution.

- Precipitation reactions are common in nature and in industry.

SOLUBILITY AND PRECIPITATION REACTIONS

- ***Solubility*** - the maximum concentration of a substance that can be achieved under specified conditions.

- Substances that have a relatively ***large solubility*** are said to be ***soluble.***

- A substance will ***precipitate*** when solution conditions are such that its concentration exceeds its solubility.

- Substances that have a relatively ***low solubility*** are said to be ***insoluble***, and these are the substances that readily precipitate from solution.

SOLUBILITY OF COMMON IONIC COMPOUNDS IN WATER

Soluble compounds contain:	**Insoluble exceptions:**
• group 1 metal cations and the ammonium ion.	
• the halide ions.	• the halides of Ag^+, Hg_2^{2+}, Pb^{2+}
• the acetate, bicarbonate, nitrate, and chlorate ions.	
• the sulfate ion	• sulfates of Ag^+, Ba^{2+}, Ca^{2+}, Hg_2^{2+}, Pb^{2+} , Sr^{2+}
Insoluble compounds contain:	**Soluble exceptions:**
• carbonate, chromate, phosphate, and sulfide ions.	• compounds of these ions with group 1 metal cations or ammonium ion.
• hydroxide ion.	• hydroxides of group 1 metal cations and Ba^{2+}.

PRECIPITATION REACTION EXAMPLE

- **Molecular Equation:**

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

- ***PbI_2 precipitates*** from solution, which is consistent with the solubility rules.

- **Net ionic equation:**

$$Pb^{2+}(aq) + 2I^{-}(aq) \longrightarrow PbI_2(s)$$

FIGURE 4.4

A precipitate of PbI_2 forms when solutions containing Pb^{2+} and I^- are mixed. (credit: Der Kreole/Wikimedia Commons)

PRECIPITATION REACTION EXAMPLE

- **Molecular Equation:**

$$\mathrm{NaCl}(aq) + \mathrm{AgNO_3}(aq) \longrightarrow \mathrm{AgCl}(s) + \mathrm{NaNO_3}(aq)$$

- ***AgCl precipitates*** from solution, which is consistent with the solubility rules.

- **Net ionic equation:**

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

ACID-BASE REACTIONS

- An ***acid-base reaction*** is one in which a hydrogen ion, H^+, is transferred from one chemical species to another.

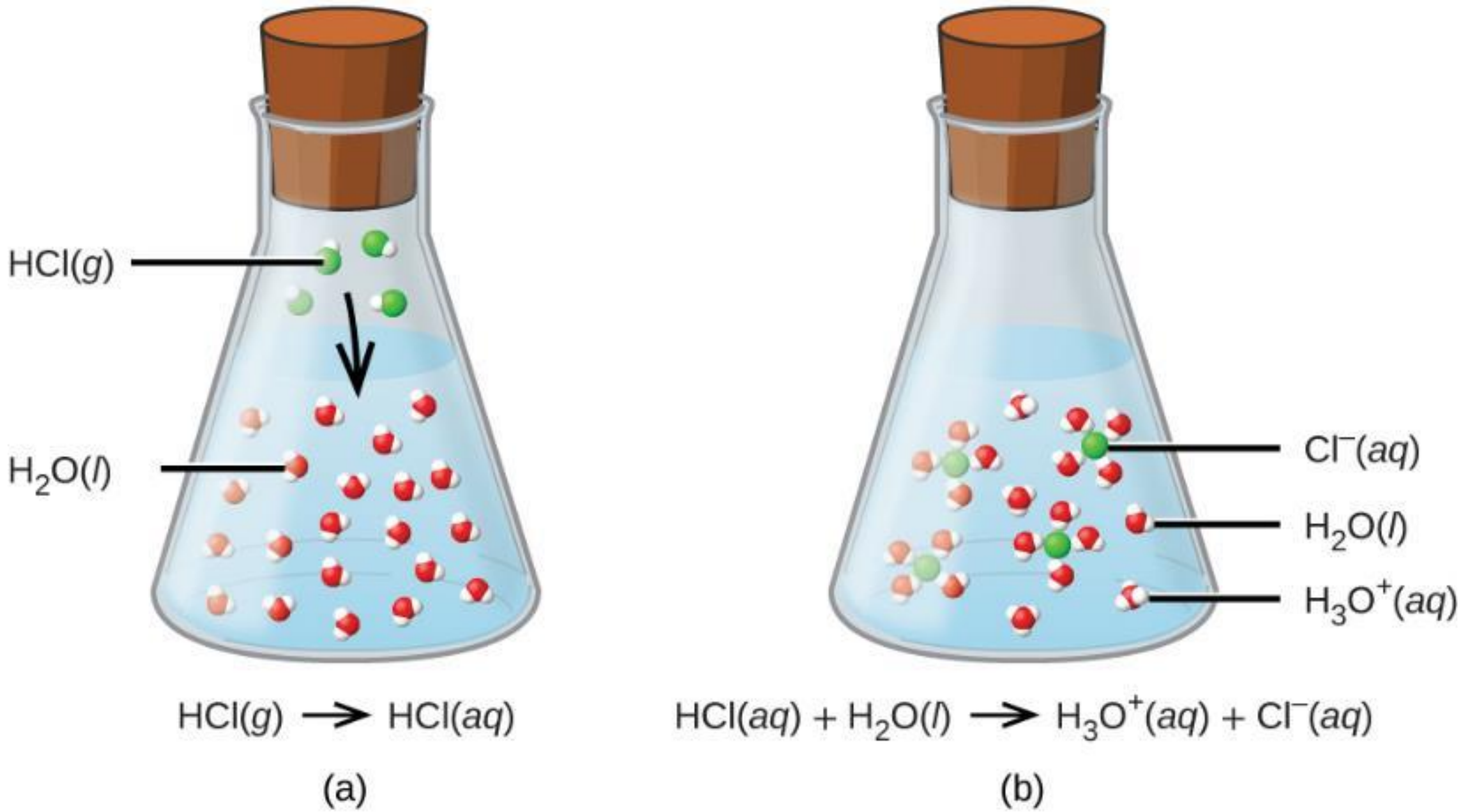
- An ***acid*** is a substance that will dissolve in water to yield ***hydronium ions, H_3O^+***.

- **Example:** HCl is a strong acid

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

- This is an acid-base reaction, H^+ ions are transferred from HCl molecules to H_2O molecules.

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).

STRONG ACIDS

- Virtually every HCl molecule that dissolves in water will undergo this reaction.

- Acids that ***completely react*** in this fashion are called ***strong acids***.

COMMON STRONG ACIDS

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Compound Formula	Name in Aqueous Solution
HBr	hydrobromic acid
HCl	hydrochloric acid
HI	hydroiodic acid
HNO_3	nitric acid
$HClO_4$	perchloric acid
H_2SO_4	sulfuric acid

WEAK ACIDS

- A far greater number of compounds behave as ***weak acids*** and only ***partially*** react with water.

- A large majority of dissolved molecules remain in their original form and only a relatively small amount of hydronium ions are generated.

WEAK ACIDS

- **Example:** Acetic Acid

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

- Only about 1% of acetic acid molecules are present in the ionized form, $CH_3CO_2^-$.

- The use of a ***double-arrow*** in the equation denotes the ***partial reaction*** aspect of this process.

- This is also an acid-base reaction.

FIGURE 4.6

(a) (b)

(a) Fruits such as oranges, lemons, and grapefruit contain the weak acid citric acid.

