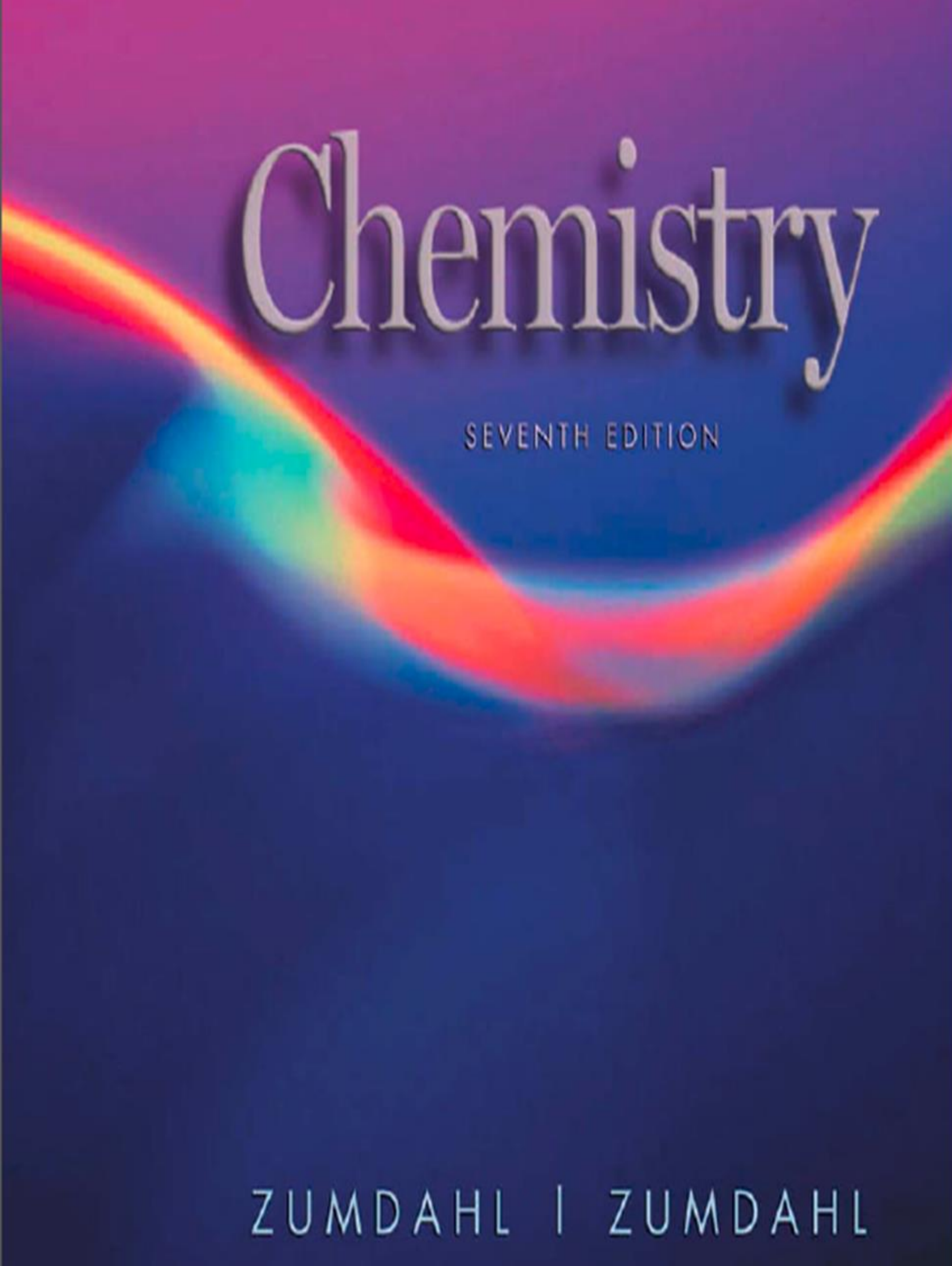


Chapter 3

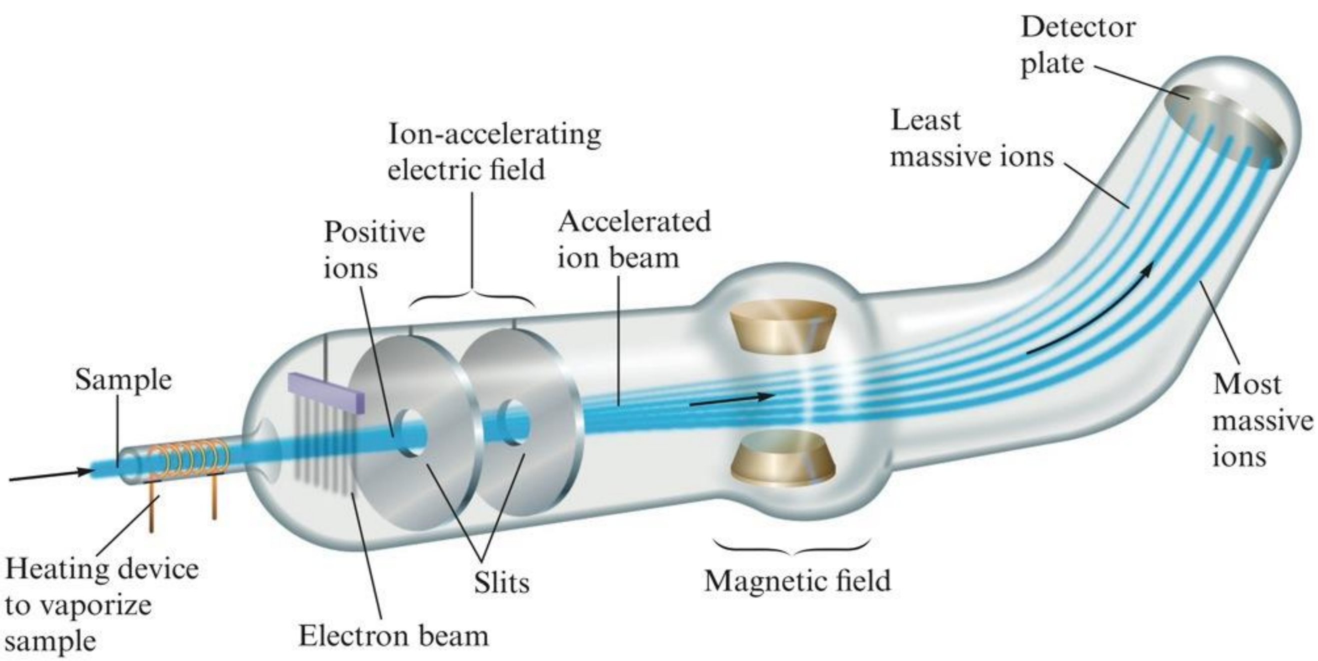
Stoichiometry

Stoichiometry – *The study of quantities of materials consumed and produced in chemical reactions.*

3.2 Atomic Masses

- The most accurate method currently available *for comparing the masses of atoms involves the use of the* **mass spectrometer.**
- **Schematic Diagram of a Mass Spectrometer**

Geoff Tompkinson/Photo Researchers, Inc.



