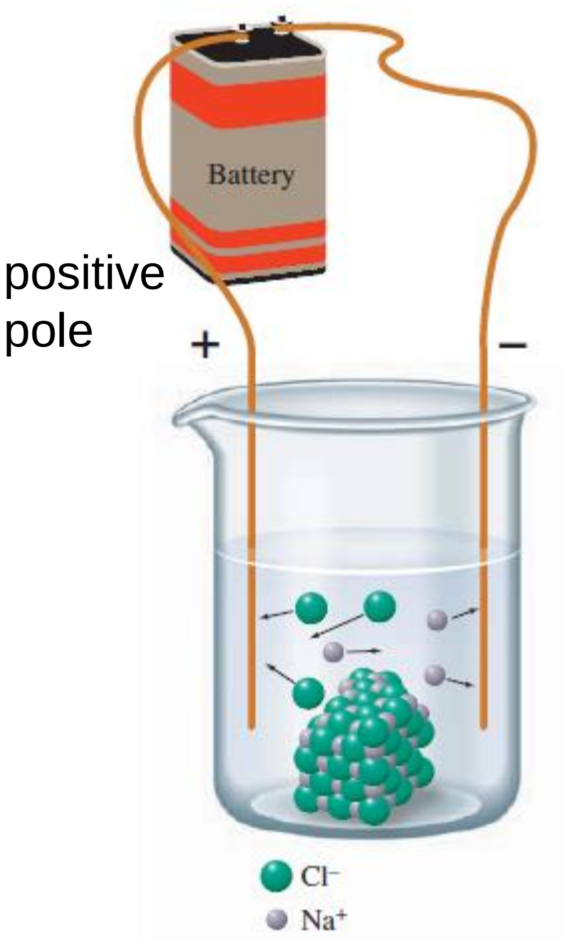
CHAPTER 4
CHEMICAL REACTIONS

Dr. Yuan Dan

4.1 Ionic Theory of Solutions and Solubility Rules

- Ionic theory of solutions



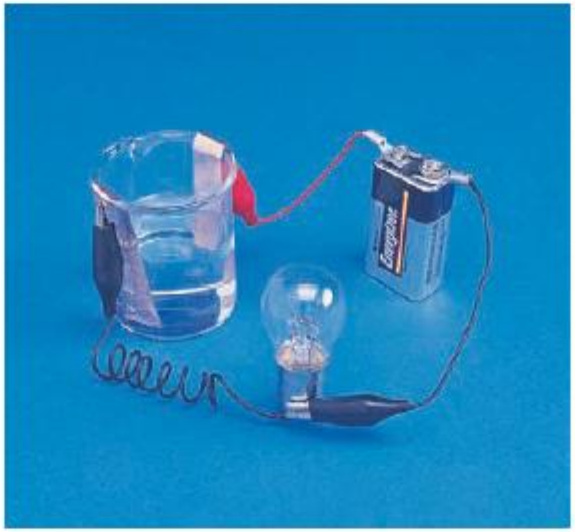
- Pure water is not conducting.
- Pure water has no conductivity.
- An aqueous solution of ions is a conductor.

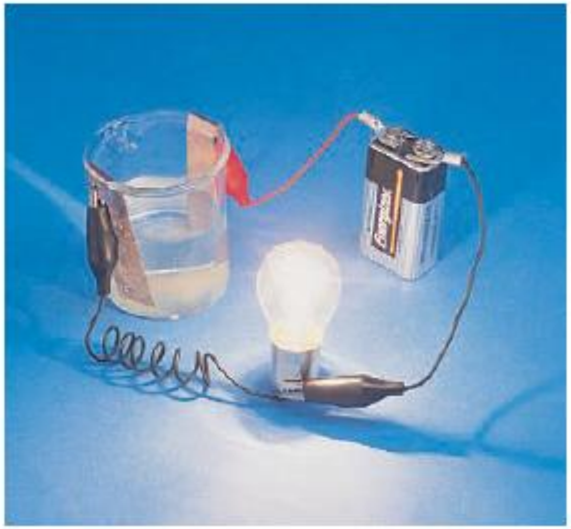
4.1 Ionic Theory of Solutions and Solubility Rules