(b) Vinegars contain the weak acid acetic acid. The hydrogen atoms that may be transferred during an acid-base reaction are highlighted in the inset molecular structures. (credit a: modification of work by Scott Bauer; credit b: modification of work by Brücke-Osteuropa/Wikimedia Commons)

BASES

- 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.

- **Examples:** $NaOH$, KOH, $Ca(OH)_2$, $Ba(OH)_2$

- These bases, along with other hydroxides, ***completely dissociate*** in water, and are considered ***strong bases***.

STRONG BASES

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

- The dissociation process is essentially complete when NaOH is dissolved in water.

- This process is a dissociation (physical process), not an acid-base reaction.

WEAK BASES

• Some compounds produce hydroxide ions when dissolved by chemically reacting with water molecules.

• In all cases, these compounds react only ***partially*** and are classified as ***weak bases***.

• Example: Ammonia, NH_3

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

• This is an acid-base reaction - H^+ is transferred from water molecules to ammonia molecules.

FIGURE 4.7

(a) (b)

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)

NEUTRALIZATION REACTIONS

- A ***neutralization reaction*** is a specific type of acid-base reaction in which the reactants are an acid and a base, the products are often a salt and water, and neither reactant is the water itself:

$$\text{Acid} + \text{base} \longrightarrow \text{salt} + \text{water}$$

- **Example:**

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

- $MgCl_2$ is a salt.

OXIDATION-REDUCTION (REDOX) REACTIONS

- Some ***redox reactions*** involve the transfer of electrons between reactant species to yield ionic products:

$$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$$

- It is helpful to split the overall reaction into individual equations called **half-reactions.**

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

$$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(s)$$

OXIDATION-REDUCTION (REDOX) REACTIONS

- The Na atoms ***lose*** electrons.

- The Cl atoms ***gain*** electrons.

- For redox reactions of this sort:
  - ***Oxidation*** = loss of electrons
  - ***Reduction*** = gain of electrons

- Na is oxidized
- Cl_2 is reduced

REDUCING AND OXIDIZING AGENTS

- Na functions as a ***reducing agent (reductant)***, since it ***provides electrons*** for (or reduces) chlorine.

- Cl_2 functions as an ***oxidizing agent (oxidant)***, as it effectively ***removes electrons*** from (oxidizes) sodium.

OXIDATION-REDUCTION (REDOX) REACTIONS

- Some redox processes do not involve the transfer of electrons:

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

- The product of this reaction is a covalent compound, so transfer of electrons in the explicit sense is not involved.

- The ***oxidation number (or oxidation state)*** of an element in a compound is the charge its atoms would possess *if the compound was ionic*.

RULES FOR ASSIGNING OXIDATION NUMBERS

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.

RULES FOR ASSIGNING OXIDATION NUMBERS

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 − ½ (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)

RULES FOR ASSIGNING OXIDATION NUMBERS

4) The sum of the oxidation numbers for all atoms in a molecule or polyatomic ion equals the charge on the molecule or ion.

EXAMPLE 4.5

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

(a) H_2S

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 (x):

charge on $H_2S = 0 = (2 \times 1) + 1x$

$x = -2$

EXAMPLE 4.5

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

(b) SO_3^{2-}

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 (x):

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

$x = +4$

EXAMPLE 4.5

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

(c) Na_2SO_4

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 (x) is calculated as directed by guideline 4:

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

$x = +6$

OXIDATION-REDUCTION (REDOX) REACTIONS

- Using the oxidation number concept, an all-inclusive definition of a redox reaction has been established.

- ***Oxidation-reduction (redox) reactions*** are those in which one or more elements involved undergo a change in oxidation number.

- ***Oxidation*** = increase in oxidation number
- ***Reduction*** = decrease in oxidation number

TYPES OF REDOX REACTIONS

- ***Combustion reactions*** in which the reductant (also called a *fuel*) and the oxidant (often, but not necessarily, molecular oxygen) react vigorously and produce significant amounts of heat, and often light, in the form of a flame.

- **Example:** Solid rocket fuel reaction

$$10Al(s) + 6NH_4ClO_4(s) \longrightarrow 4Al_2O_3(s) + 2AlCl_3(s) + 12H_2O(g) + 3N_2(g)$$

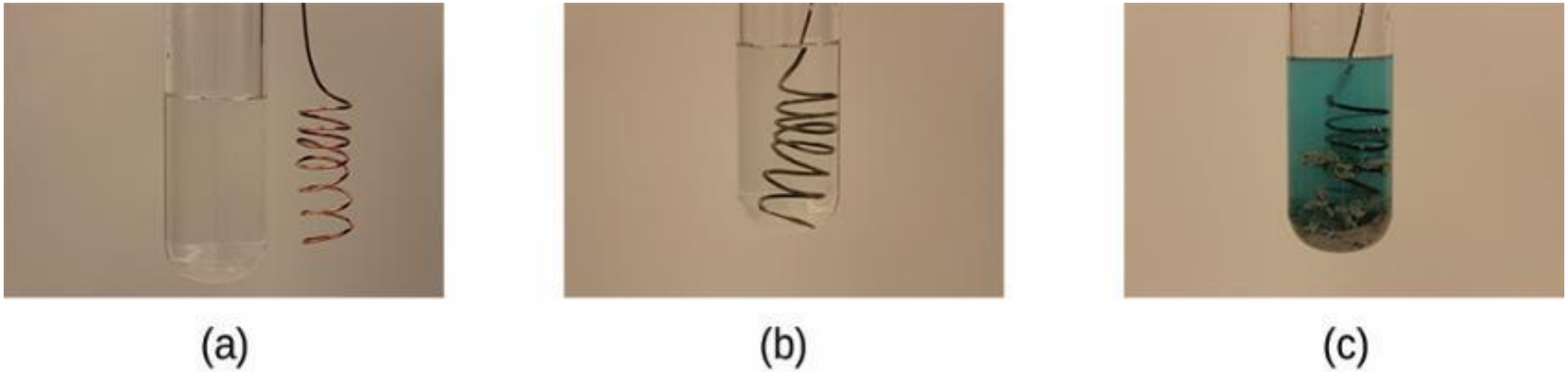
TYPES OF REDOX REACTIONS

- ***Single-displacement (replacement) reactions*** are redox reactions in which an ion in solution is displaced (or replaced) via the oxidation of a metallic element.

- **Example:**

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

FIGURE 4.8



(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)

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 the chemical change in other ways.
- These reactions are difficult to balance by inspection.
- One very useful approach to balance these types of redox reactions is to use the half-reaction method.

STEPS FOR BALANCING REDOX REACTIONS

1. Write the two individual half-reactions: the oxidation and the reduction.

2. Balance all elements except oxygen and hydrogen.

3. Balance oxygen atoms by adding H_2O molecules.

4. Balance hydrogen atoms by adding H^+ ions.

5. Balance charge by adding electrons.

STEPS FOR BALANCING REDOX REACTIONS

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.

STEPS FOR BALANCING REDOX REACTIONS

8. For reactions occurring in basic media (excess hydroxide ions), carry out these additional steps:

- Add OH^- ions to both sides of the equation in numbers equal to the number of H^+ ions.
- On the side of the equation containing both H^+ and OH^- ions, combine these ions to yield water molecules.
- Simplify the equation by removing any redundant water molecules.

9. Finally, check to see that both the number of atoms and the total charge are balanced.

EXAMPLE 4.7

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

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

Step 1: *Write the two half-reactions*.

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

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

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

EXAMPLE 4.7

***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* H_2O *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 seven water molecules are added to the right side.