3.3 The Mole (abbreviated mol)

Mole: *The number equal to the number of carbon atoms in exactly 12 grams of pure* ^{12}C

The SI definition of the mole is *the amount of a substance that contains as many entities as there are in exactly 12 g of carbon-12.*

Avogadro's number is $\underline{6.022 \times 10^{23}}$. One mole of anything is 6.022×10^{23} units of that substance.

The mass of 1 mole of an element *is equal to its atomic mass in grams.*

The mole is defined such that a sample of a natural element with a mass equal to the element's atomic mass expressed in grams contains 1 mole of atoms

E x 3.3: Aluminum (Al) is a metal with a high strength-to-mass ratio and a high resistance to corrosion; thus it is often used for structural purposes. Compute both the number of moles of atoms and the number of atoms in a 10.0-g sample of aluminum.

Solution

- The mass of 1 mole (6.022×10^{23} atoms) of aluminum is 26.98 g.

$$\boxed{moles = \frac{mass\ (g)}{molar\ mass}}$$

- $\therefore\ moles = \frac{10\ g}{26.98\ g/mol}$ =0.371 mol Al atoms

$$\boxed{\textit{The number of atoms} = \text{number of moles x } 6.02 \times 10^{23}}$$

- ∴ The number of atoms in 10 g of Al= 0.37 mol x 6.02×10^{23} atoms/mol

  = 2.23×10^{23} atoms

Ex 3.4: A silicon chip used in an integrated circuit of a microcomputer has a mass of 5.68 mg. How many silicon (Si) atoms are present in the chip?

Solution

Convert from milligrams of silicon to grams of silicon, then to moles of silicon, and finally to atoms of silicon:

$$moles = \frac{mass\ (g)}{molar\ mass}$$

- $\therefore moles = \dfrac{5.68 \text{ x}10^{-3} \text{ g}}{28.09 \text{ g/mol}}$ = 2.02×10^{-4} mol Si
- *The number of atoms* = number of moles x 6.02×10^{23}
- The number of atoms in 5.68×10^{-3} g of Si= 2.02×10^{-4} mol x 6.02×10^{23}
- = 1.22×10^{20} atoms

3.4 Molar Mass: *the mass in grams of one mole of the compound.*

Ex 3.6: Juglone, a dye known for centuries, is produced from the husks of black walnuts. It is also a natural herbicide (weed killer) that kills off competitive plants around the black walnut tree but does not affect grass and other noncompetitive plants. The formula for juglone is $\mathbf{C_{10}H_6O_3}$.

a. Calculate the molar mass of juglone.

b. A sample of $\mathbf{1.56 \times 10^{-2}}$ **g** of pure juglone was extracted from black walnut husks. How many moles of juglone does this sample represent?

Solution

a. The molar mass is:

$$
\begin{aligned}
10\text{ C:}\quad & 10 \times 12.01\text{ g} = 120.1\text{ g} \\
6\text{ H:}\quad & 6 \times 1.008\text{ g} = 6.048\text{ g} \\
3\text{ O:}\quad & 3 \times 16.00\text{ g} = \underline{48.00\text{ g}} \\
\text{Mass of 1 mol } C_{10}H_6O_3 & = 174.1\text{ g}
\end{aligned}
$$

b. 1.56 x 10^{-2} g of pure juglone:

$$\color{red}{moles} = \frac{mass\ (g)}{molar\ mass g/mol}$$

a. $= \dfrac{1.56\ x\ 10^{-2}}{174.1\ g/mol}$ = 8.96 x 10^{-5} mol juglone

- **Ex 3.7** Calcium carbonate ($CaCO_3$), also called *calcite,* is the principal mineral found in limestone, marble, chalk, pearls, and the shells of marine animals such as clams

a.Calculate the molar mass of calcium carbonate.

b. A certain sample of calcium carbonate contains 4.86 moles. What is the mass in grams

of this sample? What is the mass of the $CO_3{}^{-2}$ ions present? [Ca=40, C=12,and O=16]

Solution

a. Molar mass of $CaCO_3$= 40 + 12 +48 =100 g/mol

b.The mass in grams of 4.86 moles of this sample

- $moles = \dfrac{mass\ (g)}{molar\ mass g/mol}$ $\quad \therefore mass = moles\ x\ molar\ mass$
- = 4.86 mol x 100 g/mol
- = 486 g $CaCO_3$
- **The mass of 4.86 moles of $CO_3{}^{-2}$ ions is**
- $mass = moles\ x\ molar\ mass\ \ of\ CO_3{}^{-2}\ ions$

= 4.86 mol x 60 g/mol = 292 g $CO_3{}^{-2}$

3.5. Percent Composition of Compounds

Mass percent of an element:

$$\text{mass \%} = \frac{\text{mass of element in compound}}{\text{mass of compound}} \times 100\%$$

For ethanol, which has the formula C_2H_5OH

Molar mass of ethanol = (2x12.01)+(6x1.008)+16=46.07 g/mol

$$\text{Mass percent of C} = \frac{24.02 \text{ g}}{46.07 \text{ g}} \times 100\% = 52.14\%$$

$$\text{Mass percent of H} = \frac{6.048 \text{ g}}{46.07 \text{ g}} \times 100\% = 13.13\%$$

$$\text{Mass percent of O} = \frac{16.00 \text{ g}}{46.07 \text{ g}} \times 100\% = 34.73\%$$

E x 3.9: Carvone is a substance that occurs in two forms having different arrangements of the atoms but the same molecular formula ($C_{10}H_{14}O$) and mass. One type of carvone gives caraway seeds their characteristic smell, and the other type is responsible for the smell of spearmint oil. Compute the mass percent of each element in carvone.

