Analytical Chemistry

College of Pharmacy - Universty of Anbar / First Year 2021 - 2022

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Chapter 1

Review of Elementary Concepts

1.1 Analytical Chemistry

Analytical chemistry deals with methods for the identification of one or more of the components in a sample of matter and the determination of the relative amounts of each. The identification process is called a qualitative analysis while the determination of amount is termed a quantitative analysis. We will deal largely with the latter.

The results of a quantitative analysis are expressed in such relative terms as the percent of the analyte (the substance being determined) in the sample, the parts of analyte per thousand, per million, or even per billion parts of sample, the grams or milliliters of analyte per liter of sample, or the mole fraction of the analyte in the sample.

Most quantitative analytical measurements are preformed on solutions of the sample, therefore the study of analytical chemistry makes use of solution concepts with which the student should have considerable familiarity.

Quantitative analysis is classified into two types of analysis:

1- ***Volumetric analysis***, which concentrates on the exact volume measurement of the solution during titration. The volumetric methods of analysis include acid-base titration, precipitation titration, oxidation-reduction titration, and complex formation titration.

2- ***Gravimetric analysis***, which based upon the measurement of the weight of a substance of known composition that is chemically related to the analyte. There are two types of gravimetric analysis, precipitation methods and volatilization method.

1.2 The Chemical Composition of Solutions

Both aqueous and organic solvents find widespread use in chemical analysis. Nonpolar solvents, such as hydrocarbons and halogenated hydrocarbons, are employed when the analyte itself is nonpolar. Organic solvents, such as alcohols, ketones, and ethers, which are intermediate in polarity and which form hydrogen bonds with solutes, are considerably more useful than their less polar counterparts because they dissolve a larger variety of both organic and inorganic species. Aqueous solvents, including solutions of the common inorganic acids and bases, are perhaps the most widely used of all for analytical purposes. Our discussion will therefore focus on the behavior of solutes in water: reactions in nonaqueous polar media will be considered in less detail.

Solutions are classified according to the nature of particles of the solute to: true solution, suspended solution, and colloidal solution.

1- ***True solution***, in which the solute disappears between the molecules of the solvent, like NaCl in water.

2- ***Suspended solution***, in which the particles of the solute can be distinguished. The solute particles are separated and settled in the bottom of the container, and do not pass through filter paper.

3- ***Colloidal solution***, in which the particles of solute are suspended but do not settle in the bottom of the container, and pass through filter paper.

The presence of the solutes affects the properties of the solvent. They lower the vapour pressure, therefore the temperature increases above its boiling point to reach its usual vapour pressure. The boiling points of the solvent also increase in the presence of the solute, and if the solute is ionic its effect will doubled. Pure water boils at 100^{o}C, but in the presence of the solute it boils at higher temperature. The presence of the solute also lowers the freezing point of the solvent. Pure water freezes at 0^{0}C, while the presence of sugar for example it freezes at -1.86^{o}C.

1.3 Electrolytes and Non-electrolytes

Electrolytes are solutes which ionize in a solvent to produce an electrically conducting media. Strong electrolytes ionize completely whereas weak electrolytes are only partially ionized in the solvents (Table 1.1).

Table 1.1 Classification of electrolytes

Strong electrolytes	Weak electrolytes
1- Inorganic acids HNO_3, $HClO_4$, H_2SO_4, HCl, HI, HBr, $HClO_3$, $HBrO_3$	1- Many inorganic acids such as H_2CO_3, H_3PO_4, H_2S, H_2SO_3, H_3BO_3
2- Alkali and alkaline-earth hydroxides	2- Most organic acids
3- Most salts	3- Ammonia and most organic bases
	4- Halides, cyanides, and thiocyanates of Hg, Zn, and Cd

Non-electrolytes are solutes which do not ionize in their solvents, and therefore the solution does not conduct electricity. Examples are solutions of sugar, and alcohol in water.

1.4 Self-ionization of Solvents

Many common solvents are weak electrolytes which react with themselves to form ions (this process is termed autoprotolysis). Some examples are:

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$2CH_3OH \rightleftharpoons CH_3OH_2^+ + CH_3O^-$$

$$2HCOOH \rightleftharpoons HCOOH_2^+ + HCOO^-$$

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

The positive ion formed by the autoprotolysis of water is called the hydronium ion, the proton being bonded to the parent molecule via a covalent bond involving one of the unshared electron pairs of the oxygen. Chemists use the term H^+ instead of H_3O^+.

1.5 Acids and Bases

The classification of substances as acids or bases was founded upon several characteristic properties that these compounds impart to an aqueous solution. Typical properties include the red and blue colors that are associated with the reaction of acids and bases with litmus, the sharp taste of a dilute acid solution, the bitter taste and slippery feel of a basic solution, and the formation of a salt by interactions of an acid with a base.

**Arrhenius acids and bases*

Arrhenius defined acids as *hydrogen-containing substances that dissociate into hydrogen ions and anions when dissolved in water:*

$HCl \longrightarrow H^+ + Cl^-$

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

and bases *as compounds containing hydroxyl groups that give hydroxides ions and cations upon the same treatment:*

$NaOH \longrightarrow Na^+ + OH^-$

$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$

The relative strengths of acids and bases could be compared by measuring the degree of dissociation in aqueous solution. A completely ionized acid called strong acid, like HCl, and a partially ionized acid called weak acid, like CH_3COOH. The same rule applied for strong and weak bases.

** Bronsted and Lowry acids and bases*

Bronsted and Lowry proposed independently in 1932 that an acid *is any substance that is capable of donating a proton:* a base is *any substance that can accept a proton.* The loss of a proton by an acid gives rise to an entity that is a potential proton acceptor and thus a base; it is called the conjugated base of the parent acid. The reaction between an acid and water is a typical example:

H_2O + acid $\rightleftharpoons$ conjugate base + H_3O^+

It is important to recognize that the acidic character of a substance will be observed only in the presence of a proton acceptor; similarly basic behavior requires the presence of a proton donor. Neutralization in the Bronsted-Lowry sense can be expressed as:

$$\text{acid 1 + base 2} \rightleftharpoons \text{base 1 + acid 2}$$

This process will be spontaneous in the direction that favors production of the weaker acid and base. The dissolving of many solutes can be regarded as neutralizations, with the solvent acting as either a proton donor or acceptor. Thus:

$$\text{acid 1 + base 2} \rightleftharpoons \text{base 1 + acid 2}$$

$$HCl + H_2O \rightleftharpoons Cl^- + H_3O^+$$

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

$$H_2O + NH_3 \rightleftharpoons OH^- + NH_4^+$$

Note that acids can be anionic, cationic, or electrically neutral. It is also seen that water acts as a proton acceptor (a base) with respect to the first three solutes and as a proton donor or acid with respect to the last one; solvents that possess both acidic and basic properties are called amphiprotic.

Acids and bases differ in the extent to which they react with solvents. The reaction between hydrochloric acid and water is essentially complete; this solute is thus classed as acid in the solvent water. Acetic acid and ammonium ion react with water to a lesser degree, with the result that these substance are progressively weaker acids.

The extent of reaction between a solute acid or base and a solvent is also dependent upon the tendency of the latter to donate or accept protons. Thus, for example perchloric, hydrochloric and hydrobromic acids are all classed as strong acid in water. If glacial acetic acid, a poorer proton acceptor is used as the solvent instead, only perchloric acid undergoes complete dissociation and remains a strong acid, the process can be expressed by the equation:

$$HClO_4 + CH_3COOH \rightleftharpoons ClO_4^- + CH_3COOH_2^+$$

Acid 1 base 2 base 1 acid 2

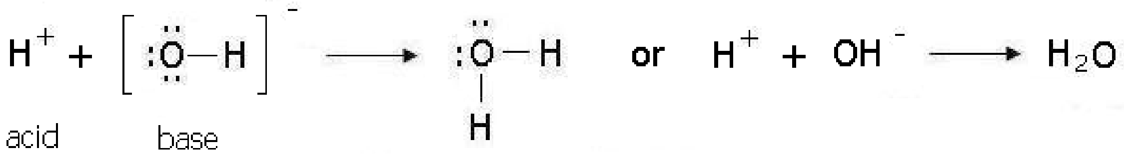
Because they undergo only partial dissociation, hydrochloric acid and hydrobromic acids are weak acids in glacial acetic acid.

A consequence of the Bronsted theory is that the most effective proton donors (that is the strongest acids) give rise, upon loss of their protons to the least effective proton acceptors (the weakest conjugate bases).

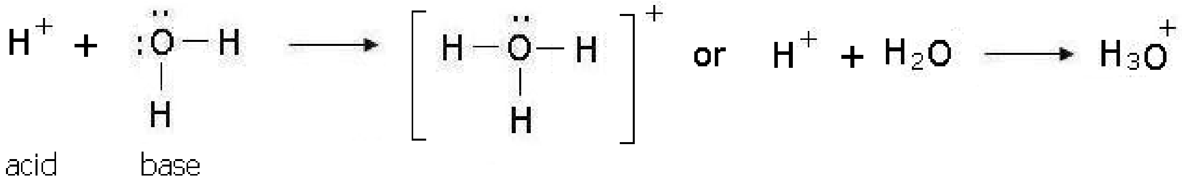
The general solvent theory includes not only species that qualify as acids or bases in the Bronsted-Lowry sense but also extends the concept of acid-base behavior to solvents that do not necessarily contain protons.