- Electrolytes: a substance that dissolves in water to give an electrically conducting solution. *i.e.* ionic solids that dissolve in water, some molecular substances (*e.g.* HCl)
- Nonelectrolyte: a substance that dissolves in water to give a nonconducting or very poorly conducting solution. *e.g.* sugar

4.1 Ionic Theory of Solutions and Solubility Rules

- Observing the Electrical Conductivity of a Solution





  - Requires a complete circuit;
  - Tells whether the solution is a good or moderate conductor

4.1 Ionic Theory of Solutions and Solubility Rules

- Strong and Weak Electrolytes
  - Strong electrolyte: an electrolyte that exists in solution almost entirely as ions. *e.g.* NaCl
  - Weak electrolyte: an electrolyte that dissolves in water to give a relatively small percentage of ions. Generally molecular substances.

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

Exception: HCl

double arrow
an reversible reaction

4.1 Ionic Theory of Solutions and Solubility Rules

- Solubility Rules
  - Soluble *vs* insoluble

TABLE 4.1 Solubility Rules for Ionic Compounds

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

4.2 Molecular and Ionic Equations

- Chemical Equations

Molecular equations

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

precipitate

Complete ionic equations (ions level)

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

Net ionic equations (remove spectator ions)

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

P132 Example 4.2

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

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

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

a. $\mathbf{H(\mathit{aq}) + OH(\mathit{aq}) \rightarrow H_2O(\mathit{l})}$

b.

$\mathbf{HC_2H_3O_2(\mathit{aq}) + OH(\mathit{aq}) \rightarrow C_2H_3O_2(\mathit{aq}) + H_2O(\mathit{l})}$

4. Chemical Reactions

- Types of Chemical Reactions

Precipitation reactions

Acid-base reactions (transfer of protons)

Oxidation-reduction reactions (transfer of electrons)

4.3 Precipitation Reactions

- An exchange (or metathesis) reaction is a reaction between compounds that, when written as a molecular equation, appears to involve the exchange of parts between the two reactants.

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

  - Net ionic equation?
  - The reaction will not occur if AgCl is soluble.

P135 Example 4.3

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

a. Aqueous solutions of sodium chloride and iron(II) nitrate are mixed. $\mathbf{NaCl(\mathit{aq}) + Fe(NO_3)_2(\mathit{aq}) \rightarrow NR}$

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

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

4.4 Acid-Base Reactions

- Acid-base indicators:
- litmus (red in acid; blue in base)
- Phenolphthalein (colorless in acid; pink in base)

TABLE 4.2 **Common Acids and Bases**

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

4.4 Acid-Base Reactions

- Definitions of Acid and Base

According to Arrhenius

- An acid is a substance that produces H^+ when it dissolves in water

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

- A base is a substance that produces OH^- when it dissolves in water

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

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

4.4 Acid-Base Reactions

- Definitions of Acid and Base

  According to Brϕnsted and Lowry

  - An acid is the species (molecule or ion) that donates a proton to another species in a proton-transfer reaction
  - A base is the species (molecule or ion) that accepts a proton in a proton-transfer reaction

H^+

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

4.4 Acid-Base Reactions

- Definitions of Acid and Base

  According to Brϕnsted and Lowry

$$H^+$$

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

hydronium ion

4.4 Acid-Base Reactions

- Strong and Weak Acids and Bases

TABLE 4.3

Common Strong Acids and Bases

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

- A strong acid is an acid that ionizes completely in water; it is a strong electrolyte.

- A weak acid is an acid that partly ionizes in water; it is a weak electrolyte.

4.4 Acid-Base Reactions

- Strong and Weak Acids and Bases

TABLE 4.3

Common Strong Acids and Bases

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

- A strong base is a base that is present in aqueous solution entirely as ions, one of which is OH^-; it is a strong electrolyte.
- A weak base is a base that partly ionizes in water; it is a weak electrolyte.