- **The molar mass of $C_{10}H_{14}O$:**

$$\begin{array}{ccccccc} 120.1\text{ g} & + & 14.11\text{ g} & + & 16.00\text{ g} & = & 150.2\text{ g} \\ C_{10} & + & H_{14} & + & O & = & C_{10}H_{14}O \end{array}$$

- **The mass percent of each element:**
  - Mass percent of C $= \dfrac{120.1\text{ g C}}{150.2\text{ g } C_{10}H_{14}O} \times 100\% = 79.96\%$
  - Mass percent of H $= \dfrac{14.11\text{ g H}}{150.2\text{ g } C_{10}H_{14}O} \times 100\% = 9.394\%$
  - Mass percent of O $= \dfrac{16.00\text{ g O}}{150.2\text{ g } C_{10}H_{14}O} \times 100\% = 10.65\%$

Empirical formula

- Empirical formula = CH
    - Simplest whole-number ratio
- Molecular formula = (empirical formula)$_n$
  [n = integer]

Molecular formula

- The formula of the constituent molecules always an integer multiple of the empirical formula
- C_6H_6 = $(CH)_6$
    - Actual formula of the compound

For ionic substances

• The same as the empirical formula

- Any molecule that can be represented as $(CH_5N)_n$, where n is an integer, has the **empirical formula** CH_5N. To specify the exact formula of the molecule involved, the **molecular formula,** we must know the molar mass.

$$
\begin{aligned}
1\,\text{C:}\quad & 1 \times 12.01\ \text{g} = 12.01\ \text{g} \\
5\,\text{H:}\quad & 5 \times 1.008\ \text{g} = 5.040\ \text{g} \\
1\,\text{N:}\quad & 1 \times 14.01\ \text{g} = \underline{14.01\ \text{g}} \\
\text{Formula mass of } CH_5N & = 31.06\ \text{g/mol}
\end{aligned}
$$

PROBLEM-SOLVING STRATEGY

Determining Molecular Formula from Empirical Formula

- Obtain the empirical formula.
- Compute the mass corresponding to the empirical formula.
- Calculate the ratio

$$\frac{\text{Molar mass}}{\text{Empirical formula mass}}$$

- The integer from the previous step represents the number of empirical formula units in one molecule. When the empirical formula subscripts are multiplied by this integer, the molecular formula results. This procedure is summarized by the equation:

$$\text{Molecular formula} = (\text{empirical formula}) \times \frac{\text{molar mass}}{\text{empirical formula mass}}$$

3.8 Chemical Equations

- **Chemical equation** with the **reactants** (here methane and oxygen) *on the left side of an arrow* and the **products** (carbon dioxide and water) *on the right side*

$$\underbrace{CH_4 + O_2}_{\text{Reactants}} \longrightarrow \underbrace{CO_2 + H_2O}_{\text{Products}}$$

- All atoms present in the reactants must be accounted for among the products. In other words, there must be the same number of each type of atom on the product side and on the reactant side of the arrow. Making sure that this rule is obeyed is called **balancing a chemical equation** for a reaction.

$$\underset{1\,C\quad 4\,H}{CH_4} + \underset{4\,O}{2O_2} \longrightarrow \underset{1\,C\quad 2\,O}{CO_2} + \underset{4\,H\quad 2\,O}{2H_2O}$$

Reactants	Products
1 C	1 C
4 H	4 H
4 O	4 O

The Meaning of a Chemical Equation

The chemical equation for a reaction gives two important types of information: the nature of the reactants and products and the relative numbers of each.

$$HCl(aq) + NaHCO_3(s) \longrightarrow CO_2(g) + H_2O(l) + NaCl(aq)$$

3.10 Calculations Involving a Limiting Reactant

- When chemicals are mixed together to undergo a reaction, they are often mixed in **stoichiometric quantities**, that is, in exactly the correct amounts so that all reactants.

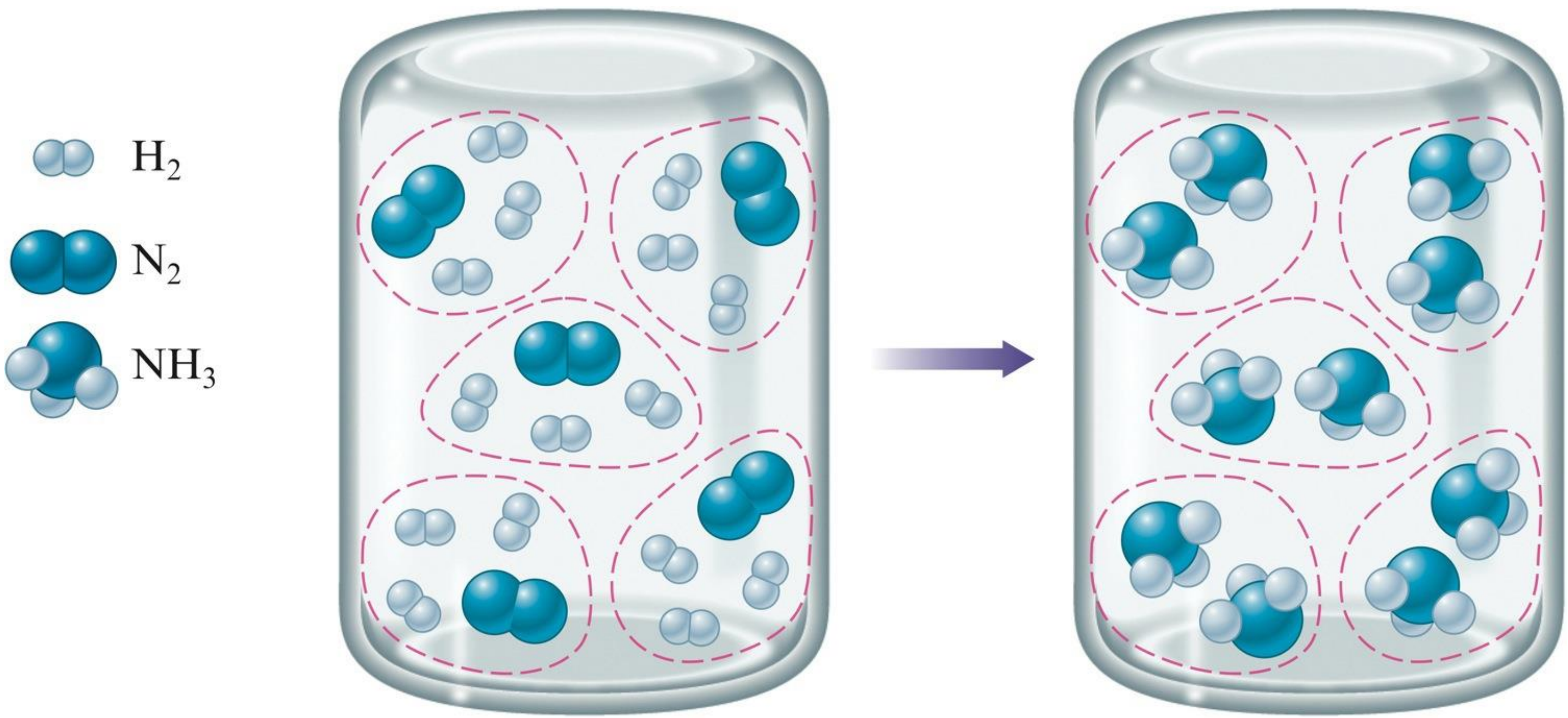
$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