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

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

EXAMPLE 4.7

Step 4: Balance hydrogen atoms by adding $\mathbf{H^+}$ ***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 H^+ ions are added to the left side.

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

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

EXAMPLE 4.7

***Step 5: Balance charge by adding electrons*.** The iron half-reaction shows a total charge of 2+ on the left side (1 Fe^{2+} ion) and 3+ on the right side (1 Fe^{3+} 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 × 2−) + (14 × 1+) = 12+ on the left side (1 $Cr_2O_7^{2-}$ ion and 14 H^+ ions). The total charge on the right side is (2 × 3+) = 6+ (2 Cr^{3+} ions). Adding six electrons to the left side will bring that side's total charge to (12 + 6−) = 6+, and charge balance is achieved.

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

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

EXAMPLE 4.7

***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.

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

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

EXAMPLE 4.7

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

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

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

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

EXAMPLE 4.7

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

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

	Reactants	**Products**
Fe	6	6
Cr	2	2
O	7	7
H	14	14
Charge	24+	24+

4.3 REACTION STOICHIOMETRY

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- 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.

- ***Coefficients*** provide the ***relative numbers*** of these chemical species.

- The ***quantitative relationships*** between the amounts of reactants and products are known as the reaction's ***stoichiometry.***

STOICHIOMETRY

- The general approach to using stoichiometric relationships is similar in concept to food preparation.

- ***Example:*** A recipe for making eight pancakes calls for 1 cup pancake mix, ¾ cup milk, and one egg.

- ***This recipe can be written as an equation:***

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

STOICHIOMETRY

1 cup mix + ¾ cup milk + 1 egg ⟶ 8 pancakes

- If two dozen pancakes are needed, the amount of ingredients must be increased proportionally according to the amounts given in the recipe.

$$24\ pan\cancel{c}akes \left(\frac{1\,egg}{8\ pan\cancel{c}akes}\right) = 3\,eggs$$

STOICHIOMETRY

- ***Balanced chemical equations*** are used in a similar fashion as recipes.

- From a balanced chemical equation we can determine:
  - The amount of one reactant required to react with a given amount of another reactant.
  - The amount of reactant needed to yield a given amount of product.

- The coefficients in the balanced equation are used to derive ***stoichiometric factors*** that permit computation of the desired quantity.

STOICHIOMETRIC FACTORS

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

- This equation shows that ammonia molecules are produced from hydrogen molecules in a 2:3 ratio.

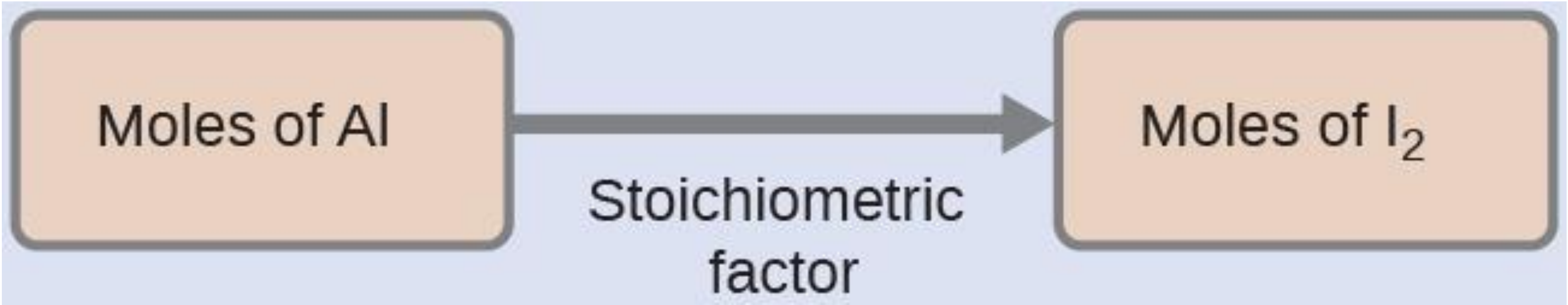
- Stoichiometric factors may be derived using any amount (number) unit:

$$\frac{2\ NH_3\ molecules}{3\ H_2\ molecules} = \frac{2\ doz\ NH_3\ molecules}{3\ doz\ H_2\ molecules} = \frac{2\ mol\ NH_3\ molecules}{3\ mol\ H_2\ molecules}$$

EXAMPLE 4.8

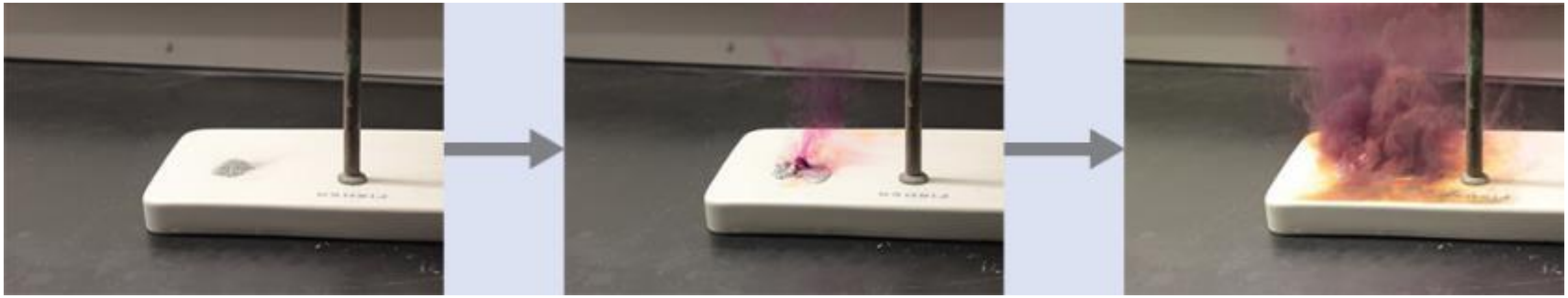
How many moles of I_2 are required to react with 0.429 mol of Al according to the following equation?

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



$$0.429\ \cancel{mol}\ Al \times \frac{3\ mol\ I_2}{2\ \cancel{mol}\ Al} = 0.644\ mol\ I_2$$