4.4 Acid-Base Reactions

- Neutralization Reactions
  - A reaction of an acid and a base that results in an ionic compound and possibly water

$$2HCl(aq) + Ca(OH)_2(aq) \longrightarrow CaCl_2(aq) + 2H_2O(l)$$

acid base salt

$$HCN(aq) + KOH(aq) \longrightarrow KCN(aq) + \underline{H_2O(l)}$$

acid base salt driving force

  - Net ionic equations?

4.4 Acid-Base Reactions

- Neutralization Reactions

$$\underset{\text{acid}}{H_2SO_4(aq)} + \underset{\text{base}}{2NH_3(aq)} \longrightarrow \underset{\text{salt}}{(NH_4)_2SO_4(aq)}$$

Without formation of H_2O

$$H^+$$

$$H^+(aq) + NH_3(aq) \longrightarrow NH_4^+(aq)$$

P141 Example 4.5

Write the molecular equation and then the net ionic equation for the neutralization of nitrous acid, HNO_2, by sodium hydroxide, NaOH, both in aqueous solution. Use an arrow with H^+ over it to show the proton transfer.

net ionic equation

$$\mathbf{HNO_2}(aq) + \mathbf{OH^-}(aq) \longrightarrow \mathbf{NO_2^-}(aq) + \mathbf{H_2O}(l)$$

H^+

4.4 Acid-Base Reactions

- Acid-Base Reactions with Gas Formation

$$Na_2CO_3(aq) + 2HCl(aq) \longrightarrow 2NaCl(aq) + \underbrace{H_2O(l) + CO_2(g)}_{H_2CO_3(aq)}$$

Carbonic acid

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

P144 Example 4.6

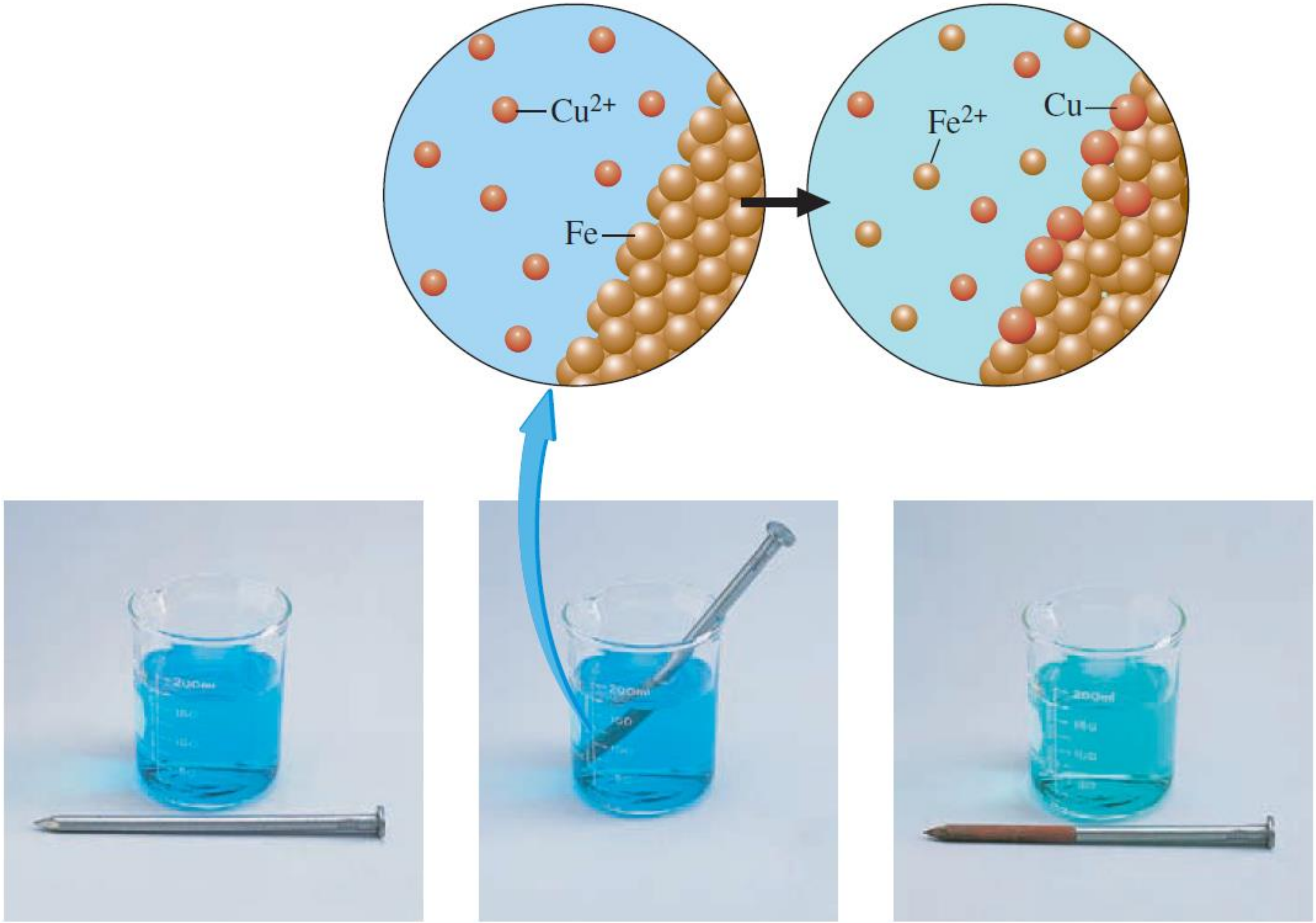
Write the molecular equation and the net ionic equation for the reaction of zinc sulfide with hydrochloric acid.