$$CH_4(g) + H_2O(g) \longrightarrow 3H_2(g) + CO(g)$$

- **Limiting reactant** (or **limiting reagent**), which is *the reactant that is consumed first and that therefore limits the amounts of products that can be formed.*

A. The Concept of Limiting Reactants

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

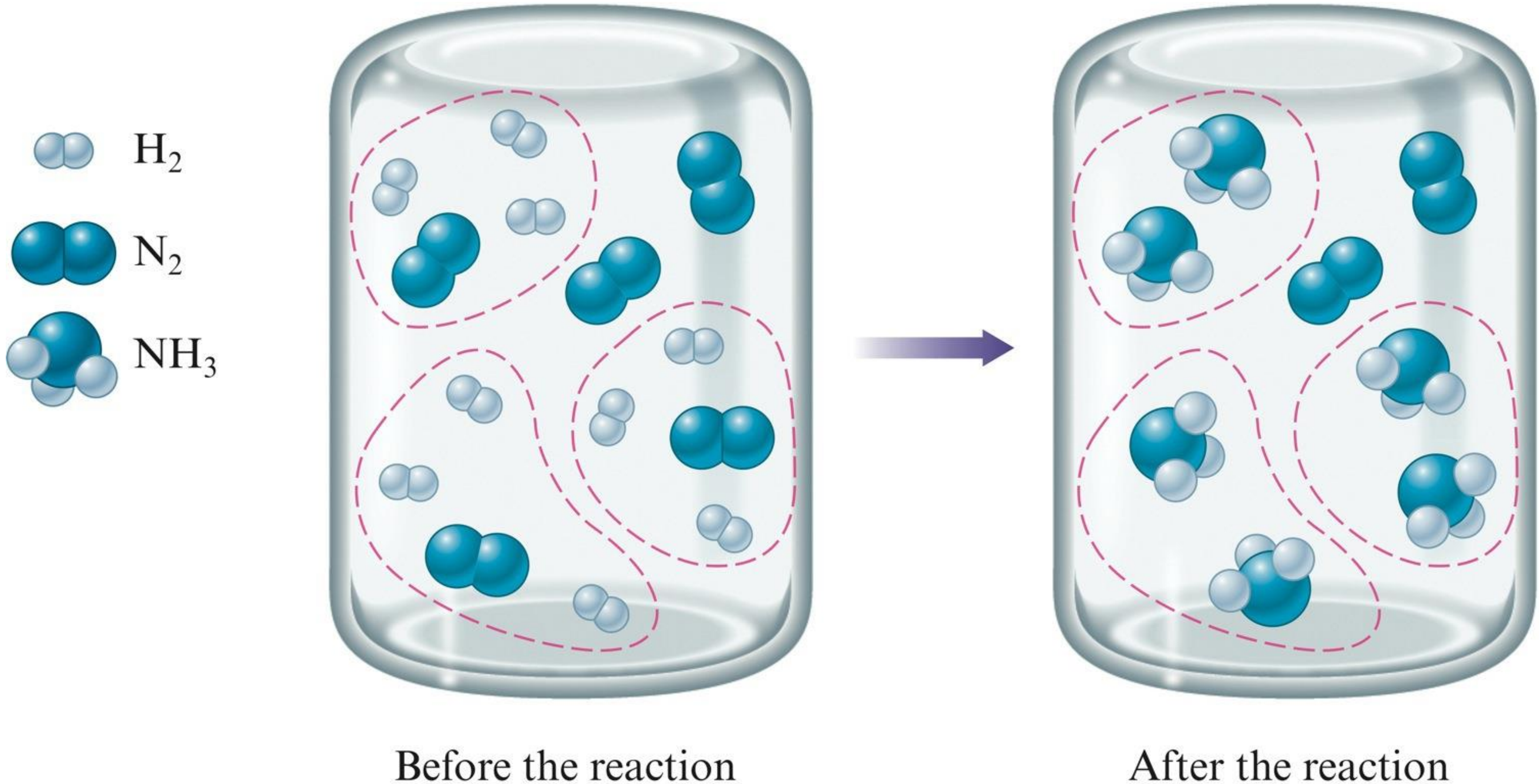


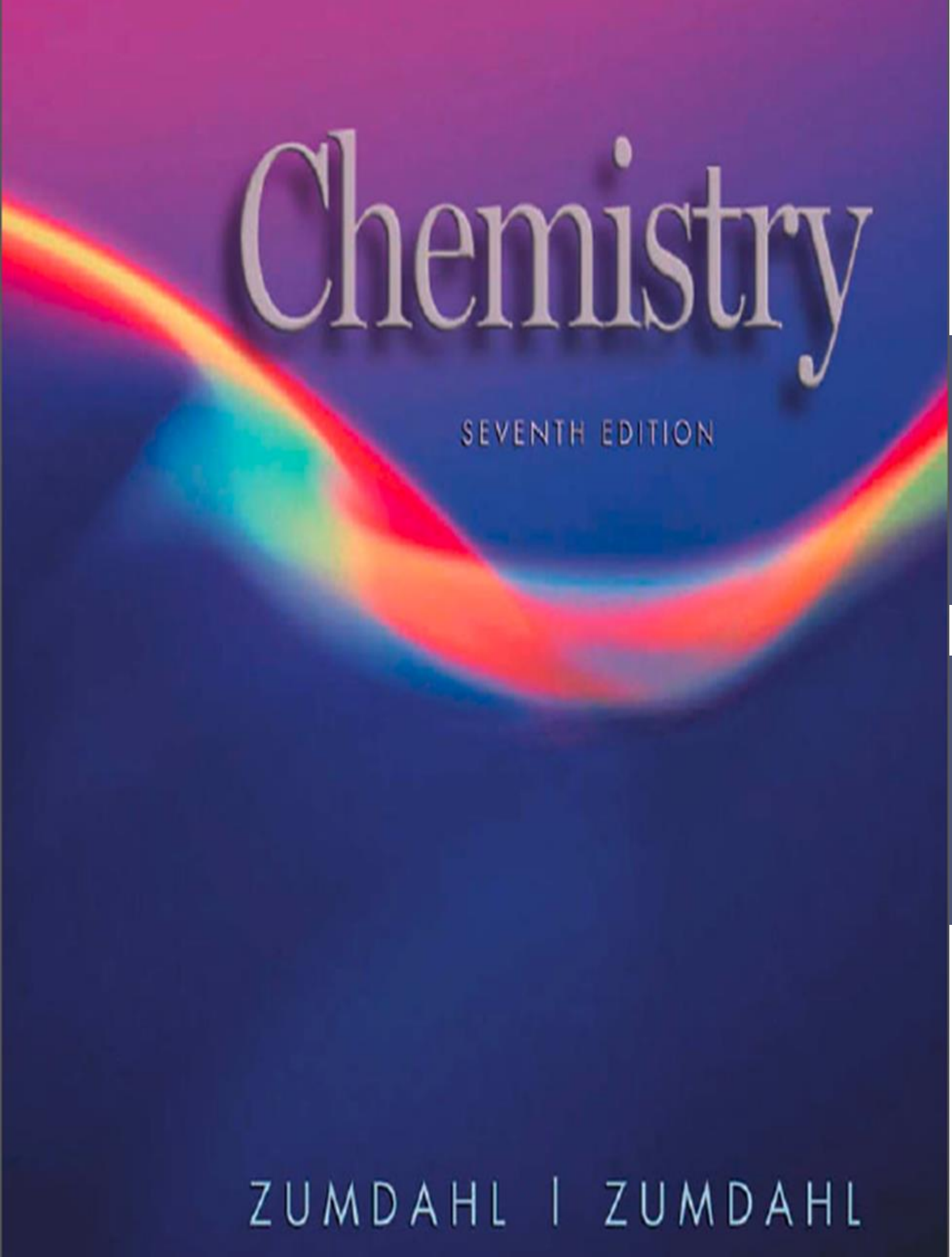
Before the reaction

After the reaction

A. The Concept of Limiting Reactants

- Limiting reactant mixture



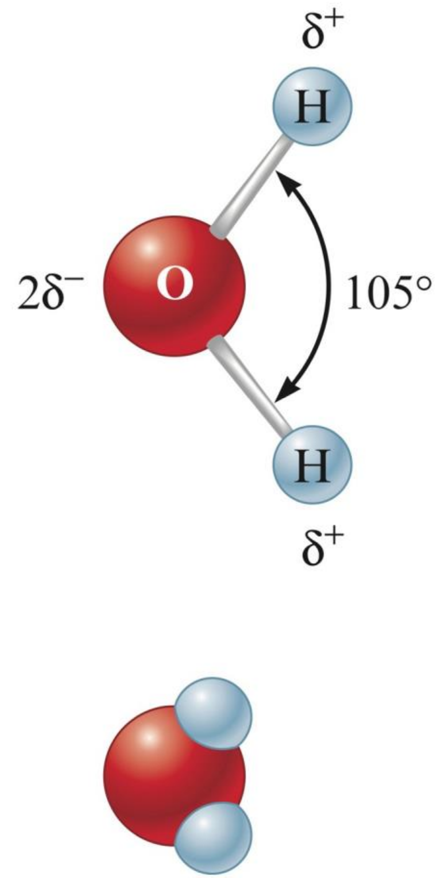


Chapter 4

Types of Chemical Reactions and Solution Stoichiometry

4.1 Water, the Common Solvent

- One of the most important substances on Earth.
- Can dissolve many different substances.
- A polar molecule because of its unequal charge distribution



4.2 The Nature of Aqueous Solutions: Strong and Weak Electrolytes

- Solute – substance being dissolved.
- Solvent – dissolving medium(e.g. liquid water).
- Electrolyte – substance that when dissolved in water produces a solution that can conduct electricity.
- Strong Electrolytes – conduct current very efficiently. Completely ionized in water.(e.g NaCl in H_2O)
- Weak Electrolytes – conduct only a small current. A small degree of ionization in water.(e.g CH_3COOH in H_2O)