FIGURE 4.9



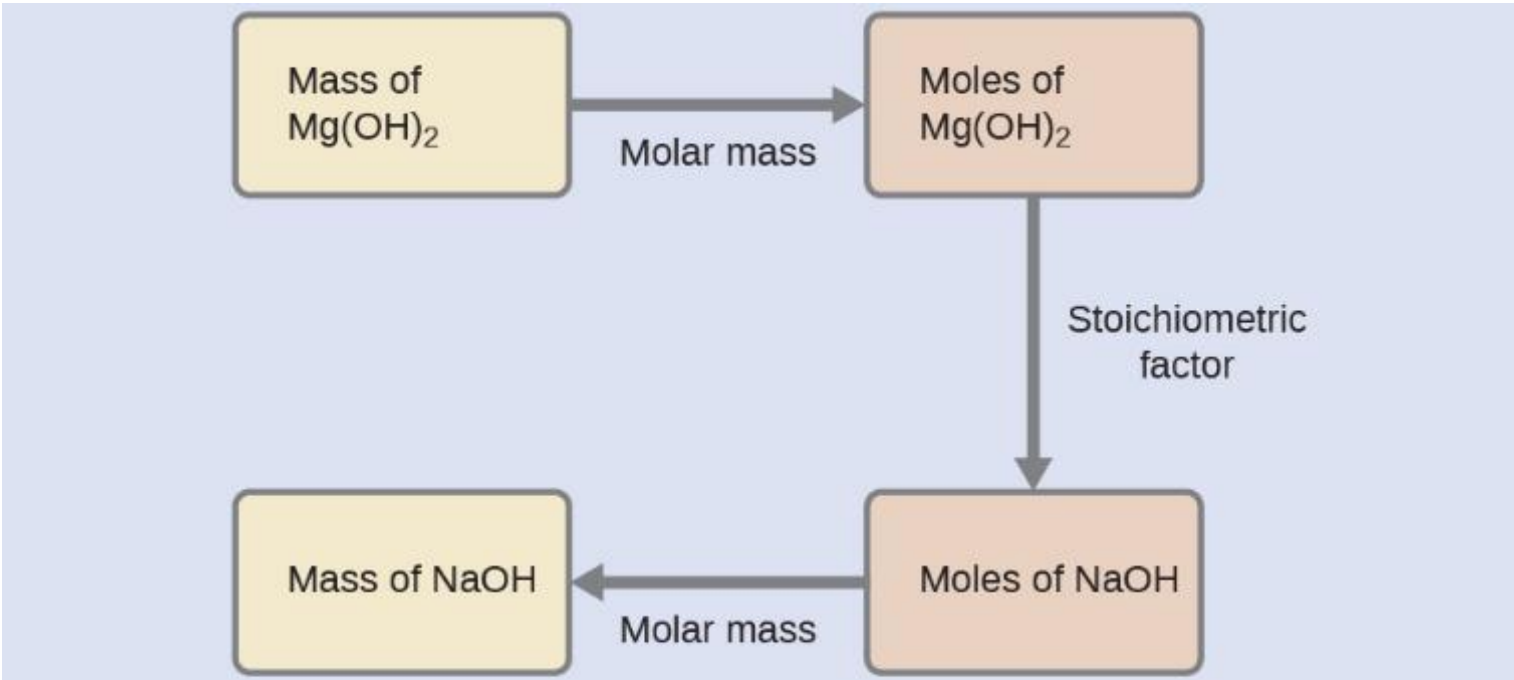
Aluminum and iodine react to produce aluminum iodide. The heat of the reaction vaporizes some of the solid iodine as a purple vapor. (credit: modification of work by Mark Ott)

EXAMPLE 4.10

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?

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

EXAMPLE 4.10



$$16\ \cancel{g\ Mg(OH)_2} \times \frac{1\ mol\ \cancel{Mg(OH)_2}}{58.3\ \cancel{g\ Mg(OH)_2}} \times \frac{2\ \cancel{mol\ NaOH}}{1\ \cancel{mol\ Mg(OH)_2}}$$

$$\times \frac{40.0\ g\ NaOH}{1\ \cancel{mol\ NaOH}} = 22\ g\ NaOH$$

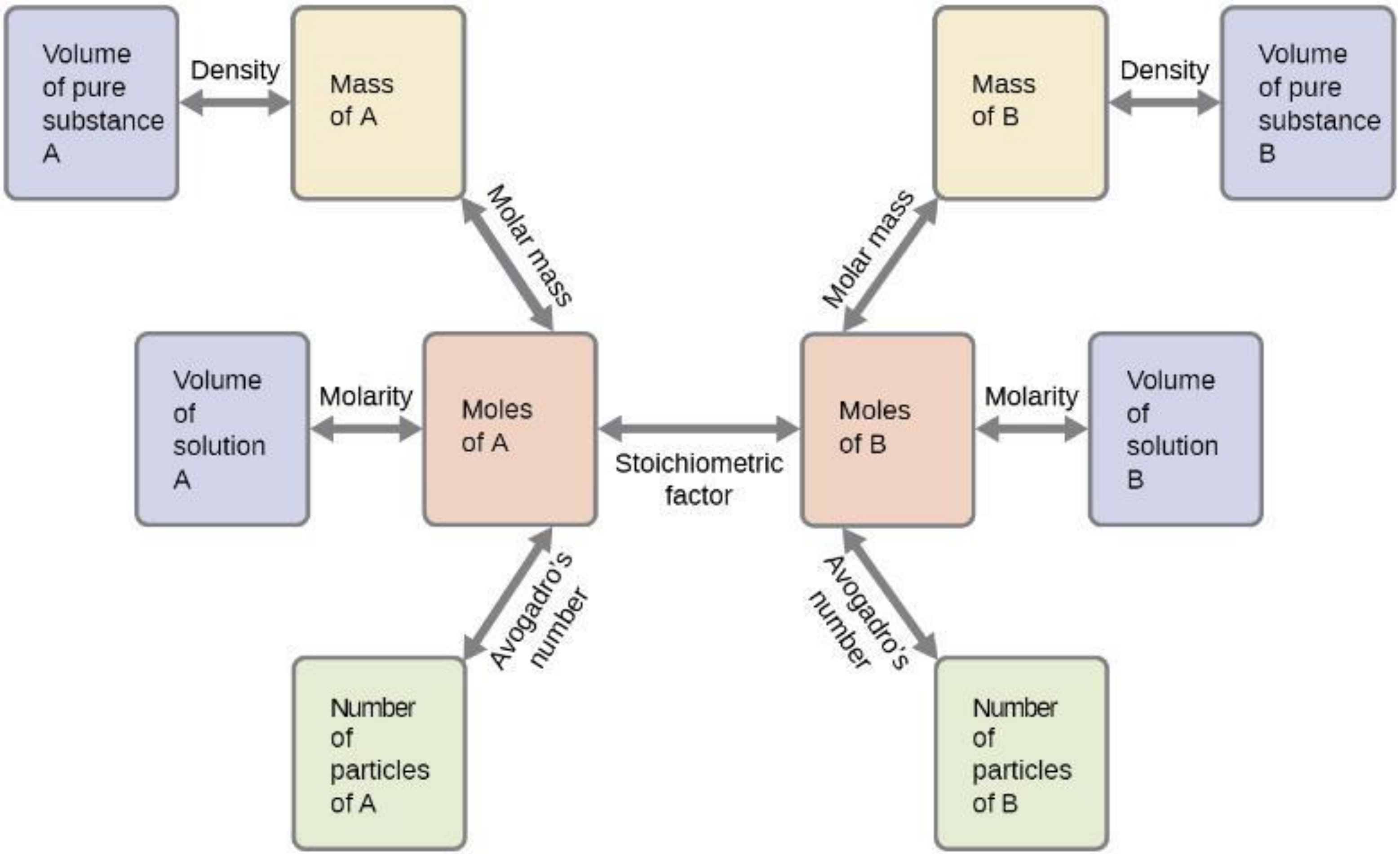
STOICHIOMETRY

- Examples 4.8 and 4.10 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).

- ***All of these calculations share a common essential component: the use of stoichiometric factors derived from balanced chemical equations.***

FIGURE 4.10



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

FIGURE 4.11

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

4.4 REACTION YIELDS

- The relative amounts of reactants and products represented in a balanced chemical equation are often referred to as ***stoichiometric amounts.***

- All of the exercises in the preceding module involved stoichiometric amounts of reactants.

- In more realistic situations, reactants are not present in stoichiometric amounts.

LIMITING REACTANT

- Consider making grilled cheese sandwiches.

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

- Provided with 28 slices of bread and 11 slices of cheese, one may prepare 11 sandwiches per the provided recipe.

- All of the provided cheese would be used and six slices of bread would be left over.

LIMITING REACTANT

- The number of sandwiches prepared has been ***limited*** by the number of cheese slices.