$$\mathbf{ZnS(\mathit{s}) + 2HCl(\mathit{aq}) \rightarrow ZnCl_2(\mathit{aq}) + H_2S(\mathit{g})}$$

$$\mathbf{ZnS(\mathit{s}) + 2H^+(\mathit{aq}) \rightarrow Zn^{2+}(\mathit{aq}) + H_2S(\mathit{g})}$$

4.5 Oxidation-Reduction Reactions

- involving a transfer of electrons from one species to another



4.5 Oxidation-Reduction Reactions

$$Fe(s) + CuSO_4(aq) \longrightarrow FeSO_4(aq) + Cu(s)$$

$$Fe(s) + Cu^{2+}(aq) \longrightarrow Fe^{2+}(aq) + Cu(s)$$

Electron transfer

- Redox reaction
- A reaction in which electrons are transferred between species or in which atoms change oxidation numbers.

4.5 Oxidation-Reduction Reactions

- Oxidation Number (or Oxidation State)
  - The actual charge of the atom if it exists as a monoatomic ion
  - or a hypothetical charge assigned to the atom in the substance by simple rules.
  - The oxidation number of an atom that exists in a substance as a monoatomic ion equals the charge on that ion.

$$\overset{0}{2Ca(s)} + \overset{0}{O_2(g)} \longrightarrow 2\overset{+2}{Ca}\overset{-2}{O}(s)$$

oxidized reduced

4.5 Oxidation-Reduction Reactions

- Oxidation Number (or Oxidation State)

$$\overset{0}{Ca}(s) + \overset{0}{Cl_2}(g) \longrightarrow \overset{+2}{Ca}\overset{-1}{Cl_2}(s)$$

  - An oxidation-reduction reaction always involves both oxidation and reduction.
  - A redox reaction does NOT always involve oxygen.

4.5 Oxidation-Reduction Reactions

- Oxidation-Number Rules

TABLE 4.5 Rules for Assigning Oxidation Numbers

Rule	Applies to	Statement
1	Elements	The oxidation number of an atom in an element is zero.
2	Monatomic ions	The oxidation number of an atom in a monatomic ion equals the charge on the ion.
3	Oxygen	The oxidation number of oxygen is -2 in most of its compounds. (An exception is O in H_2O_2 and other peroxides, where the oxidation number is -1.)
4	Hydrogen	The oxidation number of hydrogen is $+1$ in most of its compounds. (The oxidation number of hydrogen is -1 in binary compounds with a metal, such as CaH_2.)
5	Halogens	The oxidation number of fluorine is -1 in all of its compounds. Each of the other halogens (Cl, Br, I) has an oxidation number of -1 in binary compounds, except when the other element is another halogen above it in the periodic table or the other element is oxygen.
6	Compounds and ions	The sum of the oxidation numbers of the atoms in a compound is zero. The sum of the oxidation numbers of the atoms in a polyatomic ion equals the charge on the ion.