- Nonelectrolytes – no current flows

  Dissolves but does not produce any ions.

4.3 The Composition of Solutions

molarity (M), which is defined as *moles of solute per volume of solution in liters*:

$$M = \text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Ex 4.1: Calculate the molarity of a solution prepared by dissolving 11.5 g of solid NaOH in enough water to make 1.50 L of solution.[molar mass of NaOH=40g/mol]

Solution

$$M = \text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Moles of solute = $\frac{\textit{mass of solute in g}}{\textit{molar mass of solute}} = \frac{11.5\ g}{40\ g/mol}$ = 0.288 mol NaOH

- $\text{Molarity} = \frac{\text{mol solute}}{\text{L solution}} = \frac{0.288\ \text{mol NaOH}}{1.50\ \text{L solution}} = 0.192\ M\ \text{NaOH}$

Ex 4.2: Calculate the molarity of a solution prepared by dissolving 1.56 g of gaseous HCl in enough water to make 26.8 mL of solution. .[molar mass of HCl=36.46g/mol]

Solution

$$M = \text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Moles of solute = $\frac{\boldsymbol{mass\ of\ solute\ in\ g}}{\boldsymbol{molar\ mass\ of\ solute}} = \frac{1.56\ g}{36.46\ g/mol}$ = 4.28×10^{-2} mol HCl