**** Lewis acids and bases***

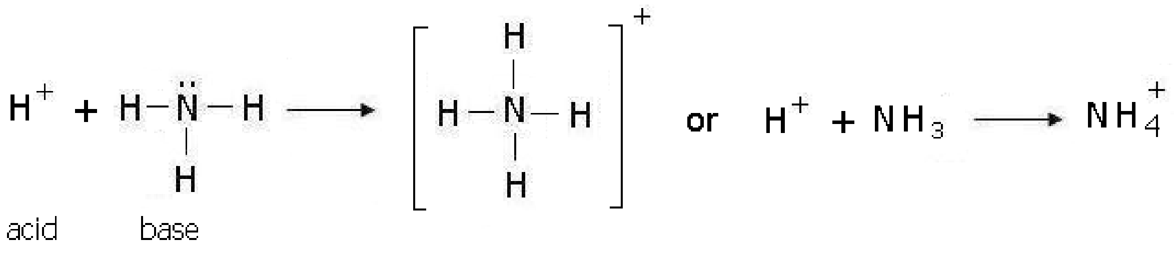
Lewis defined an acid as *an electron-pair acceptor* and a base as *an electron-pair donor*.



$$H^+ + OH^- \longrightarrow H_2O$$



$$H^+ + H_2O \longrightarrow H_3O^+$$



$$H^+ + NH_3 \longrightarrow NH_4^+$$

$$\underset{\text{acid}}{SO_3} + \underset{\text{base}}{O^{2-}} \longrightarrow SO_4^{2-}$$

$$\underset{\text{acid}}{SO_3} + \underset{\text{base}}{OH^-} \longrightarrow HSO_4^-$$

$$\underset{\text{acid}}{AlCl_3} + \underset{\text{base}}{Cl^-} \longrightarrow AlCl_4^-$$

**** Salts***

Salts are formed by the reactions of cations and anions. Some of the salts are anhydrous like NaCl, KCl, $KMnO_4$ and $K_2Cr_2O_7$. Other salts are hydrous such as $CaCl_2.2H_2O$, $CuSO_4.5H_2O$ and $ZnSO_4.7H_2O$. Salts exist in its solid state as ions, therefore, sodium chloride is ionized in its crystalline case into Na^+ which is surrounded by six ions of Cl^-, and each Cl^- is surrounded by six ions of Na^+. These ions are attached to each other by electrostatic strengths. Thus, these salts are completely ionized in solvents of dielectric constant like water.

1.6 Chemical Units of Weight

In the laboratory, the mass of a substance is ordinarily determined in such metric units as the kilogram (kg), the gram (g), the milligram (mg), the microgram (µg), the nanogram (ng), or the picogram (pg).

$$g = 10^3 \text{ mg} = 10^6 \text{ µg} = 10^9 \text{ ng} = 10^{12} \text{ pg} = 10^{-3} \text{ kg}$$

For chemical calculations, however, it is more convenient to employ mass units that express the weight relationship or stoichiometry among reacting species in terms of small whole numbers. The gram formula weight, the gram molecular weight, and the gram equivalent weight are employed in analytical work for this reason. These terms are often shortened to the formula weight, the molecular weight and the equivalent weight.

One molecular weight of a species contains 6.02×10^{23} particles of that species; this quantity is frequently referred to as the ***mole***. In a similar way, the formula weight represents 6.02×10^{23} units of the substance, whether real or not, represented by the chemical formula.

Example 1

A 25.0 g sample of H_2 contains:

$$\frac{25.0\ \text{g}}{2.016\ \text{g/mole}} = 12.4 \text{ moles of } H_2$$

$$12.4 \text{ moles} \times \frac{6.02\times10^{23} \text{ molecules}}{\text{Mole}} = 7.47\times10^{24} \text{ molecules } H_2$$

The same weight of NaCl contains:

$$\frac{25.0\ \text{g}}{58.44\ \text{g/fw}} = \text{o.428 fw NaCl}$$

which corresponds to 0.428 mole Na^+ and 0.428 mole Cl^-

1.7 Equivalent Weight

It is the mass of a given substance which will combine with or displace a fixed quantity of another substance.

For acids:

It is the weight of acid that contains one equivalent of a proton.

$$\text{equivalent weight} = \frac{\text{molar mass}}{\text{no. of equivalent hydrogen ions}}$$

Example 2

Calculate the equivalent weights for the following acids: HCl, H_2SO_4, H_3PO_4. Atomic weights for H = 1, O = 16, Cl = 35.5, S = 32, P = 31.

$$\text{equivalent weight for HCl} = \frac{\text{molar mass}}{\text{no. of equivalent hydrogen ions}}$$

$$= \frac{1 + 35.5}{1} = 36.5 \text{ gram/equivalent}$$

$$\text{for } H_2SO_4 = \frac{(2\times1) + 32 + (16\times4)}{2} = 49$$

$$\text{for } H_3PO_4 = \frac{(3\times1) + 31 + (16\times4)}{3} = 32.67$$

For bases:

It is the weight of base that contains one equivalent of an hydroxide.

$$\text{equivalent weight} = \frac{\text{molar mass}}{\text{no. of equivalent hydroxide ions}}$$

Example 3

Calculate the equivalent weights for the following bases: NaOH, $Ca(OH)_2$, $Al(OH)_3$. Atomic weights for H = 1, O = 16, Na = 23, Ca = 40, Al = 26.98.

$$\text{equivalent weight for NaOH} = \frac{\text{molar mass}}{\text{no. of equivalent hydroxide ions}}$$

$$= \frac{23 + 16 + 1}{1} = 40 \text{ gram/equivalent}$$

$$\text{for } Ca(OH)_2 = \frac{40 + [(16 + 1)]2}{2} = 37$$

$$\text{for } Al(OH)_3 = \frac{26.98 + [(16 + 1)]3}{3} = 25.99$$

For salts:

It is the weight of the salt that contains the equivalent weight of one of its ions.

$$\text{equivalent weight for salt} = \frac{\text{molar mass}}{\text{no. of metal ions} \times \text{oxidation no.}}$$

$$= \frac{\text{molar mass}}{\text{no. of acidic radical ions} \times \text{oxidation no.}}$$

Example 4

Calculate the equivalent weights for the following salts: Na_2O, Na_2CO_3, $Al_2(SO_4)_3$. Atomic weights for O = 16, C = 12, Na = 23, S = 32, Al = 26.98.

$$\text{equivalent weight for } Na_2O = \frac{\text{molar mass}}{\text{no. of metal ions} \times \text{oxidation no.}}$$

$$= \frac{(23 \times 2) + 16}{2 \times 1} = 31 \text{ gram/equivalent}$$

$$\text{for } Na_2CO_3 = \frac{(23 \times 2) + 12 + (16 \times 3)}{2 \times 1} = 53$$

$$\text{for } Al_2(SO_4)_3 = \frac{(26.98 \times 2) + [32 + (16 \times 4)]\ 3}{2 \times 3} = 56.99$$

For salts in precipitation reactions:

The equivalent weight of salts in precipitation reactions is the weight of substance in gram that precipitates quantity equivalent to quantity of 1 gram of hydrogen, or the equivalent weight of another substance in the same reaction.

$$\text{equivalent weight for salt} = \frac{\text{molar mass}}{\text{sum of oxidation numbers of the part participates in precipitate formation}}$$

Example 5

Calculate the equivalent weight for the substances participate in the reaction of AgCl precipitation. Atomic weights for Ag = 108, N = 14, O = 16, Na = 23, Cl = 35.5.

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$$

$$\text{equivalent weight for } AgNO_3 = \frac{\text{molar mass for } AgNO_3}{\text{oxidation number of Ag}}$$

$$= \frac{108 + 14 + (16 \times 3)}{1} = 170 \text{ gram/equivalent}$$

$$\text{equivalent weight for NaCl} = \frac{\text{molar mass for NaCl}}{\text{oxidation number of } Cl^-}$$

$$= \frac{35.5 + 23}{1} = 58.5$$

For oxidation-reduction agents:

The oxidation-reduction reactions involve transfer of electrons from one substance to another.

$$\begin{array}{l}\text{equivalent weight for oxidation} \\ \text{or reduction agent}\end{array} = \frac{\text{molar mass}}{\text{the difference between oxidation numbers}}$$

Example 6

Calculate the equivalent weight for $FeSO_4$ and $KMnO_4$ in the following reaction, which permanganate solution oxidizes iron sulphate. Atomic weights for Fe = 56, S = 32, O = 16, K = 39, Mn = 55.

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

The ferrous oxidized to ferric:

$$Fe^{2+} \longrightarrow Fe^{3+} + e^- \quad \text{(oxidation)}$$

the difference between oxidation numbers = +3 – (+2) = +1

$$\text{equivalent weight for } FeSO_4 = \frac{\text{molar mass for } FeSO_4}{1}$$

$$= \frac{152}{1} = 152 \text{ gram/equivalent}$$

the manganese gain 5 electrons:

$$Mn^{7+} + 5e^- \longrightarrow Mn^{2+} \quad \text{(reduction)}$$

the difference between oxidation numbers = +7 – (+2) = 5

$$\text{equivalent weight for } KMnO_4 = \frac{\text{molar mass for } KMnO_4}{5}$$

$$= \frac{158}{5} = 31.6$$

1.8 Methods Expressing Solutions concentration

1- ***Mass percentage w/w%*** $= \dfrac{\text{g solute}}{\text{g solution}} \times 100$

5% solution of NaCl means that 5 g of NaCl dissolved in 95 g water.

Example 7

Calculate the mass percentage of 200 g solution contains 25 g sodium sulphate.

$$\text{mass percentage w/w\%} = \frac{\text{g solute}}{\text{g solution}} \times 100$$

$$= \frac{25}{200} \times 100 = 12.5\%$$

Example 8

Calculate the mass percentage for a solution prepared by dissolving 15 g of $AgNO_3$ in 100 cm^3 water. The density of water is 1 g/cm^3.

$$\text{weight of solvent} = \text{volume} \times \text{density}$$

$$= 100\ cm^3 \times 1\ g/cm^3$$

$$= 100\ g$$

$$\text{weight of solution} = 100\ g\ \text{solvent} + 15\ g\ \text{solute}$$

$$= 115\ g$$

$$\text{mass percentage w/w\%} = \frac{\text{g solute}}{\text{g solution}} \times 100$$

$$= \frac{15}{115} \times 100$$

$$= 13.04\%$$

2- ***Volume percentage v/v%*** $= \dfrac{\text{ml solute}}{\text{ml solution}} \times 100$

10% solution of alcohol means that 10 ml alcohol is added to enough solvent in order to reach 100 ml volume (addition of 90 ml solvent).