P147 Example 4.7

To obtain the oxidation number of the chlorine atom in each of the following:

(a) $HClO_4$ (perchloric acid),

(b) ClO_3^- (chlorate ion).

4.5 Oxidation-Reduction Reactions

- Describing Oxidation-Reduction Reactions

Half-reaction:

$$\overset{0}{Fe}(s) \longrightarrow \overset{+2}{Fe}{}^{2+}(aq) + 2e^- \qquad \text{(electrons lost by Fe)}$$

$$\overset{+2}{Cu}{}^{2+}(aq) + 2e^- \longrightarrow \overset{0}{Cu}(s) \qquad \text{(electrons gained by } Cu^{2+}\text{)}$$

4.5 Oxidation-Reduction Reactions

- Describing Oxidation-Reduction Reactions

oxidation

$$\overset{0}{Fe(s)} + \overset{+2}{Cu^{2+}(aq)} \longrightarrow \overset{+2}{Fe^{2+}(aq)} + \overset{0}{Cu(s)}$$

reducing agent

oxidizing agent

reduction

4.5 Oxidation-Reduction Reactions

- Some Common Oxidation-Reduction Reactions

Combination reaction

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

Decomposition reaction

$$2HgO(s) \xrightarrow{\Delta} 2Hg(l) + O_2(g)$$

Displacement reaction

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

Combustion reaction

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

4.5 Oxidation-Reduction Reactions

- Some Common Oxidation-Reduction Reactions

Displacement reaction

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

$$2K(s) + 2H^+(aq) \longrightarrow 2K^+(aq) + H_2(g)$$

TABLE 4.6 Activity Series of the Elements

React vigorously with acidic solutions and water to give H_2	Li, K, Ba, Ca, Na
React with acids to give H_2	Mg, Al, Zn, Cr, Fe, Cd, Co, Ni, Sn, Pb
	H_2
Do not react with acids to give H_2*	Cu, Hg, Ag, Au

4.6 Balancing Simple Oxidation–Reduction Equations

- Half-Reaction Method

$$Zn(s) + Ag^{+}(aq) \longrightarrow Zn^{2+}(aq) + Ag(s)$$

$$Zn \longrightarrow Zn^{2+} + 2e^{-} \qquad \text{(oxidation half-reaction)}$$

$$Ag^{+} + e^{-} \longrightarrow Ag \qquad \text{(reduction half-reaction)}$$

$$1 \times (Zn \longrightarrow Zn^{2+} + 2e^{-})$$

$$2 \times (Ag^{+} + e^{-} \longrightarrow Ag)$$

$$Zn + 2Ag^{+} + \cancel{2e^{-}} \longrightarrow Zn^{2+} + 2Ag + \cancel{2e^{-}}$$

P153 Example 4.8

The combination (oxidation–reduction) reaction of magnesium metal and nitrogen gas:

$$Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$$

Apply the half-reaction method to balance this equation.

$$3Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$$

4.7 Molar Concentration

- Molar Concentration (Molarity, *M*)

$$\text{solution}\begin{cases}\text{solute}\\ \\ \text{solvent}\end{cases}$$

  - Concentration: the quantity of solute in a standard quantity of solution. dilute *vs.* concentrated.
  - Molar concentration (molarity, *M*): the moles of solute dissolved in one liter of solution

$$\text{Molarity } (M) = \frac{\text{moles of solute}}{\text{liters of solution}}$$

4.7 Molar Concentration

- Molar Concentration (Molarity, *M*)

FIGURE 4.18

Preparing a 0.200 *M* $CuSO_4$ solution

Left: 0.0500 mol $CuSO_4{\cdot}5H_2O$ (12.48 g) is weighed on a platform balance. *Center:* The copper(II) sulfate pentahydrate is transferred carefully to the volumetric flask. *Right:* Water is added to bring the solution level to the mark on the neck of the 250-mL volumetric flask. The molarity is 0.0500 mol/0.250 L = 0.200 *M*.