Volume of solution in liter = 26.8 mLx10^{-3}L/mL= 2.68 x 10^{-2} L

- $\text{Molarity} = \frac{4.28 \times 10^{-2}\ \text{mol HCl}}{2.68 \times 10^{-2}\ \text{L solution}} = 1.60\ M\ \text{HCl}$

Ex 4.3: Give the concentration of each type of ion in the following solutions:
a. 0.50 M $Co(NO_3)_2$ **b.** 1 M $Fe(ClO_4)_3$

Solution

a. When solid $Co(NO_3)_2$ dissolves, the cobalt(II) cation and the nitrate anions separate:

$$\underset{0.5\ M}{Co(NO_3)_2(s)} \xrightarrow{H_2O} \underset{0.5\ M}{Co^{2+}(aq)} + \underset{2 \times 0.5\ M = 1\ M}{2NO_3^-(aq)}$$

b. When solid $Fe(ClO_4)_3$ dissolves, the iron(III) cation and the perchlorate anions separate:

$$\underset{1\ M}{Fe(ClO_4)_3(s)} \xrightarrow{H_2O} \underset{1\ M}{Fe^{3+}(aq)} + \underset{3 \times 1\ M = 3M}{3ClO_4^-(aq)}$$

Ex 4.4: Calculate the number of moles of Cl^- ions in 1.75 L of 1.0×10^{-3} M $ZnCl_2$.

Solution

When solid $ZnCl_2$ dissolves, it produces ions as follows:

$$ZnCl_2(s) \xrightarrow{H_2O} Zn^{2+}(aq) + 2Cl^-(aq)$$

1×10^{-3}M 1×10^{-3}M 2×10^{-3}M

$$M = \text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

∴Moles of Cl = molarity x liters of solution

$= 2 \times 10^{-3} \times 1.75\text{L} = 3.5 \times 10^{-3}$ mol Cl^-

Ex 4.5: Typical blood serum is about 0.14 M NaCl. What volume of blood contains 1.0 mg NaCl? [molar mass of 58.45 g/mol]

Solution

We must first determine the number of moles represented by 1.0 mg NaCl

Moles of solute $= \dfrac{\text{mass of solute in g}}{\text{molar mass of solute}} = \dfrac{1.0x10^{-3}\ g}{58.45\ g/mol} = 1.7\text{x}10^{-5}$ mol NaCl

$$M = \text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

$$\therefore volume\ (liters\ of\ solution) = \frac{moles\ of\ solute}{molarity}$$

$$V = \frac{1.7\text{x}10{-}5\ \text{mol}}{0.14\ mol/L} = 1.2\ \text{x}\ 10^{-4}\ \text{L}$$

Thus 0.12 mL of blood contains 1.7 x 10^{-5} mol NaCl or 1.0 mg NaCl.

A standard solution

- Is a solution whose concentration is accurately known.

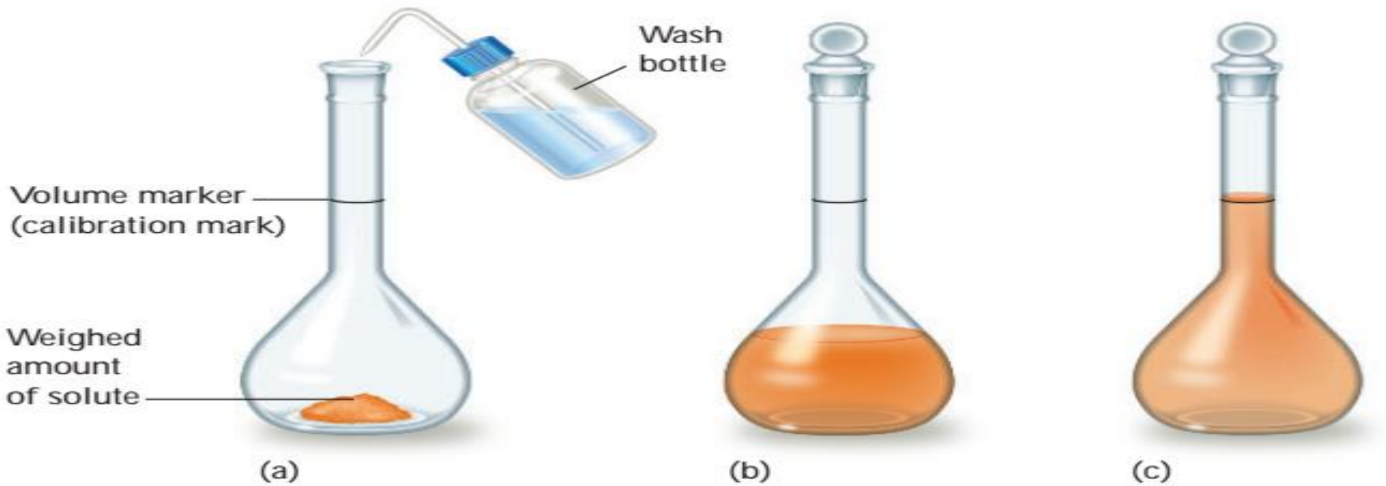


FIGURE 4.10
Steps involved in the preparation of a standard aqueous solution. (a) Put a weighed amount of a substance (the solute) into the volumetric flask, and add a small quantity of water. (b) Dissolve the solid in the water by gently swirling the flask (*with the stopper in place*). (c) Add more water (with gentle swirling) until the level of the solution just reaches the mark etched on the neck of the flask. Then mix the solution thoroughly by inverting the flask several times.

Exercise 4.6

To analyze the alcohol content of a certain wine, a chemist needs 1.00 L of an aqueous 0.200 *M* $K_2Cr_2O_7$ (potassium dichromate) solution. How much solid $K_2Cr_2O_7$ must be weighed out to make this solution? [molar mass of $K_2Cr_2O_7$ = 294.2 g/mol]

Solution:-

$$M = \frac{moles}{volume} \qquad \therefore moles = M \; x \; V$$

$$\therefore moles = 0.200 \; x \; 1.00 = 0.2 \; moles$$

$$mass = moles \; x \; molar \; mass$$

$$\therefore mass = 0.200 \; x \; 294.2 = 58.5 \; g$$

* Thus, to make 1.00 L of 0.200 M $K_2Cr_2O_7$, the chemist must weigh out 58.8 g $K_2Cr_2O_7$, transfer it to a 1.00-L volumetric flask, and add distilled water to the mark on the flask.