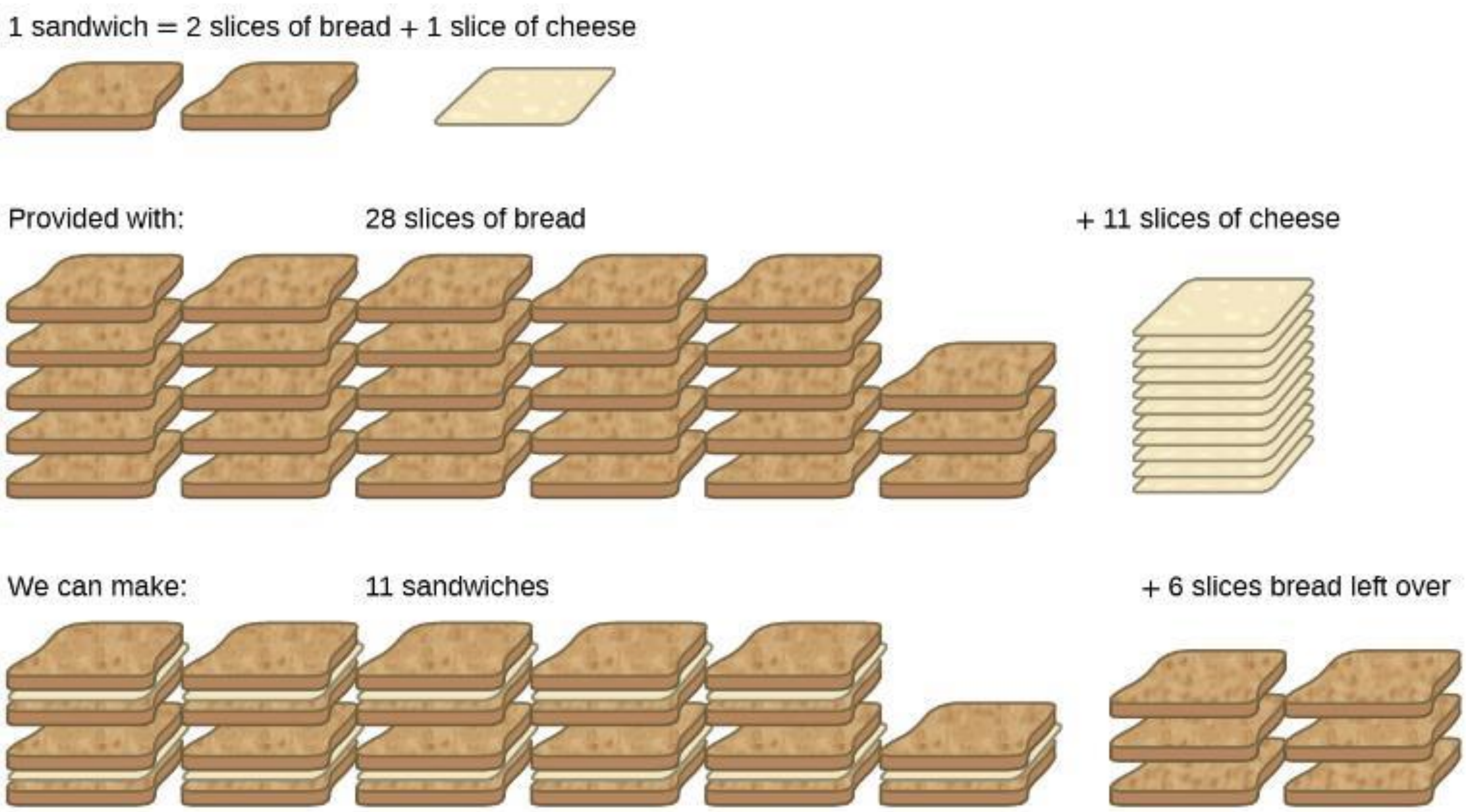
- Cheese is the ***limiting reactant.***

- The limiting reactant will always be entirely consumed, thus limiting the amount of product that may be generated.

- The bread slices have been provided in ***excess.***

- Bread is the ***excess reactant.***

FIGURE 4.12



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

LIMITING REACTANT

- Now consider a chemical process.

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

- Imagine combining 3 moles of H_2 and 2 moles Cl_2.
- One approach for determining the limiting reactant involves comparing the amount of product expected for the complete reaction of each reactant.
- The reactant yielding the ***lesser*** amount of product is the limiting reactant.

LIMITING REACTANT

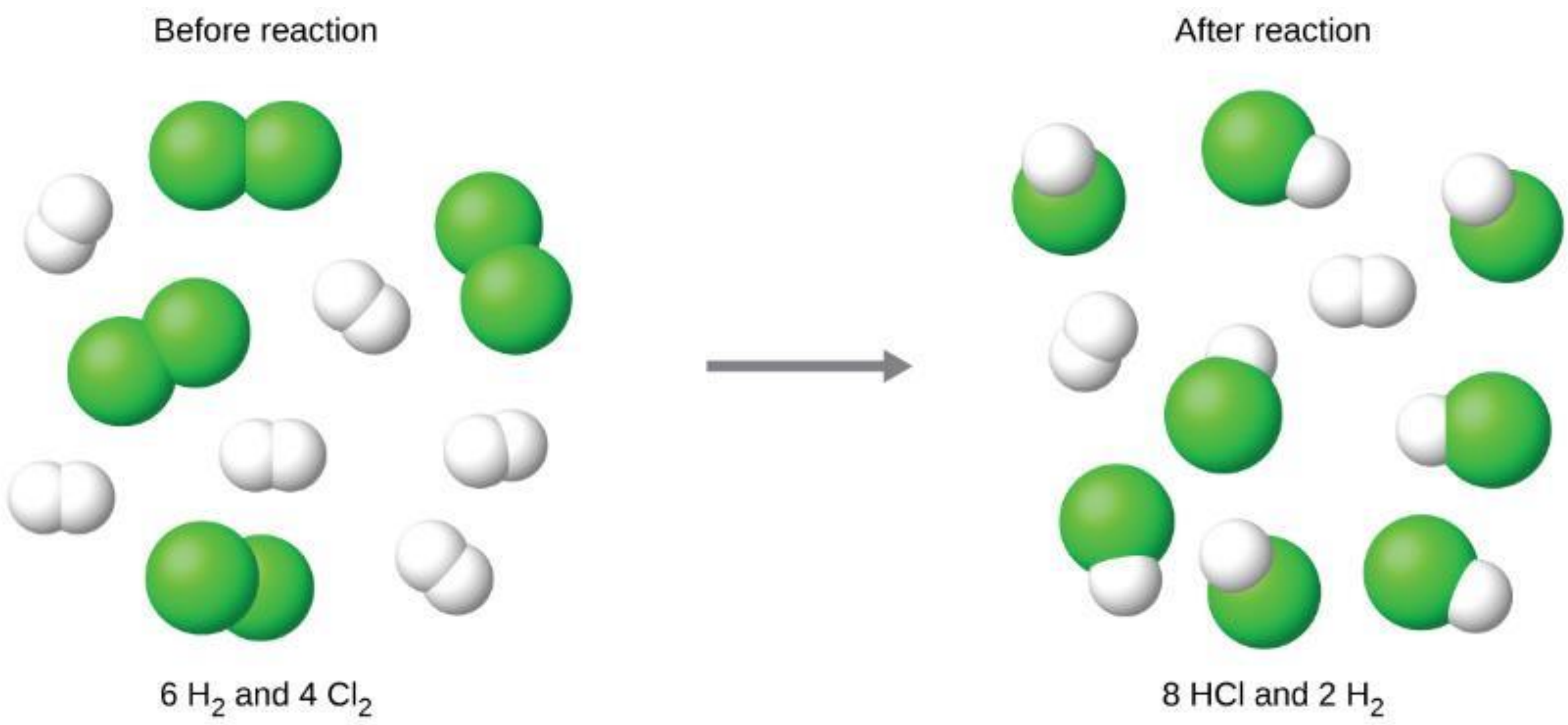
$$3\,\cancel{mol}\,H_2 \times \frac{2\,mol\,HCl}{1\,\cancel{mol}\,H_2} = 6\,mol\,HCl$$

$$2\,\cancel{mol}\,Cl_2 \times \frac{2\,mol\,HCl}{1\,\cancel{mol}\,Cl_2} = 4\,mol\,HCl$$

- The Cl_2 will be consumed once 4 moles HCl is produced.
- Unreacted H_2 will remain once this reaction is complete.