Example 9

10 g of organic solvent (density 1.5 g/cm^3) was added to 90 g water, the density of the solution become 1.1 g/cm^3. Calculate the v/v% and the w/w% concentrations of the organic substance in the solution.

weight of solution = 90 g + 10 g = 100 g

$$\text{mass percentage w/w\%} = \frac{10\text{ g}}{100\text{ g}} \times 100$$

$$= 10\%$$

$$\text{volume of solution} = \frac{\text{weight}}{\text{density}} = \frac{100}{1.1} = 90.90\text{ ml}$$

$$\text{volume of solute} = \frac{\text{weight}}{\text{density}} = \frac{10}{1.5} = 6.67\text{ ml}$$

$$\text{volume percentage v/v\%} = \frac{6.67\text{ ml}}{90.90\text{ ml}} \times 100 = 7.3\%$$

3- ***Mass/volume percentage w/v%*** $= \dfrac{\text{g solute}}{\text{ml solution}} \times 100$

Example 10

Calculate the weight of sodium chloride salt in 500 ml solution of a 0.85 %w/v concentration.

$$\text{w/v\%} = \frac{\text{g solute}}{\text{ml solution}} \times 100$$

$$0.85 = \frac{\text{g}}{500} \times 100 = 4.25\ \text{g}$$

4- ***Parts per million (ppm)*** $= \dfrac{\text{mg solute}}{\text{kg solvent}}$

and there are:

$$\text{Parts per thousand (ppt)} = \frac{\text{g solute}}{\text{kg solvent}}$$

$$\text{Parts per billion (ppb)} = \frac{\text{µg solute}}{\text{kg solvent}}$$

Example 11

A weight of a sample 345 g contains 3 mg Hg, what is the concentration of Hg in the sample in ppm?

$$\text{parts per million (ppm)} = \frac{\text{mg solute}}{\text{kg solvent}}$$

$$\text{(ppm)} = \frac{3}{0.345} = 7.35\ \text{ppm}$$

Example 12

A sample contains 4.8 parts per billion arsine, if the weight of the sample is 525 g, how many μg arsine present in the sample?

$$\text{parts per billion (ppb)} = \frac{\text{μg solute}}{\text{kg solvent}}$$

$$4.8 = \frac{\text{μg arsine}}{0.525}$$

$$\text{μg arsine} = 2.52$$

5- *Molar concentration (M)*

It is the number of molar weights of the solute in 1 liter of solvent.

$$\text{Molarity (M)} = \frac{\text{no. of molar weights of solute}}{\text{volume of solution in liter}}$$

$$\text{no. of molar weights} = \frac{\text{weight of substance in g}}{\text{molar mass}}$$

$$\text{Molar concentration (M)} = \frac{\dfrac{\text{weight of substance in g}}{\text{molar mass}}}{\dfrac{\text{volume of solution in ml}}{1000}}$$

$$= \frac{\text{weight of substance in g} \times 1000}{\text{molecular weight} \times \text{volume of solution in ml}}$$

$$\text{weight of substance} = \text{M} \times \text{molecular weight} \times \frac{\text{volume ml}}{1000}$$

Example 13

Calculate the molar concentration (M) of a solution prepared by dissolving 29.35 g of NaCl in 200 ml water. Atomic weights for Na = 22.99, Cl = 35.45.

$$M = \frac{\text{weight of substance in g} \times 1000}{\text{molecular weight} \times \text{volume of solution in ml}}$$

$$= \frac{29.35 \times 1000}{200 \times 58.44} = 2.5 \text{ molar}$$

Example 14

Calculate the weight of $AgNO_3$ needed to prepare 500 ml solution of a concentration 0.1250 M. Molecular weight of $AgNO_3$ is 169.9.

$$M = \frac{\text{weight of substance in g} \times 1000}{\text{molecular weight} \times \text{volume of solution in ml}}$$

$$\text{weight of } AgNO_3 = M \times \text{molecular weight} \times \frac{\text{volume ml}}{1000}$$

$$\text{weight of } AgNO_3 = 0.125 \times 169.9 \times \frac{500}{1000}$$

$$= 10.62 \text{ g}$$

6- *Normal concentration (N)*

It is the number of equivalent weights of the solute dissolved in liter of the solvent.

$$\text{Normality (N)} = \frac{\text{no. of equivalent weights of solute}}{\text{volume of solution in liter}}$$

$$\text{no. of equivalent weights} = \frac{\text{weight of substance in g}}{\text{equivalent weight}}$$

$$\text{Normal concentration (N)} = \frac{\dfrac{\text{weight of substance in g}}{\text{equivalent weight}}}{\dfrac{\text{volume of solution in ml}}{1000}}$$

$$= \frac{\text{weight of substance in g} \times 1000}{\text{equivalent weight} \times \text{volume of solution in ml}}$$

$$\text{weight of substance} = \text{N} \times \text{equivalent weight} \times \frac{\text{volume ml}}{1000}$$

Example 15

Calculate the number of grams of Na_2SO_4 needed to prepare 200 ml solution of 0.5 N concentration. Equivalent weight of Na_2SO_4 = 71.

$$\text{weight of substance} = \text{N} \times \text{equivalent weight} \times \frac{\text{volume ml}}{1000}$$

$$\text{weight of } Na_2SO_4 \quad = 0.5 \times 71 \times \frac{200}{1000} = 7.1 \text{ g}$$

Example 16

Calculate the molar (M) and normal (N) concentrations for a solution prepared by dissolving 10.6 g from sodium carbonate Na_2CO_3 in a liter of the solution. Molecular weight of Na_2CO_3 = 106.

$$\text{no. of moles of } Na_2SO_4 = \frac{\text{weight}}{\text{molecular weight}}$$

$$= \frac{10.6}{106} = 0.1$$

$$\text{Molarity (M)} = \frac{\text{no. of moles of solute}}{\text{volume of solution in liter}} = \frac{0.1}{1} = 0.1$$

$$\text{no. of equivalent weights of } Na_2SO_4 = \frac{\text{weight}}{\text{equivalent weight}} = \frac{10.6}{106/2}$$

$$= 0.2$$

$$\text{Normality (N)} = \frac{\text{no. of equivalent weights}}{\text{volume of solution in liter}} = \frac{0.2}{1} = 0.2$$

**** Relationship between Molarity (M) and Normality (N)***

$$N = M \times \text{no. of equivalents}$$

Example 17

Calculate the molar (M) concentration of H_3PO_4 solution of 0.250 N, to produce phosphate ion PO_4^{3-}.

$$N = M \times \text{no. of equivalents}$$

$$0.25 = M \times 3$$

$$M = 0.0833 \text{ Molar}$$

7- *Molal concentration (m)*

It is the number of molar masses (moles) of the dissolved substance in 1000 g of the solvent, whatever is the total volume of the solution.

$$\text{Molal concentration (m)} = \frac{\text{weight of substance in g} \times 1000}{\text{molecular weight} \times \text{weight of solvent in g}}$$

Example 18

Calculate the molal (m) concentration m for ethanol in a solution prepared by dissolving 92.2 g ethanol in 500 g water. Molecular weight for ethanol = 46.1.

$$\text{Molal concentration (m)} = \frac{\text{weight of substance in g} \times 1000}{\text{molecular weight} \times \text{weight of solvent in g}}$$

$$= \frac{92.9 \times 1000}{46.1 \times 500} = 4 \text{ m}$$

** The mole fraction*

The mole fraction for solvent is the number of moles of solvent relative to the total number of moles, and the mole fraction for solute is the number of moles of solute relative to the total number of moles. If we multiply the mole fraction by 100 the product is mole percent.

Example 19

Calculate the mole fraction for ethanol C_2H_5OH and water in a solution prepared by dissolving 13.80 g of ethanol in 27 g water. Atomic weight for O=16, C=12, H=1.

$$\text{no. of moles of ethanol} = \frac{\text{weight}}{\text{molecular weight}} = \frac{13.80}{46} = 0.30 \text{ mole}$$

$$\text{no. of moles of water} = \frac{\text{weight}}{\text{molecular weight}} = \frac{27}{18} = 1.50 \text{ mole}$$

the total number of moles = 0.30 + 1.50 = 1.80 mole

$$\text{mole fraction for ethanol} = \frac{\text{moles of ethanol}}{\text{total no. of moles}} = \frac{0.30}{1.80} = 0.167$$

$$\text{mole fraction for water} = \frac{\text{moles of water}}{\text{total no. of moles}} = \frac{1.50}{1.80} = 0.833$$

The highest value for mole fraction is 1, so it is possible to calculate mole fraction for water by determining mole fraction for ethanol:

mole fraction for water = 1 – mole fraction for ethanol

= 1- 0.167 = 0.833

**** Solutions Normality***

The concentration of an acid can be calculated as follow: $N = \frac{D \times \% \times 1000}{\text{equivalent weight} \times 100}$

D = density.

To dilute a solution:

$$\underset{\text{before dilution}}{N_1 \times V_1} = \underset{\text{after dilution}}{N_2 \times V_2}$$

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Chapter 2

The Evaluation of The Reliability of Analytical Data

2.1 Introduction

Every physical measurement is subject to a degree of uncertainty that, at best, can be decreased only to an acceptable level. The determination of the magnitude of this uncertainty is often a difficult task that requires additional effort, ingenuity, and good judgment on the part of the scientist.

A direct relationship exists between the accuracy of an analytical measurement and the time and effort spend.

2.2 The Mean and Median

The mean, arithmetic mean, and average ($\bar{x}$) are synonymous terms for the numerical value obtained by dividing the sum of a set of replicate measurements by the number of individual results in the set.

The median of a set is that result about which all others are equally distributed, half being numerically greater and half being numerically smaller. If the set consists of an odd number of measurements, selection of the median may be made directly; for a set containing an even number of measurements, the average of the central pair is taken.