Dilution

- The process of adding water to a concentrated or stock solution to achieve the molarity desired for a particular solution.
- Dilution with water does not alter the numbers of moles of solute present.
- Moles of solute before dilution = moles of solute after dilution

$$M_1V_1 = M_2V_2$$

4.4 Types of Chemical Reactions

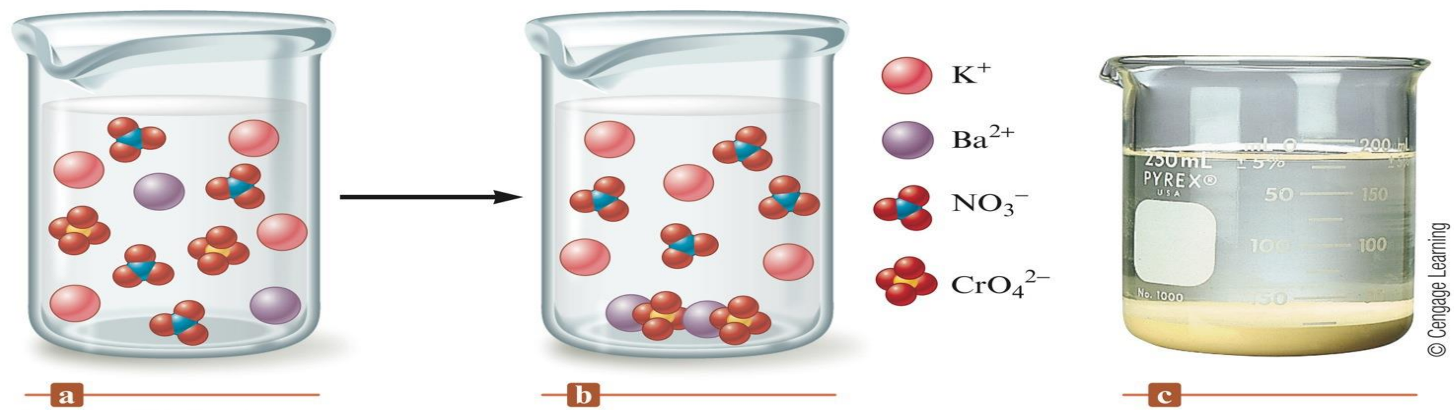
- Precipitation reactions
- Acid–base reactions
- Oxidation–reduction reactions

4.5 Precipitation Reactions

When two solutions are mixed, an insoluble substance(solid) sometimes forms. Such a reaction is called a **precipitation reaction**, and *the solid that forms* is called a **precipitate**

$$K_2CrO_4(aq) + Ba(NO_3)_2(aq) \longrightarrow \text{products}$$

$$Ba^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow BaCrO_4(s)$$



- *Soluble* – solid dissolves in solution; (*aq*) is used in reaction equation.
- *Insoluble* – solid does not dissolve in solution; (*s*) is used in reaction equation.
- *Insoluble* and *slightly soluble* are often used interchangeably.

➢ Simple Rules for Solubility

1. Most nitrate (NO_3^-) salts are soluble.
2. Most alkali metal (group 1A) salts and NH_4^+ are soluble.
3. Most Cl^-, Br^-, and I^- salts are soluble (except Ag^+, Pb^{2+}, Hg_2^{2+}).
4. Most sulfate salts are soluble (except $BaSO_4$, $PbSO_4$, Hg_2SO_4, $CaSO_4$).
5. Most OH^- are only slightly soluble (NaOH, KOH are soluble, $Ba(OH)_2$, $Ca(OH)_2$ are marginally soluble).
6. Most S^{2-}, CO_3^{2-}, CrO_4^{2-}, PO_4^{3-} salts are only slightly soluble, except for those containing the cations in Rule 2.

Exercise 4.8

Using the solubility rules, predict what will happen when the following pairs of solutions are mixed.

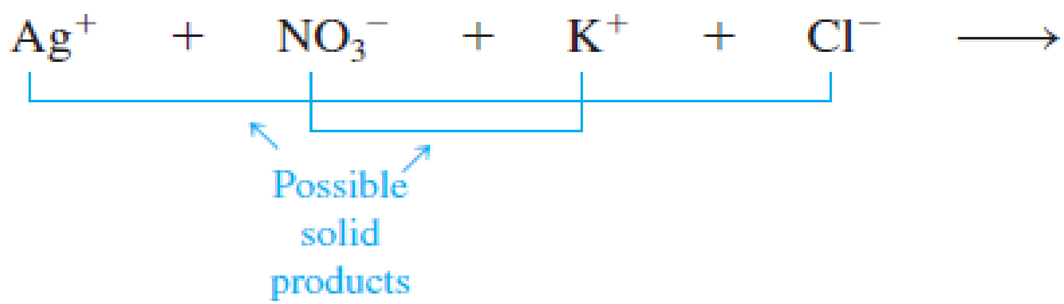
a. $KNO_3(aq)$ and $BaCl_2(aq)$

b. $Na_2SO_4(aq)$ and $Pb(NO_3)_2(aq)$

c. $KOH(aq)$ and $Fe(NO_3)_3(aq)$

Solution:-

a.



$$\boldsymbol{KNO_3(aq) + BaCl_2(aq) \rightarrow KCl(aq) + Ba(NO3)_2(aq)}$$

∴No precipitated formed

- b

$$Na^{+} \quad + \quad SO_4^{\,2-} \quad + \quad Pb^{2+} \quad + \quad NO_3^{\,-} \quad \longrightarrow$$

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

- When these solutions are mixed, $PbSO_4$ will precipitate from the solution

- c

$$3KOH(aq) + Fe(NO_3)_3(aq) \longrightarrow Fe(OH)_3(s) + 3KNO_3(aq)$$

- The solubility rules indicate that both K and NO_3 salts are soluble. However, $Fe(OH)_3$ is only slightly soluble (Rule 5) and hence will precipitate

4.8 Acid–Base Reactions

An acid is *a proton donor.*

A base is *a proton acceptor*

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

Acid–Base Titrations

Volumetric analysis is *a technique for determining the amount of a certain substance by doing a titration.*

Equivalence point or the stoichiometric point. is *the point in the titration where enough titrant has been added to react exactly with the analyte*

An indicator: *a substance added at the beginning of the titration that changes color* at (or very near) the equivalence point.