- Cl_2 is the ***limiting reactant*** and H_2 is the ***excess reactant.***

FIGURE 4.13



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.

THEORETICAL AND ACTUAL YIELDS

- The amount of product that *may be* produced by a reaction as calculated per the stoichiometry of an appropriate balanced chemical equation, is called the ***theoretical yield*** of the reaction.

- The amount of product obtained is called the ***actual yield***, and it is often less than the theoretical yield for a number of reasons.
  - Competing side reactions.
  - Incomplete reaction.
  - Difficult recovery of product.

PERCENT YIELD

- The extent to which a reaction's theoretical yield is achieved is commonly expressed as its ***percent yield:***

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

- When calculating percent yield, both yields must be expressed using the same units, so that these units will cancel.

EXAMPLE 4.13

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?

EXAMPLE 4.13

First determine the theoretical yield.

$$1.274\ \cancel{g}\ CuSO_4 \times \frac{1\ \cancel{mol}\ CuSO_4}{159.62\ \cancel{g}\ CuSO_4} \times \frac{1\ \cancel{mol}\ Cu}{1\ \cancel{mol}\ CuSO_4}$$

$$\times \frac{63.55\ g\ Cu}{1\ \cancel{mol}\ Cu} = 0.5072\ g\ Cu$$

EXAMPLE 4.13

Next calculate the percent yield.

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

$$percent\ yield = \frac{0.392\ g\ Cu}{0.5072\ g\ Cu} \times 100 = 77.3\%$$

FIGURE 4.14

(a) (b)

(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

- **Quantitative Analysis –** The determination of the amount or concentration of a substance in a sample.

- We will discuss two main types of quantitative analysis:

  1) Titration

  2) Gravimetric Analysis

TITRATION

- **Titrations involve two solutions:**

  1) Titrant – Solution containing a known concentration of one reactant.

  2) Analyte – Solution containing a reactant of unknown amount or concentration.

- 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.

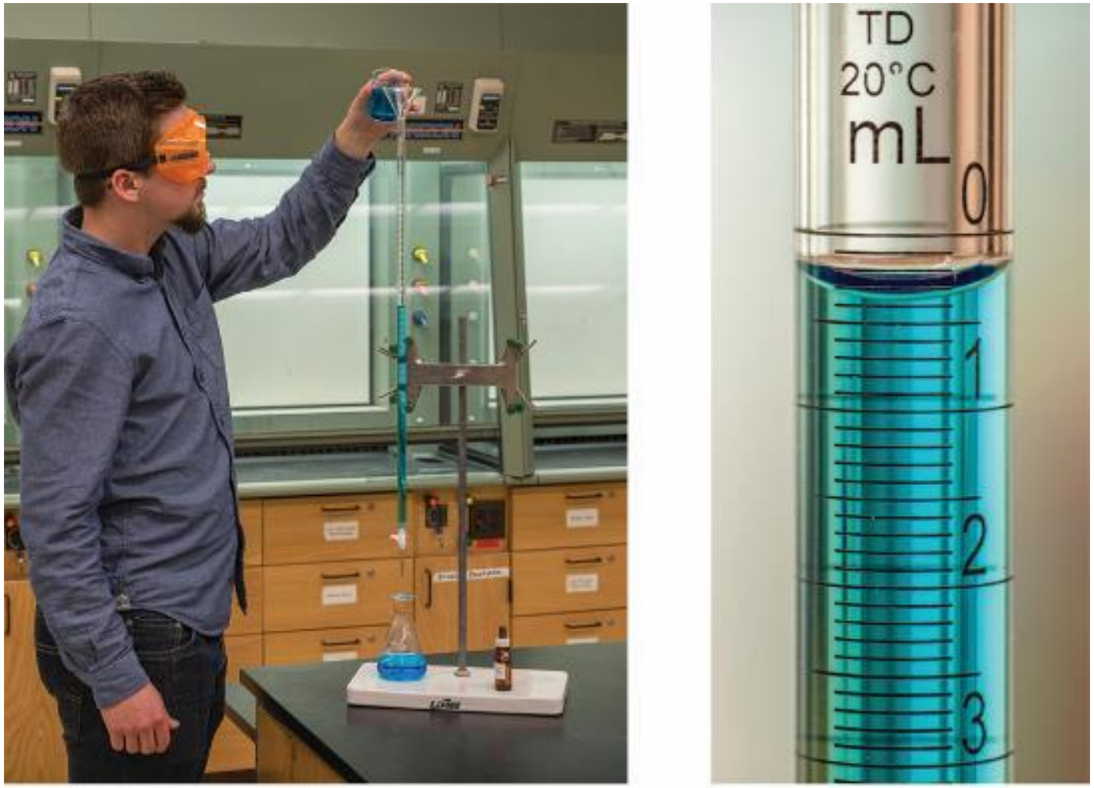
TITRATION

- ***Indicators*** are added to the analyte solution to impart a change in color at or very near the equivalence point of the titration.

- The volume of titrant actually measured is called the ***end point.***

- The difference between the equivalence and end points should be negligible.

FIGURE 4.15



(a) (b)

(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)