P154 Example 4.9

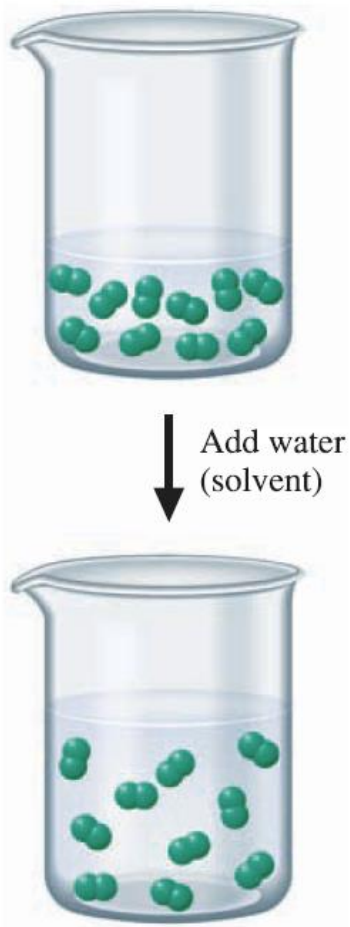
A sample of $NaNO_3$ weighing 0.38 g is placed in a 50.0 mL volumetric flask. The flask is then filled with water to the mark on the neck, dissolving the solid. What is the molarity of the resulting solution?

$$\text{Molarity} = \frac{4.\underline{4}7 \times 10^{-3}\ \text{mol NaNO}_3}{50.0 \times 10^{-3}\ \text{L soln}} = \mathbf{0.089}\ \boldsymbol{M}\ \mathbf{NaNO_3}$$

4.8 Diluting Solutions

- the moles of solute has not changed during the dilution

$$M_i \times V_i = M_f \times V_f$$



P157 Example 4.11

You are given a solution of 14.8 M NH_3. How many milliliters of this solution do you require to give 100.0 mL of 1.00 M NH_3 when diluted？

$$M_iV_i = M_fV_f$$

$$V_i = \frac{M_fV_f}{M_i}$$

$$V_i = \frac{1.00 \cancel{M} \times 100.0 \text{ mL}}{14.8 \cancel{M}} = \mathbf{6.76\ mL}$$

4.9 Gravimetric Analysis

Analytical Chemistry $\begin{cases} \text{Qualitative analysis} \\ \\ \text{Quantitative analysis} \end{cases}$

- Gravimetric analysis: a type of quantitative analysis in which the amount of a species in a material is determined by converting the species to a product that can be isolated completely and weighed.
- Precipitation reactions are frequently used.

4.9 Gravimetric Analysis

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

P159 Example 4.12

A 1.000-L sample of polluted water was analyzed for lead(II) ion, Pb^{2+}, by adding an excess of sodium sulfate to it. The mass of lead(II) sulfate that precipitated was 229.8 mg. What is the mass of lead in a liter of the water? Give the answer as milligrams of lead per liter of solution.

P159 Example 4.12

$$\% \text{ Pb} = \frac{207.2 \text{ g/mol}}{303.3 \text{ g/mol}} \times 100\% = 68.32\%$$