The endpoint of the titration: *The point where the indicator actually changes color*

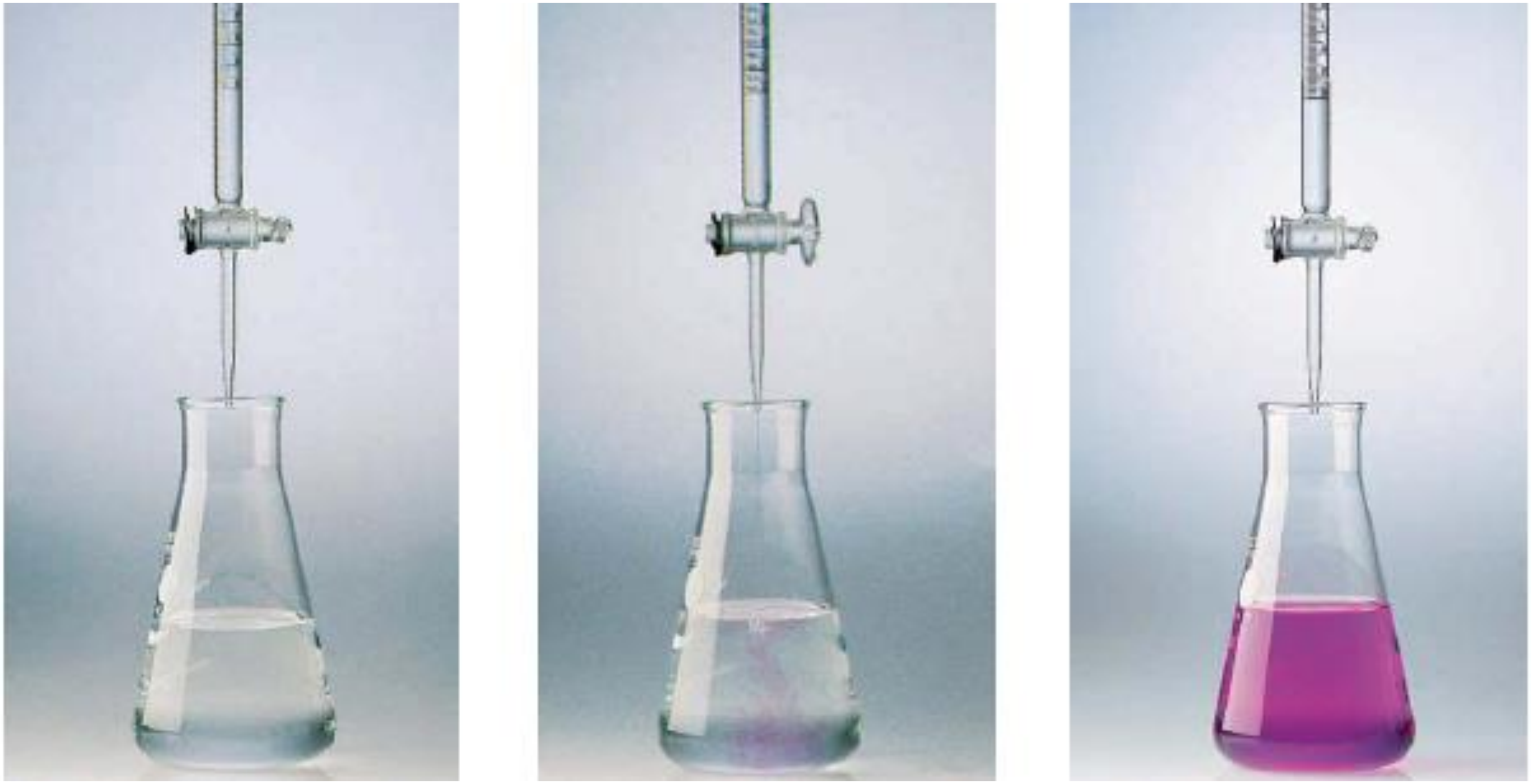


FIGURE 4.18

The titration of an acid with a base. (a) The titrant(the base) is in the buret, and the flask contains the acid solution along with a small amount of indicator. (b) As base is added drop by drop to the acid solution in the flask during the titration, the indicator changes color, but the color disappears on mixing. (c) The stoichiometric (equivalence) point is marked by a permanent indicator color change. The volume of base added is the difference between the final and initial buret readings.

4.9 Oxidation–Reduction Reactions

- Reactions like this one, in which one or more electrons are transferred, are called **oxidation–reduction reactions** or **redox reactions.**

Oxidation States

The oxidation states (or oxidation numbers) of the atoms in a covalent compound as the imaginary charges the atoms would have if the shared electrons were divided equally between identical atoms bonded to each other or, for different atoms, were all assigned to the atom in each bond that has the greater attraction for electrons.

Table 4.2 ▶ Rules for Assigning Oxidation States

The Oxidation State of . . .	Summary	Examples
• An atom in an element is zero	Element: 0	Na(*s*), $O_2(g)$, $O_3(g)$, Hg(*l*)
• A monatomic ion is the same as its charge	Monatomic ion: charge of ion	Na^+, Cl^-
• Fluorine is −1 in its compounds	Fluorine: −1	HF, PF_3
• Oxygen is usually −2 in its compounds Exception: peroxides (containing O_2^{2-}), in which oxygen is −1	Oxygen: −2	H_2O, CO_2
• Hydrogen is +1 in its covalent compounds	Hydrogen: +1	H_2O, HCl, NH_3

Ex 4.16: Assign oxidation states to all atoms in the following.

a. CO_2 **b.** SF_6 **c.** NO_3

Solution

a.

CO_2

↗ ↖

+4 −2 for each oxygen

C + 2O=0, C+2(-2)=0

$\therefore C = +4$

b.

SF_6

↗ ↖

+6 −1 for each fluorine

S + 6F=, S+6(-1)=0

$\therefore$ **S = +6**

c.

NO_3^-

↗ ↖

+5 −2 for each oxygen

N + 3O= -1, N + 3(-2)=-1

$\therefore N = +5$