Example 1

Calculate the mean and the median for 10.06, 10.20, 10.08, 10.10.

$$\text{mean} = (\bar{x}) = \frac{10.06 + 10.20 + 10.08 + 10.10}{4} = 10.11$$

Since the set contain an even number of measurements, the median is the average of the middle pair:

$$\text{median} = \frac{10.08 + 10.10}{2} = 10.09$$

Ideally, the mean and the median should be numerically identical; more often than not, however, this condition is not realized, particularly when the number of measurements in the set is small.

2.3 Precision

The term precision is used to describe the reproducibility of results. It can be defined as the agreement between the numerical values of two or more measurements that have been made in an identical fashion. Several methods exist for expressing the precision of data.

**** Absolute methods for expressing precision***

The deviation from the mean ($x_i - \bar{x}$) is a common method for describing precision and is simply the numerical difference, without regard to sign, between an experimental value and the mean for the set of data that include the value. To illustrate, suppose that a chloride analysis yielded the following results:

Sample	**Percent Chloride**	**Deviation from Mean ($x_i - \bar{x}$)**	**Deviation from Median**
x_1	24.39	0.077	0.03
x_2	24.19	0.123	0.17
x_3	24.36	0.047	0.00
	3[72.94	3[0.247	3[0.20

($\bar{x}$) = 24.313 = 24.31 Avg = 0.082 = 0.08 Avg = 0.067 = 0.07

$w = x_{\max} - x_{\min} = 24.39 - 24.19 = 0.20$

Precision can also be reported in terms of deviation from the median. In the preceding example, deviations from 24.36 would be recorded, as shown in the last column of the table. The spread or range (*w*) in a set of data is the numerical difference between the highest and lowest result and also a measure of precision. In the previous example, the spread would be 0.20% chloride.

Two other measures of precision are the standard deviation and the variance.

**** Relative precision***

We have thus far considered the expression of precision in absolute terms. It is often more convenient, however, to indicate the precision relative to the mean (or the median) in terms of percentage or as parts per thousand. For example, for sample $x_{1,}$

$$\text{relative deviation from mean} = \frac{0.077 \times 100}{24.31} = 0.32 \cong 0.3\%$$

Similarly, the average deviation of the set from the median can be expressed as:

$$\text{relative average deviation from median} = \frac{0.067 \times 1000}{24.36} = 3 \text{ ppt}$$

2.4 Accuracy

The term accuracy denotes the nearness of a measurement to its accepted value and is expressed in terms of error. Accuracy involves a comparison with respect to a true or accepted value; in contrast, precision compares a result with other measurements in the same way.

The accuracy of a measurement is often described in terms of absolute error, which can be defined as:

$$E = x_i - x_t$$

The absolute error E is the difference between the observed value x_i and the accepted value x_t. The value may itself be subjected to considerable uncertainty.

Returning to the previous example, suppose that the accepted value for the percentage of chloride in the sample is 24.36%. The absolute error of the mean is thus 24.31 – 24.36 = - 0.05% chloride; here we ordinarily retain the sign of the error to indicate whether the result is high or low.

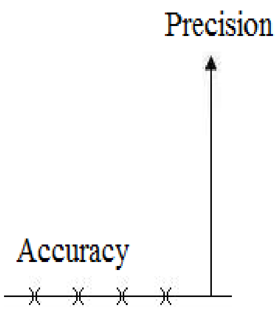
Often a more useful quantity than the absolute error is the relative error expressed as a percentage or in part per thousand of the accepted value. Thus, for the chloride analysis we have been considering,

$$\text{relative error} = \frac{0.05 \times 100}{24.36} = -\,0.21 = 0.2\%$$

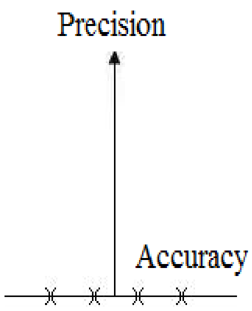
$$\text{relative error} = \frac{0.05 \times 1000}{24.36} = -\,2.1 = -\,2 \text{ ppt}$$

2.5 Precision and Accuracy of Experimental Data

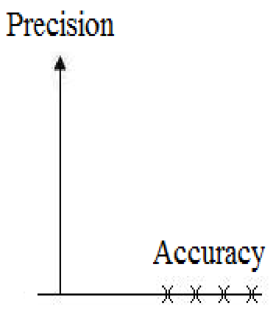
The precision of a measurement is readily determined by replicate experiments performed under identical conditions. Unfortunately, an estimate of the accuracy is not equally available because this quantity requires sure knowledge of the vary information that is being sought, namely, the true value. It is tempting to ascribe a direct relationship between precision and accuracy. The danger of this approach is illustrated in the following figure:



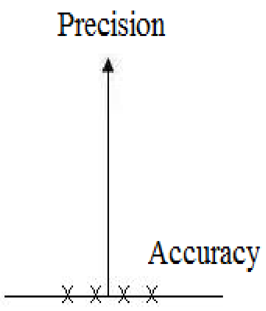
poor precision and
poor accuracy
4



good precision and
poor accuracy
3



poor precision and
good accuracy
2



high precision and
high accuracy
1

2.6 Classification of Errors

The uncertainties that arise in a chemical analysis, and that are responsible for the behavior illustrated in the last figure, may be classified into two broad categories, depending upon their origin.

* ***Determinate errors:*** those that have a definite value which can (in principle, if not in practice) be measured and accounted for.

****Indeterminate errors:*** result from extending a system of measurement to its maximum. These errors cannot be positively identified and do not have a definite measurable value; instead, they fluctuate in a random manner.

2.7 Types of Determinate Errors

1- Personal errors

These errors are the result of the ignorance, carelessness, prejudices, or physical limitations of the experimenter. For example, they may arise from the use of an improper technique in transferring a sample, from disregard of temperature corrections for a measuring device, from over- or underwashing a precipitate, or from transposing numbers when recording an experimental measurement.

2- Instrumental errors

Instrumental errors are attributable to imperfections in the tools with which the analyst works or to the effects of environmental factors upon these tools. For example, volumetric equipment such as burets, pipets, and volumetric flasks frequently deliver or contain volumes slightly different from those indicated by their graduations, particularly when they are employed at temperatures which differ significantly from the temperature at which they were calibrated. Calibration at the proper temperature will obviously eliminate this type of determinate error.

3- Method errors

Determinate errors are often introduced from nonideal chemical behavior of the reagents and reactions upon which the analysis is based. Such sources of nonideality include the slowness of some reactions, the incompleteness of others, the lack of stability of some species, the nonspecificity of most reagents, and the possible occurrence of side reactions which interfere with the measurement process. For example, in a gravimetric analysis the chemist is confronted with the problem of isolating the element to be determined as a solid of the greatest possible purity. If he fails to wash it sufficiently, the precipitate will be contaminated with foreign substances and have a spuriously high weight. On the other hand, sufficient washing to remove these contaminants may cause weighable quantities to be lost owing to the solubility of the precipitate; here, a negative determinate error will result.

2.8 Effect of Determinate Error upon the Results of an Analysis

Determinate errors generally fall into either of two categories, ***constant*** or ***proportional***. The magnitude of a constant error stays essentially the same as the size of the quantity measured is varied. Proportional errors increase or decrease according to the size of the sample taken for analysis.

**** Constant errors.*** For any given analysis, a constant error will become more serious as the size of the quantity measured decreases. This problem is illustrated by the solubility losses that attend the washing of a precipitate.

Example 2

Suppose that directions call for washing of the precipitate with 200 ml of water, and that 0.50 mg is lost in this volume of wash liquid. If 500 mg of precipitate are involved, the relative error due to solubility loss will be:

$$\frac{-(0.50 \times 100)}{500} = -0.1\%$$

Loss of the same quantity from 50 mg of precipitate will result in a relative error of – 1.0%.

The amount of reagent required to bring about the color change in a volumetric analysis is another example of constant error. This volume, usually small, remains the same regardless of the total volume of reagent required. Again, the relative error will be more serious as the total volume decreases. Clearly, one way of minimizing the effect of constant error is to use as large a sample as is consistent with the method at hand.

*** Proportional errors.** Interfering contaminants in the sample, if not eliminated in some manner, will cause an error of the proportional variety. For example, a method widely employed for the analysis of copper involves reaction of the copper(II) ion with potassium iodide; the quantity of iodine produced in the reaction is then measured. Iron(III), if present, will also liberate iodine from potassium iodide. Unless steps are taken to prevent this interference, the analysis will yield erroneously high results for the percentage of copper since the iodine produced will be a measure of the sum of the copper and iron in the sample. The magnitude of this error is fixed by the fraction of iron contamination and will produce the same relative effect regardless of the size of sample taken for analysis. If the sample size is doubled, for example, the amount of iodine librated by both the copper and the iron contaminant will also be doubled.

2.9 Effects of Indeterminate Error

As suggested by its name, indeterminate error arises from uncertainties in a measurement that are unknown and cannot be controlled by the scientist. The effect of such uncertainties is to produce a scatter of results for replicate measurements.

2.10 The standard deviation

The absolute standard deviation, *s*, describes the spread of individual measurements about the mean and is given as:

$$s = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \overline{x})^2}{N - 1}}$$

where x_i is one of *n* individual measurements, and $\overline{x}$ is the mean. Frequently, the relative standard deviation, s_r, is reported. The percent relative standard deviation is obtained by multiplying s_r by 100%.

$$s_r = \frac{s}{\overline{x}}$$

Example 3

Calculate the standard deviation *s* for a subset consisting of the following values of the replicate measurements from the calibration of a 10 ml pipette.