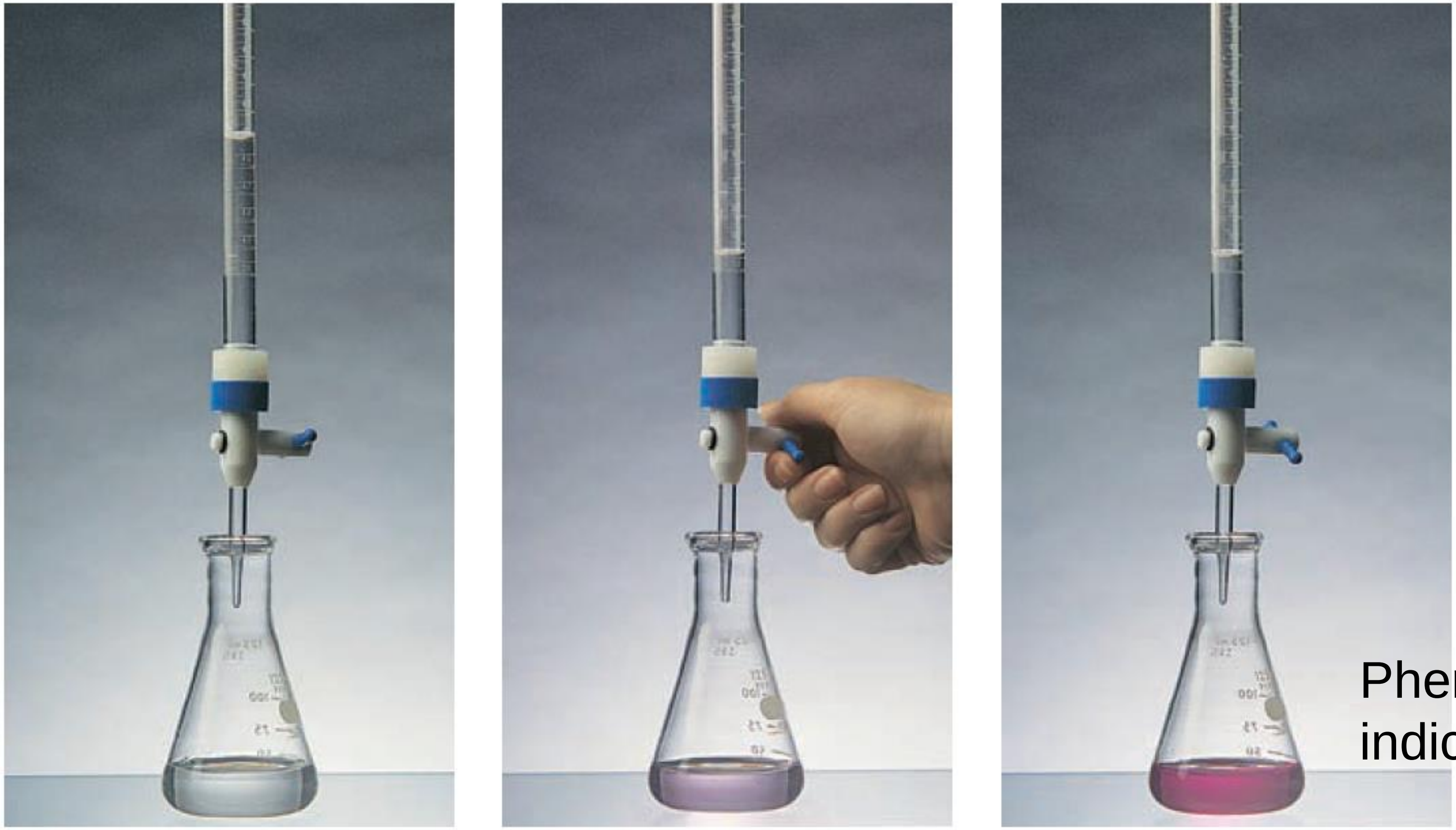
$$\text{Amount Pb in sample} = 229.8 \text{ mg } PbSO_4 \times 0.6832 = 157.0 \text{ mg Pb}$$

4.10 Volumetric Analysis

- Titration: a procedure for determining the amount of substance A by adding a carefully measured volume of a solution with known concentration of B until the reaction of A and B is just complete.
- Volumetric analysis is a method based on titration.

4.10 Volumetric Analysis

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



buret

Phenolphthalein indicator

P161 Example 4.14

A flask contains a solution with an unknown amount of HCl. This solution is titrated with 0.207 M NaOH. It takes 4.47 mL NaOH to complete the reaction. What is the mass of the HCl? 0.0338 g HCl