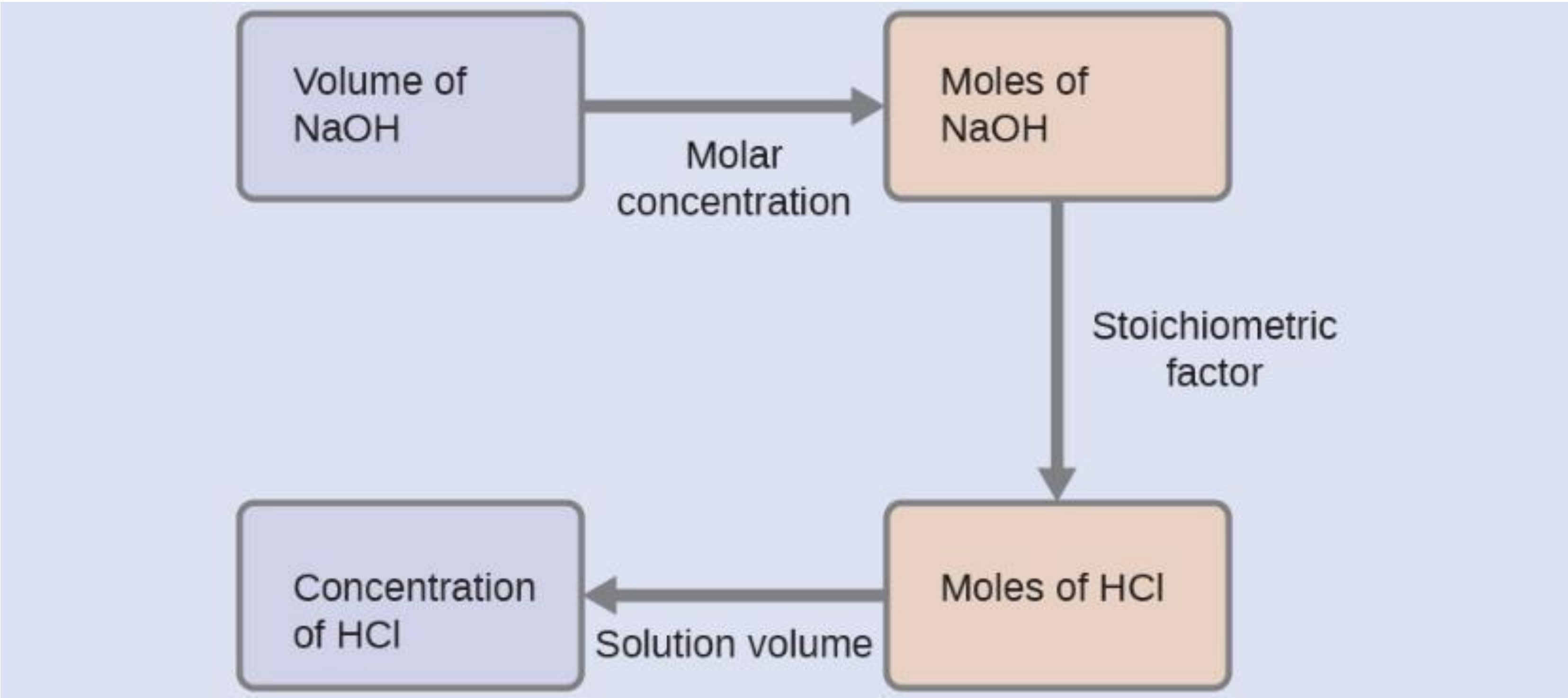
EXAMPLE 4.14

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?

EXAMPLE 4.14



$$35.23\ \cancel{mL}\ NaOH \times \frac{1\ \cancel{L}}{1000\ \cancel{mL}} \times \frac{0.250\ \cancel{mol}\ NaOH}{1\ \cancel{L}} \times \frac{1\ mol\ HCl}{1\ \cancel{mol}\ NaOH}$$

$$= 8.81 \times 10^{-3}\ mol\ HCl$$

EXAMPLE 4.14

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

$$M = \frac{8.81 \times 10^{-3}\ mol\ HCl}{50.00\ \cancel{m}L \times \dfrac{1\ L}{1000\ \cancel{m}L}} = 0.176\ M$$

GRAVIMETRIC ANALYSIS

- ***Gravimetric Analysis –*** A type of analysis 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 system, used along with the known stoichiometry of the compounds involved, permit calculation of the analyte concentration.

- Commonly, the analyte is separated by subjecting it to a precipitation reaction.

FIGURE 4.16

The precipitate may be removed from a reaction mixture by filtration.

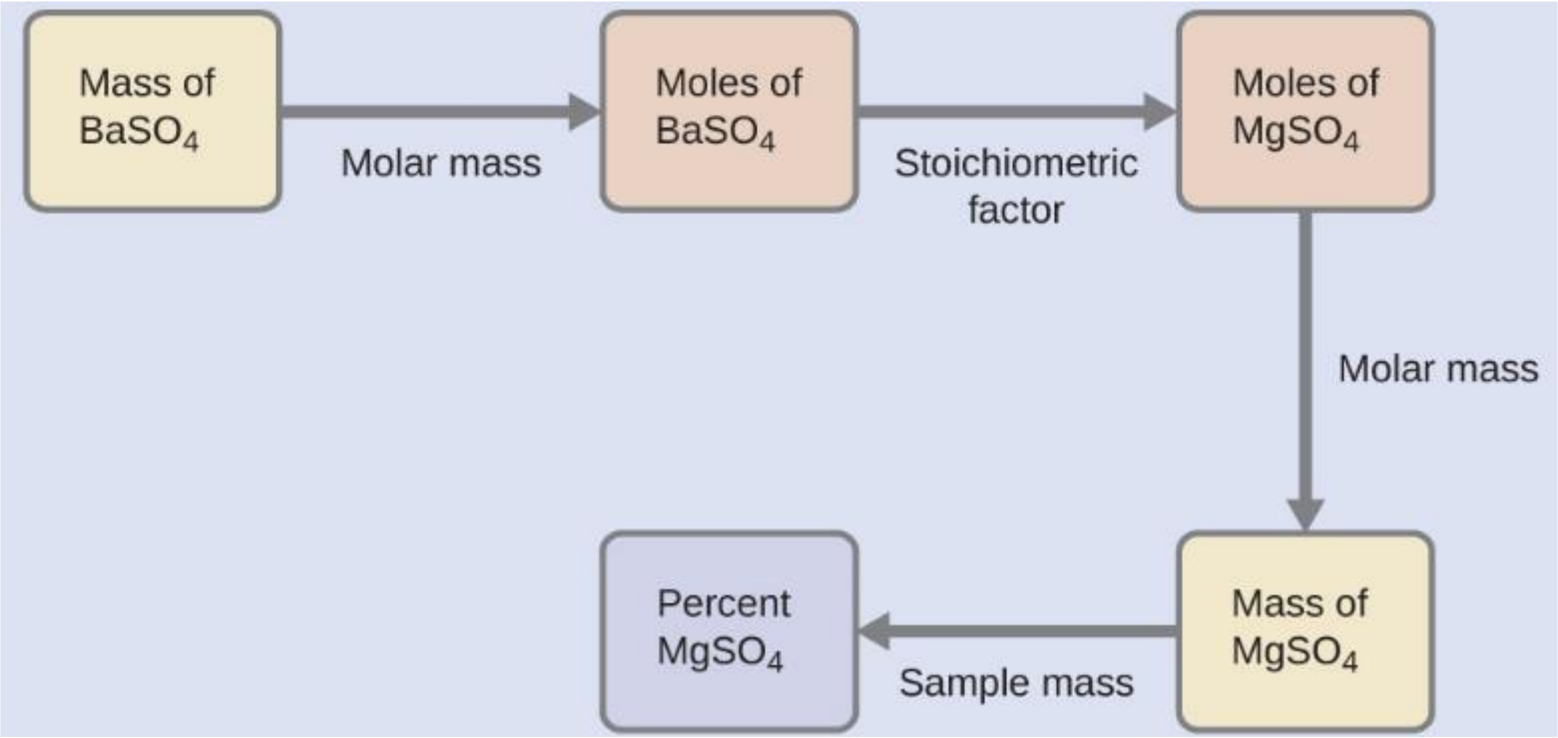
EXAMPLE 4.15

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 $MgSO_4$ in the mixture?

EXAMPLE 4.15



$$0.6168\ \cancel{g}\ BaSO_4 \times \frac{1\ mol\ \cancel{BaSO_4}}{233.43\ g\ \cancel{BaSO_4}} \times \frac{1\ mol\ \cancel{MgSO_4}}{1\ mol\ \cancel{BaSO_4}}$$

$$\times \frac{120.37\ g\ MgSO_4}{1\ mol\ \cancel{MgSO_4}} = 0.3181\ g\ MgSO_4$$

EXAMPLE 4.15

$$mass\ percent\ MgSO_4 = \frac{mass\ MgSO_4}{mass\ sample} \times 100$$

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

COMBUSTION ANALYSIS

- The elemental composition of hydrocarbons and related compounds may be determined via a gravimetric method known as ***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.