Trial	**Vol. water delivered, ml**
1	9.990
2	9.986
3	9.973
4	9.983
5	9.980

x_i	$\lvert x_i - \bar{x} \rvert$	$(x_i - \bar{x})^2$
9.990	7.6×10^{-3}	57.8×10^{-6}
9.986	3.6×10^{-3}	13.0×10^{-6}
9.973	9.4×10^{-3}	88.4×10^{-6}
9.983	0.6×10^{-3}	0.4×10^{-6}
9.980	2.4×10^{-3}	5.8×10^{-6}
$5 \overline{)\,49.912}$ $9.9824 = \bar{x}$		$\sum_{i=1}^{5} (x_i - \bar{x})^2 = 165.4 \times 10^{-6}$

$$s = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N - 1}} \qquad s = \sqrt{\frac{165.4 \times 10^{-6}}{5 - 1}} = 6.4 \times 10^{-3} = \pm 0.006$$

We can also calculate s_r:

$$s_r = \frac{s}{\bar{x}} \qquad s_r = \frac{0.006}{9.982} = 6.010$$

2.11 The Variance

The variance is another common measure of spread; it is the square of the standard deviation. The standard deviation, rather than the variance, is usually reported because the units for standard deviation are the same as that for the mean value.

To calculate the variance of the last example:

$$\text{Variance} = s^2 = (0.006)^2 = 0.000036$$

2.12 Rejection of Data

When a set of data contains an outlying result that appears to differ excessively from the average (or the median), the decision must be made to retain or to reject it.

Of the numerous statistical criteria suggested to aid in deciding whether to retain or reject a measurement, the Q test is to be preferred. Here the difference between the questionable result and its nearest neighbor is divided by the spread of the entire set. The resulting ratio, Q, is then compared with rejection values that are critical for a particular degree of confidence. Table 2-1 provides critical values of Q at the 90% confidence level. Q = rejection quotient, Q_{crit} = critical Q-value, Q_{exp} = experimental Q-value.

Table 2-1 Critical Values for Rejection Quotient *Q*

Number of Observations	**Q_{crit} (90% confidence) Reject if Q_{exp} >**
2	-
3	0.94
4	0.76
5	0.64
6	0.56
7	0.51
8	0.47
9	0.44
10	0.41

Example 4

The analysis of a calcite sample yielded CaO percentage of 55.95, 56.00, 56.04, 56.08, and 56.23, respectively. The last value appears anomalous; should it be retained or rejected?

The difference between 56.23 and 56.08 is 0.15. The spread (56.23 – 55.95) is 0.28. Thus,

$$Q_{exp} = \frac{0.15}{0.28} = 0.54$$

For five measurements, Q_{crit} is 0.64. Since 0.54 < 0.64, retention is indicated.

Analytical Chemistry

College of Pharmacy - Universty of Anbar / First Year 2021 - 2022

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Chapter 3

Gravimetric Analysis

3.1 Introduction

A gravimetric analysis is based upon the measurement of the weight of a substance of known composition that is chemically related to the analyte. Two types of gravimetric methods exist.

1- *Precipitation methods*: The species to be determined is caused to react chemically with a reagent to yield a product of limited solubility; after filtration and other suitable treatment, the solid residue of known chemical composition is weighed.

2- *Volatilization methods*: The substance to be determined is separated as a gas from the remainder of the sample; here the analysis is based upon the weight of the volatilized substance or upon the weight of the nonvolatile residue. Precipitation methods are more frequently encountered than methods involving volatilization, so we concentrate on the precipitation method.

3.2 Calculation of Results from Gravimetric Data

A gravimetric analysis requires two experimental measurements: specifically, the weight of sample taken and the weight of a product of known composition derived from the sample. Ordinarily these data are converted to a percentage of analyte by a simple mathematical manipulation.

If A is the analyte, we may write:

$$\%\,A = \frac{\text{weight of A}}{\text{weight of sample}} \times 100 \qquad (3\text{-}1)$$

Usually the weight of A is not measured directly. Instead, the species that is actually isolated and weight either contains A or can be chemically related to A. In either case, a *gravimetric factor* is needed to convert the weight of the precipitate to the corresponding weight of A. The properties of this factor are conveniently demonstrated with examples.

Example 1

How many grams of Cl are contained in a precipitate of AgCl that weights 0.204 g? Atomic weights for Ag = 107.86, Cl = 35.45.

We write the equation:

$$AgNO_3 + NaCl \longrightarrow AgCl\downarrow + NaNO_3$$

$$\begin{array}{ccc} Cl^- & \longleftarrow & AgCl \\ 35.45 & \equiv & 143.3 \\ x & & 0.204 \end{array}$$

$$x = 0.204 \times \frac{35.45}{143.3} = 0.0505\ g$$

The value $\frac{35.45}{143.3}$ is called the *gravimetric factor* (GF).

Example 2

To what weight of $AlCl_3$ would 0.204 g of AgCl correspond? Atomic weights for Ag = 107.86, Cl = 35.45, Al = 26.98.

We know that each $AlCl_3$ yield three AgCl. Therefore,

$$\begin{array}{ccc} AlCl_3 & \equiv & 3AgCl \\ 133.3 & \equiv & 3 \times 143.3 \\ x & & 0.204 \end{array}$$

$$x = 0.204 \times \frac{133.3}{3 \times 143.3} = 0.0633\ g$$

Example 3

What weight of Fe_2O_3 can be obtained from 1.63 g of Fe_3O_4? What is the gravimetric factor for this conversation? Atomic weights for Fe = 55.84, O = 16.

It is necessary to assume that all Fe in the Fe_3O_4 is transformed into Fe_2O_3 and ample oxygen is available to accomplish this change. That is:

$$2Fe_3O_4 + [O] = 3Fe_2O_3$$

$$\begin{array}{ccc} 2Fe_3O_4 & \equiv & 3Fe_2O_3 \\ 2 \times 231.5 & \equiv & 3 \times 159.7 \\ 1.63 & & x \end{array}$$

$$x = 1.63 \times \frac{3 \times 159.7}{2 \times 231.5} = 1.687 = 1.69 \text{ g}$$

$$\text{gravimetric factor } \frac{3 \times 159.7}{2 \times 231.5} = 1.035$$

Example 4

A 0.703 g sample of a commercial detergent was ignited at a red heat to destroy the organic matter. The residue was then taken up in hot HCl which converted the P to H_3PO_4. The phosphate was precipitated as $MgNH_4PO_4.6H_2O$ by addition of Mg^{2+} followed by aqueous NH_3. After being filtered and washed, the precipitate was converted to $Mg_2P_2O_7$ by ignition at 1000°C. This residue weighed 0.432 g. Calculate the percent P in the sample. Atomic weights for P = 30.97, Mg = 24.3, O = 16.

$$\begin{array}{ccc} P & \equiv & Mg_2P_2O_7 \\ 30.97 & \equiv & 222.54 \\ x & & 0.432 \end{array}$$

$$x = 0.432 \times \frac{2 \times 30.97}{222.54} = 0.120 \text{ g}$$

$$\% \text{ P} = \frac{0.120}{0.703} \times 100 = 17.1\%$$

Example 5

At elevated temperatures sodium oxalate is converted to sodium carbonate:

$$Na_2C_2O_4 \longrightarrow Na_2CO_3 + CO$$

Ignition of a 1.3906 g sample of impure sodium oxalate yielded a residue weighing 1.1436 g. Calculate the percentage purity of the sample. Atomic weights for Na = 22.98, C = 12, O = 16.

Here it must be assumed that the difference between the initial and final weights represents the carbon monoxide evolved during the ignition; it is this weight loss that forms the basis for the analysis. From the equation for the process, we see that:

1.3906 – 1.1436 = 0.247 weight of CO

$$\begin{array}{ccc} Na_2C_2O_4 & \equiv & CO \\ 133.96 & \equiv & 28 \\ x & & 0.247 \end{array}$$

$$x = 0.247 \times \frac{133.96}{28} = 1.181 \text{ g}$$

$$\% \; Na_2C_2O_4 = \frac{1.181}{1.3906} \times 100 = 84.97\%$$

Example 6

Calculate the percentage of SO_3 in a sample of gypsum of a 0.7560 g weight, produced 0.9875 g of $BaSO_4$ precipitate. Atomic weights for Ba = 137.34, O = 16, S = 32.

$$\begin{array}{ccc} BaSO_4 & \equiv & SO_3 \\ 233.34 & \equiv & 80 \\ 0.9875 & & x \end{array}$$

$$x = 0.9875 \times \frac{80}{233.34} = 0.3385g$$

$$\% \ SO_3 = \frac{0.3385}{0.7560} \times 100 = 44.77\%$$

3.3 Properties of Precipitates and Precipitating Reagents

The ideal precipitating reagent for a gravimetric analysis would react specifically with the analyte to produce a solid that would:

(1) have a sufficiently low solubility so that losses from that source would be negligible.

(2) be readily filtered and washed free of contaminants.

(3) be unreactive and of known composition after drying or, if necessary, ignition.

Few precipitates or reagents possess all these desirable properties; thus, the chemist frequently finds it necessary to perform analyses using a product or a reaction that is far from ideal.

3.4 Filterability and Purity of Precipitates

Both the ease of filtration and the ease of purification are influenced by the particle of the solid phase. The relationship between particle size and ease of filtration is straightforward, coarse precipitates being readily retained by porous media which permit rapid filtration. Finely divided precipitates require dense filters, low filtration rates result. The effect of particle size upon purity of a precipitate is more complex. A decrease in soluble contaminants is found to accompany an increase in particle size.

In considering the purity of precipitates we shall use the term coprecipitation, which describes those processes by which normally soluble components of a solution are carried down during the formation of a precipitate.

3.5 Factors That Determine the Particle Size of Precipitates

Enormous variation is observed in the particle size of precipitates, depending upon their chemical composition and the conditions leading to their formation.

* **Colloidal suspensions**, the individual particles of which are so small as to be invisible to the naked eye (10^{-6} to 10^{-4} mm in diameter). These particles show no tendency to settle out from solution, nor are they retained upon common filtering media.

* **Particles** with dimensions on the order of several tenths of a millimeter. The dispersion of such particles in the liquid phase is called a crystalline suspension. The particles of a crystalline suspension tend to settle out rapidly and are readily filtered.

No sharp discontinuities in physical properties occur as the dimensions of the particles containing the solid phase increase from colloidal to those typical of crystals. Indeed, some precipitates possess characteristics intermediate between these types.

The particle size of the solid that forms is influenced in part by experimental variables as the temperature, the solubility of the precipitate in the medium in which it is being formed, reactant concentrations, and the rate at which reagents are mixed. The particle size is related to a single property called relative supersaturation, where:

$$\text{relative supersaturation} = \frac{Q - S}{S} \qquad (3\text{-}2)$$

Q is the concentration of the solute at any instant, and S is its equilibrium solubility.

During formation of sparingly soluble precipitate, each addition of precipitating reagent causes the solution to be momentarily supersaturated (that is $Q > S$). Under most circumstances, this unstable condition is relived, usually after a brief period, by precipitate formation. Experimental evidence suggests, however, that the particle size of the resulting precipitate varies inversely with the average of relative supersaturation that exists after each addition of reagent. Thus, when $(Q - S) / S$ is large, the precipitate tends to be colloidal; when this parameter is low on the average, a crystalline solid results.

3.6 Mechanics of Precipitate Formation

The effect of relative supersaturation on particle size can be rationalized by postulating two precipitation processes, ***nucleation*** and ***particle growth***. The particle size of a freshly formed precipitate is governed by the extent to which one of these steps predominates over the other.

Nucleation is a process whereby some minimum number of ions or molecules (perhaps as few as four or five) units to form a stable second phase. Further precipitation can occur either by formation of additional nuclei or by deposition of solid on the nuclei that are already present (particle growth). If the former predominates, a precipitate containing a large number of small particles results; if growth predominates, a smaller number of large particles will be produced.

The rate of nucleation is believed to increase enormously with increasing relativesupersaturation. In contrast, the rate of particle growth is only moderately enhanced by high relative supersaturations.

At low relative supersaturations, growth predominates. When the supersaturation is great, the exponential nature of nucleation may cause this process to occur. These effects are illustrated in Figure 3-1.

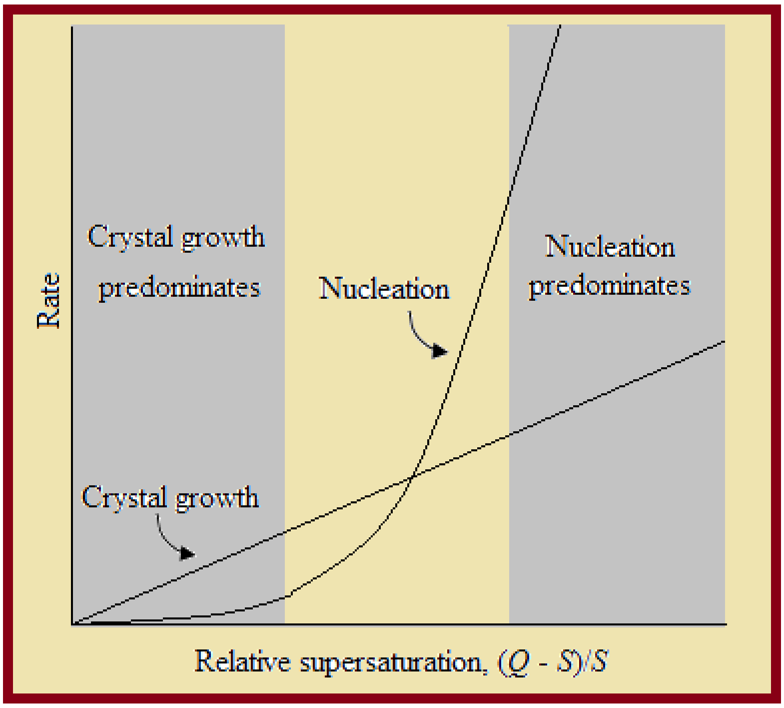


Figure 3-1 Effect of Relative Supersaturation on Precipitation Processes

3.7 Experimental Control of Particle Size

Experimental variables that minimize supersaturation and thus lead to crystalline precipitate include:

Elevated temperature (to increase *S*).

Dilute solutions (to minimize *Q*).

Low addition of the precipitating agent and

Good stirring (also to lower the average value of *Q*).

The particle size of precipitates with solubilities that are pH-dependent can often be enhanced by increasing *S* during precipitation. For example, large, easily filtered crystals of calcium oxalate can be obtained by forming the bulk of the precipitate in a somewhat acidic environment in which the salt is moderately soluble. The precipitation is then completed by slowly adding aqueous ammonia until the pH is sufficiently high for quantitative removal of the calcium oxalate; the additional precipitate produced during this step forms on the solid.

3.8 Colloidal Precipitates

Individual colloidal particles are so small that they are not retained on ordinary filtering media; furthermore, Brownian motion prevents their settling out of solution under the influence of gravity. Fortunately, however, the individual particles of most colloids can be coagulate or agglomerate to give a filterable, noncrystalline mass that rapidly settles out from a solution.

** Coagulation of colloids*

Three experimental measures induce the coagulation process are, **heating**, **stirring**, and **adding an electrolyte to the medium**. To understand the effectiveness of these measures, we need to account for the stability of a colloidal suspension.

The individual particles in a typical colloid bear either a positive or a negative charge as a consequence of ***adsorption*** of cations or anions on their surfaces. Adsorption of ions upon an ionic solid has the normal bonding forces that are responsible for crystal growth. When a silver ion adsorbed on the surface of a silver chloride particle, negative ions are attracted to this site by the same forces that hold chloride ions in the silver chloride lattice. Chloride ions on the surface exert an analogous attraction for cations in the solvent.

Thus, a silver chloride particle will be positively charged in a solution containing an excess of silver ions, and it will have a negative charge in the presence of excess chloride ion for the same reason.

Figure 3-2 illustrates schematically a colloidal silver chloride particle in a solution containing an excess of silver ions. Attached directly to the solid surface are silver ions in the primary adsorption layer. Surrounding the charge particle is a region of solution called the counter-ion layer, within which there exists an excess of negative ions sufficient to balance the charge of the adsorbed positive ions on the particle surface. The counter-ion layer forms as the result of electrostatic forces.

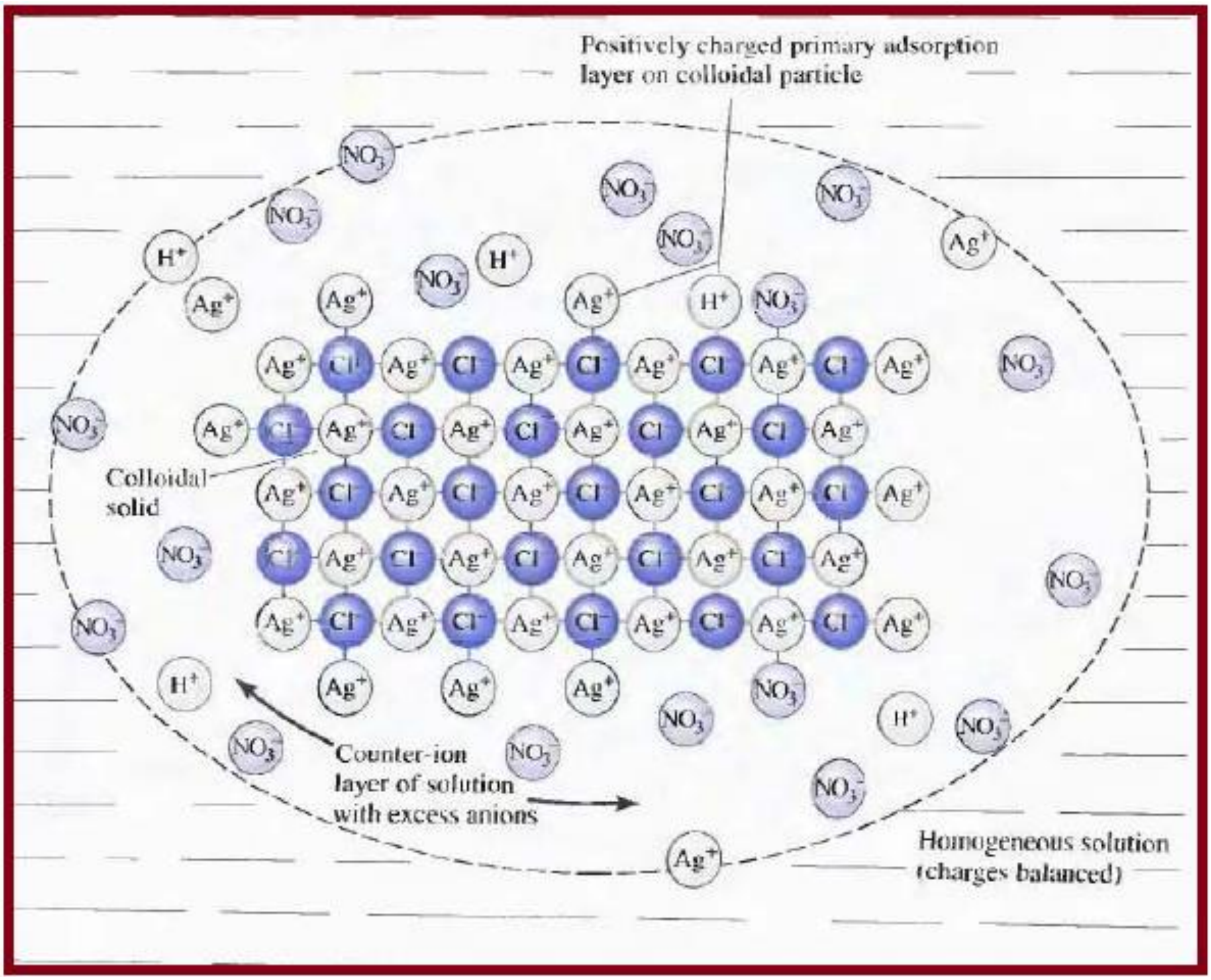


Figure 3-2 Colloidal AgCl Particle Suspended in a Solution of $AgNO_3$

The solution outside the secondary adsorption layer remains electrically neutral. **Coagulation** cannot occur if the secondary adsorption layer is too thick because the individual particles of AgCl are unable to approach one another closely enough. The primarily adsorbed silver ions and the negative counter-ion layer constitute an electric double layer that imparts stability to the colloidal suspension. As colloidal particles approach one another, this double layer exerts an electrostatic repulsive force that prevents particles from colliding and adhering.