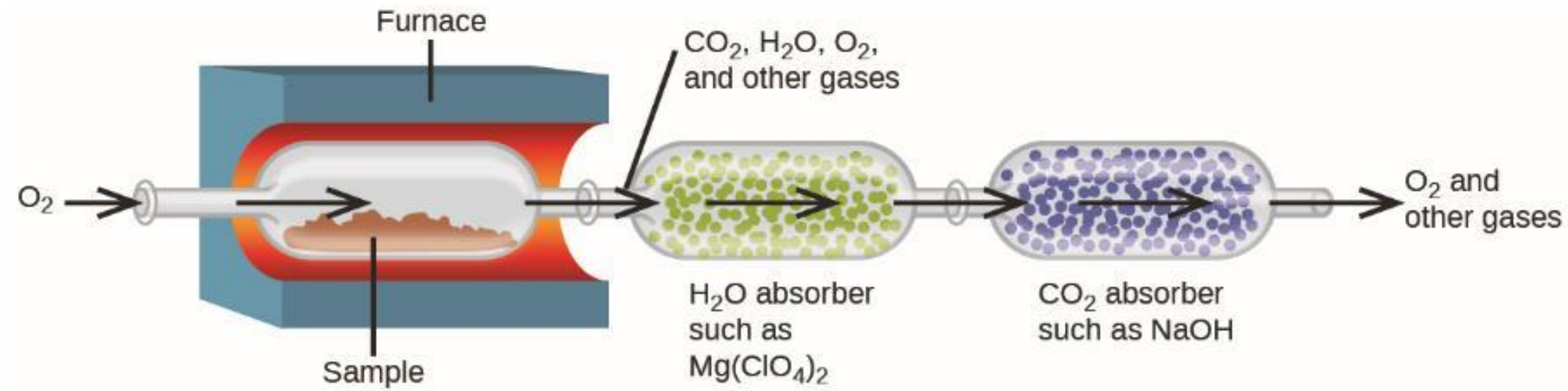
COMBUSTION ANALYSIS

- The complete combustion of hydrocarbons, for example, will yield carbon dioxide and water vapor as the only products.

- The gaseous combustion products are swept through separate, preweighed collection devices containing compounds that selectively absorb each product.

- The mass of the absorbed product can then be used in an appropriate stoichiometric calculation to derive the moles and mass of the relevant element.

FIGURE 4.17



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

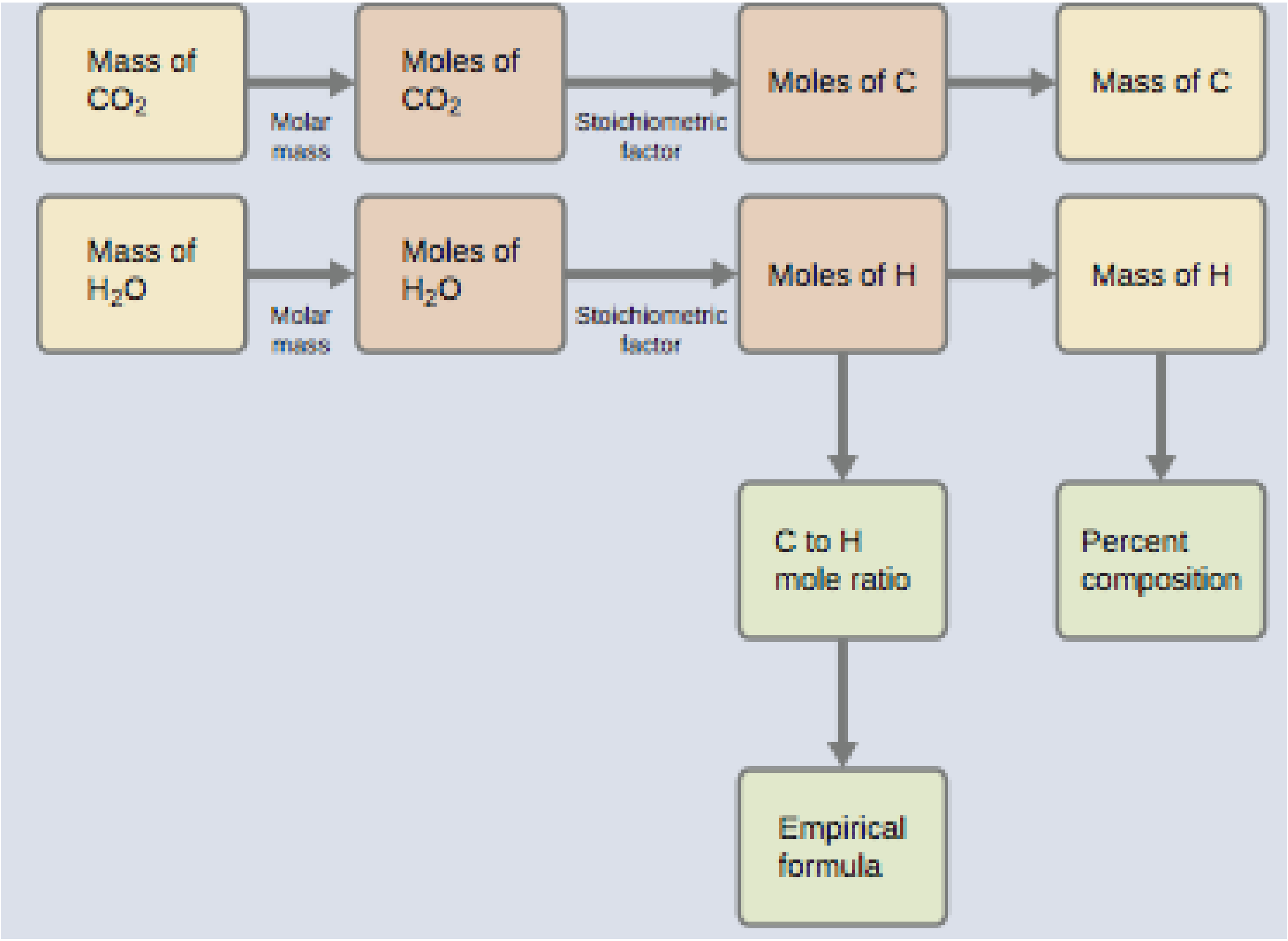
EXAMPLE 4.16

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.

$$C_xH_y(s) \ + \ \text{excess } O_2(g) \ \longrightarrow \ xCO_2(g) \ + \ \frac{y}{2}H_2O(g)$$

What is the empirical formula of polyethylene?

EXAMPLE 4.16


Mass of CO_2
Molar mass
Moles of CO_2
Stoichiometric factor
Moles of C
Mass of C
Mass of H_2O
Molar mass
Moles of H_2O
Stoichiometric factor
Moles of H
Mass of H
C to H mole ratio
Percent composition
Empirical formula

EXAMPLE 4.16

$$0.00394\ \cancel{g}\ CO_2 \times \frac{1\ \cancel{mol}\ CO_2}{44.01\ \cancel{g}} \times \frac{1\ mol\ C}{1\ \cancel{mol}\ CO_2} = 8.95 \times 10^{-5}\ mol\ C$$

$$0.00161\ \cancel{g}\ H_2O \times \frac{1\ \cancel{mol}\ H_2O}{18.02\ \cancel{g}} \times \frac{2\ mol\ H}{1\ \cancel{mol}\ H_2O} = 1.79 \times 10^{-4}\ mol\ H$$

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

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

and the empirical formula for polyethylene is CH_2.

HW problems: 3, 9, 11, 17, 20, 21, 23, 31, 41, 49, 53, 61, 67, 81, 87, 93