Coagulation of a colloidal suspension can often be brought about by a short period of healing, particularly if accompanied by stirring. Heating deceases the number of adhered ions and thus the thickness of the double layer.

An even more effective way to coagulate a colloid is to increase the electrolyte concentration of the solution. If we add a suitable ionic compound to a colloidal suspension, the concentration of counter-ions increases in the vicinity of each particle. As a result, the volume of solution that contains sufficient counter-ions to balance the charge of the primary adsorption layer decreases.

** Coprecipitation in coagulated colloids*

Adsorption is the principal type of coprecipitation that affects coagulated colloids; other types are encountered with crystalline solids.

A coagulated colloid consists of irregularly arranged particles which form a loosely packed, porous mass. Within this mass, large internal surface areas remain in contact with the solvent phase. Adhering to these surfaces will be most of the primarily adsorbed ions which were on the uncoagulated particles. Even though the counter-ion layer surrounding the original colloidal particle is properly considered to be part of the solution, it must be recognized that sufficient counter ions to impart electrical neutrality must accompany the particle through the processes of coagulation and filtration.

** Peptization of colloids*

Peptization is the process whereby a coagulated colloid reverts to its original dispersed state. Peptization occurs when pure water is used to wash such a precipitate. Washing is not particularly effective in dislodging adsorbed contaminants; it does tend to remove the electrolyte responsible for coagulation from the internal liquid in contact with the solid. As the electrolyte is removed, the counter-ion layers increase again in volume. The repulsive forces responsible for the colloidal state are thus reestablished, and particles detach themselves from the coagulated mass. The washing becomes cloudy as the freshly dispersed particles pass through the filter.

This problem is commonly resolved by washing the agglomerated colloid with a solution containing a volatile electrolyte which can subsequently be removed from the solid by heating. For example, silver chloride precipitates are ordinarily washed with dilute nitric acid. The washed precipitate is heavily contaminated by the acid, but no harm results since the nitric acid is removed when the precipitate is dried at 110°C.

3.9 Crystalline Precipitates

In general, crystalline precipitates are more easily handled than coagulated colloids. The particle size of crystalline solids can be improved by keeping the relative supersaturation low during the period in which the precipitate is formed. From Equation 3-2, it is apparent that minimizing Q or maximizing S, or both, will accomplish this purpose.

The use of dilute solutions and the slow addition of precipitating agent with good mixing tend to reduce the supersaturation in the solution. Ordinarily, S can be increased by precipitating from hot solution.

** Types of impurities in crystalline precipitate*

The specific area of crystalline precipitates is relatively small; consequently, coprecipitation by direct adsorption is negligible. However, other forms of coprecipitation, which involve incorporation of contamination within the interior of crystals, may cause serious errors. There are two types of coprecipitation:

1- ***Inclusion:*** Interfering ions whose size and charge are similar to a lattice ion may substitute into the lattice structure by chemical adsorption. The impurities are randomly distributed, in the form of individual ions or molecules, throughout the crystal. Inclusions are difficult to remove since the included material is chemically part of the crystal lattice. The only way to remove included material is through reprecipitation.

2- ***Occlusion*:** It involves a nonhomogeneous distribution of impurities, consisting of numerous ions or molecules of the contaminant, within imperfections in the crystal lattice.

Occlusion occurs when whole droplets of solution containing impurities are trapped and surrounded by a rapidly growing crystal. Because the contaminants are located within the crystal, washing does little to decrease their amount. A lower precipitation rate may significantly lessen the extent of occlusion by providing time for the impurities to escape before they become entrapped. Digestion of the precipitate for as long as several hours is even more effective in eliminating contamination by occlusion.

** Digestion of crystalline precipitates*

The heating of crystalline precipitates (without stirring) for some time after formation frequently yields a product with improved purity and filterability. The improvement in purity results from the solution and recrystallization that occur continuously and at an enhanced rate at elevated temperatures. During these processes, many pockets of imperfection become exposed to the solution; the contaminant is thus able to escape from the solid and more perfect crystals result.

Solution and recrystallization during digestion are probably responsible for the improvement in filterability as well. Bridging between adjacent particles occur to yield larger crystalline aggregates which are more easily filtered.

3.10 Direction of Coprecipitation Errors

Coprecipitated impurities may cause the results of an analysis to be either too high or too low. If the contaminant is not a compound of the ion being determined, positive errors will always result. Thus, a positive error will be observed when colloidal silver chloride adsorbs silver nitrate during a chloride analysis. On the other hand, where the contaminant contains the ion being determined, either positive or negative errors may be observed. In the determination of barium ions by precipitation as barium sulfate, for example, occlusion of barium salts occurs. If the occluded contaminant is barium nitrate, a positive error will be observed, since this compound has a greater formula weigh than the barium sulfate. If barium chloride were the contaminant, however, a negative error would arise because its formula weight is less than that of the sulfate salt.

3.11 Drying and Ignition of Precipitates

After separating the precipitate from its supernatant solution the precipitate is dried to remove any residual traces of rinse solution and any volatile impurities. The temperature and method of drying depend on the method of filtration, and the precipitate’s desired chemical form. A temperature of 110 °C is usually sufficient when removing water and other easily volatilized impurities. A conventional laboratory oven is sufficient for this purpose. The temperature required to produce a suitable product varies from precipitate to precipitate.

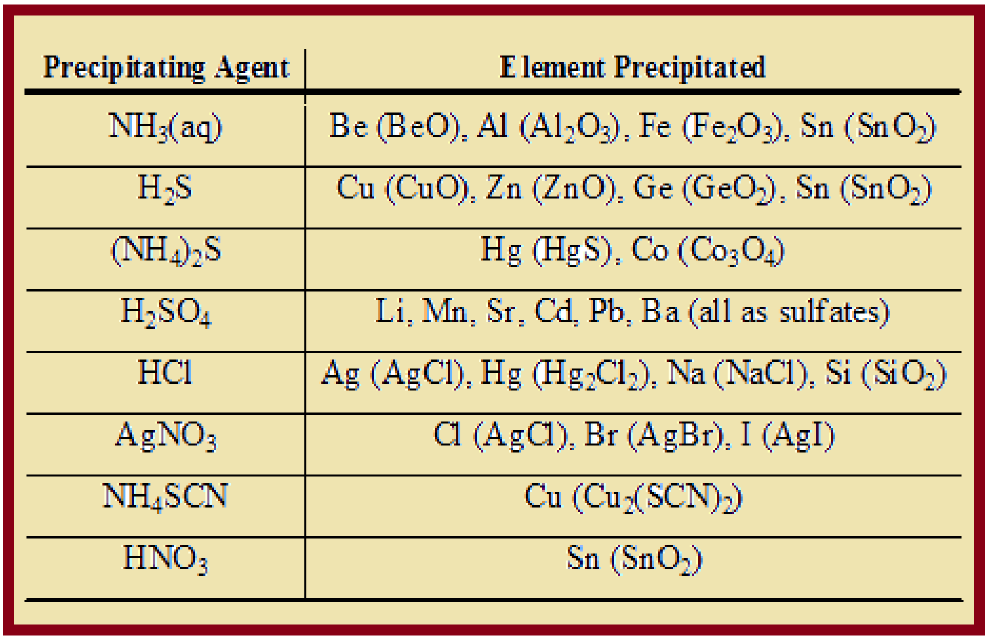
3.12 Applications of Gravimetric Method

**** Inorganic precipitating agents***

Table 3-1 lists some of the common inorganic precipitating agents. These reagents typically cause formation of a slightly soluble salt or a hydrous oxide.

The weighing form is either the salts itself or else an oxide. The lack of specificity of most inorganic reagent is clear from the many entries in the table.

Table 3-1 Some Inorganic Precipitating Agents

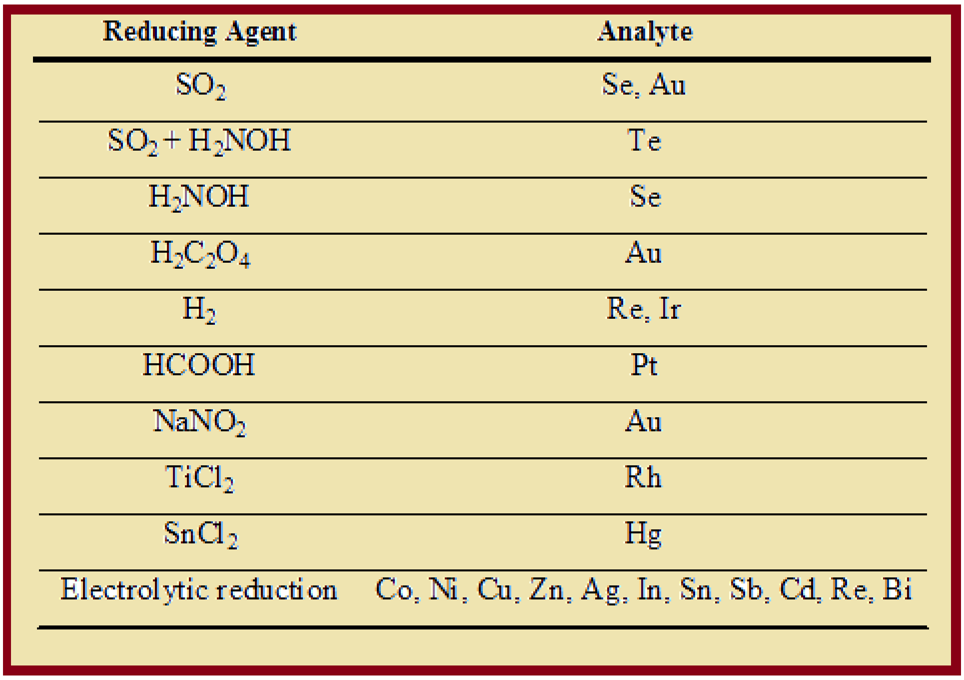


Precipitating Agent	Element Precipitated
NH_3(aq)	Be (BeO), Al (Al_2O_3), Fe (Fe_2O_3), Sn (SnO_2)
H_2S	Cu (CuO), Zn (ZnO), Ge (GeO_2), Sn (SnO_2)
$(NH_4)_2S$	Hg (HgS), Co (Co_3O_4)
H_2SO_4	Li, Mn, Sr, Cd, Pb, Ba (all as sulfates)
HCl	Ag (AgCl), Hg (Hg_2Cl_2), Na (NaCl), Si (SiO_2)
$AgNO_3$	Cl (AgCl), Br (AgBr), I (AgI)
NH_4SCN	Cu ($Cu_2(SCN)_2$)
HNO_3	Sn (SnO_2)

**** Reducing reagents***

Table 3-2 lists several reagents that convert the analyte to its elemental form for weighing.

Table 3-2 Some Reducing Reagents Employed in Gravimetric Methods



Reducing Agent	Analyte
SO_2	Se, Au
$SO_2 + H_2NOH$	Te
H_2NOH	Se
$H_2C_2O_4$	Au
H_2	Re, Ir
HCOOH	Pt
$NaNO_2$	Au
$TiCl_2$	Rh
$SnCl_2$	Hg
Electrolytic reduction	Co, Ni, Cu, Zn, Ag, In, Sn, Sb, Cd, Re, Bi

**** Organic precipitating agents***

A number of organic reagents have been developed for the gravimetric analysis of inorganic species. In general, these reagents tend to be more selective in their reactions than many of the inorganic reagents listed in Table 3.1.

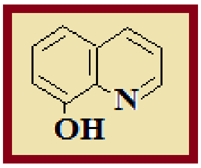
Two types of organic reagents are encountered. One forms slightly soluble nonionic complexes called coordination compounds. The other forms products in which the bonding between the inorganic species and the reagent is largely ionic.

Organic reagents which yield sparingly soluble coordination compounds typically contain at least two functional groups, each of which is capable of bonding with the cation by donation of a pair of electrons. The functional groups are located in the molecule in such a way that a five- or six-membered ring results from reaction.

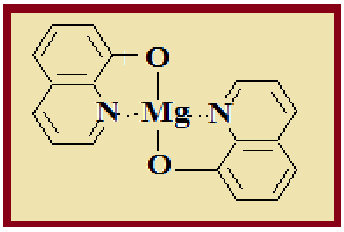
Coordination compounds which form complexes of this type are called chelating agents; their products with a cation are termed chelates.

Neutral coordination compounds are relatively nonpolar; as a consequence, their solubilities are low in water but high in organic liquids. Chelates usually possess low densities and are often intensely colored. Because they are not wetted by water, coordination compounds are readily freed of moisture at low temperatures. At the same time, however, their hydrophobic nature endows these precipitates with the annoying tendency to creep up the sides of the filtering medium during the washing operation; physical loss of solid may result unless care is taken. Three examples of coordination reagents are considered here.

8-Hydroxyquinoline. Approximately two dozen cations form sparingly soluble coordination compounds with 8-hydroxyquinoline, which is also known as oxine.

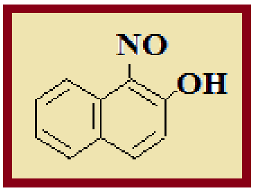


Typical of these is the product with magnesium:



The solubilities of metal oxinates vary widely from cation to cation and, moreover, are pH dependent because proton formation always accompanies the chelation reaction. Therefore, by control of pH, a considerable degree of selectivity can be imparted to 8-hydroxyquinoline.

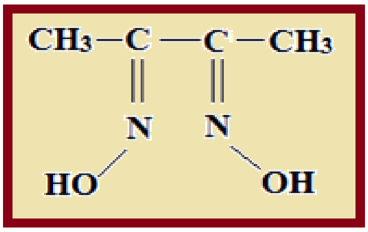
α-Nitroso-β-naphthol. This was one of the first selective organic reagents; its structure is:



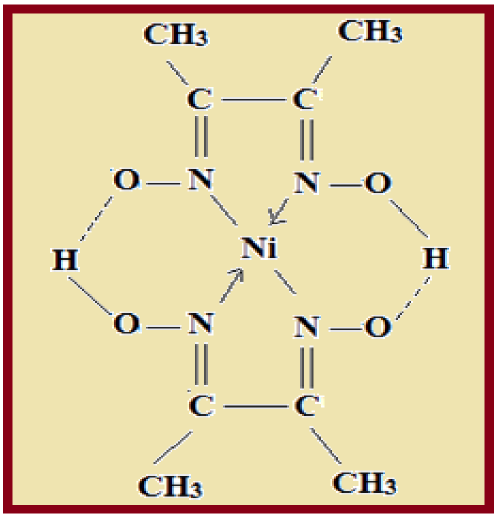
The reagent reacts with cobalt(II) to give a neutral cobalt(III) chelate having the structure CoA_3, where A^- is the conjugate base of the reagent. Note that formation of the product involves both oxidation and precipitation of the cobalt by the reagent; the precipitate is contaminated by reduction products of the reagent as a consequence. Therefore, it is common practice to ignite the chelate in oxygen to produce Co_3O_4; alternatively, the ignition is performed in a hydrogen atmosphere to produce the element as the weighed form.

The most important application of α-nitroso-β-naphthol has been for the determination of cobalt in the presence of nickel. Other ions that precipitate with the reagent include bismuth(III), chromium(III), mercury(II), tin(IV), titanium(III), tungsten(VI), uranium(VI), and vanadium(V).

Dimethylglyoxime. An organic precipitating agent of unparalleled specificity is dimethylglyoxime.

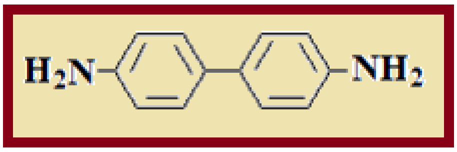


Its coordination compound with palladium is the only one that is sparingly soluble in acid solution. Similarly, only the nickel compound precipitates from a weakly alkaline environment. Nickel dimethylglyoxime is bright red and has the structure:



Sodium Tetraphenylboron. Sodium tetraphenylboron, $(C_6H_5)_4B^-Na^+$, is an important example of organic precipitating reagent that form saltlike precipitates. In cold mineral acid solutions, it is a near-specific precipitating agent for potassium ion and for ammonium ion. The precipitates are stoichiometric, corresponding to the potassium or the ammonium salt, as the case may be; they are amenable to vacuum filtration and can be brought to constant weight at 105 to 120°C. Only mercury(II), rubidium, and cesium interfere and must be removed by prior treatment.

Benzidine. Another salt-forming reagent is benzidine.



Benzidine precipitates sulfate from a slightly acidic medium as $C_{12}H_{12}N_2.H_2SO_4$. The solubility of this precipitate increases rapidly with temperature and also with the acidity of the environment; both variable must be carefully controlled. Instead of being weighed as a gravimetric precipitate, benzidine sulfate may be titrated with a standard solution of sodium hydroxide. Yet another method for completion of the analysis calls for titration of the benzidine with a standard solution of permanganate. The methods succeed in the presence of copper, cobalt, nickel, zinc, manganese(II), iron(II), chromium(III), and aluminum ions. Benzidine is well suited to the rapid, routine analysis of sulfate.

Analytical Chemistry

College of Pharmacy - Universty of Anbar / First Year 2021 - 2022

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Chapter 4

Chemical Equilibrium

4.1 Introduction

The reactions used in analytical chemistry never result in complete conversion of reactants to products. Instead, they proceed to a state of ***chemical equilibrium*** in which the ratio of concentrations of reactants and products is constant. ***Equilibrium-constant expressions*** are algebraic equations that describe the concentration relationships existing among reactants and products at equilibrium. Among other things, equilibrium-constant expressions permit calculation of the error in an analysis resulting from the quantity of unreacted analyte that remains when equilibrium has been reached.

4.2 Equilibrium Constant Expressions

The influence of concentration (or pressure if the species are gases) on the position of a chemical equilibrium is conveniently described in quantitative terms by means of an *equilibrium-constant expression.* Such expressions are derived from thermodynamics. They are important because they permit the chemist to predict the direction and completeness of a chemical reaction. An equilibrium-constant expression, however, yields no information concerning the rate at which equilibrium is approached. In fact, we sometimes encounter reactions that have highly favorable equilibrium constants but are of little analytical use because their rates are low. This limitation can often be overcome by the use of a catalyst, which speeds the attainment of equilibrium without changing its position.

For the reaction:

$$mA + nB \rightleftharpoons yC + zD$$

the equilibrium constant is:

$$K_c = \frac{[C]^y[D]^z}{[A]^m[B]^n}$$

where K_c is the equilibrium constant, the letter c denote the concentrations in mole/liter. The square-bracketed terms mean the molar concentration if the species is a dissolved solute. And mean partial pressure in atmospheres if the species is a gas; in fact, we often replace K_c with K_p in this case. K_c is large if the products more than reactants, and small if the products less than reactants, and equal to 1 if the concentrations of the products and reactants are equal at the equilibrium state.

Example 1

Write the equilibrium constant for the following reactions:

1- $2NO_{(g)} + Cl_{2(g)} \rightleftharpoons 2NOCl_{(g)}$
2- $Na_2CO_{3(s)} + BaSO_{4(s)} \rightleftharpoons Na_2SO_{4(s)} + BaCO_{3(s)}$

1- $$K_p = \frac{[NOCl_{(g)}]^2}{[NO_{(g)}]^2\,[Cl_{2(g)}]}$$

2- $$K_c = \frac{[Na_2SO_{4(s)}][BaCO_{3(s)}]}{[Na_2CO_{3(s)}][BaSO_{4(s)}]}$$

Example 2

In the thermal cracking of HI at 321.4ºC, the premier concentration of the substance was 2.08 *M*, and in the equilibrium state the concentration was 1.68*M*. Calculate K_c.

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

at the beginning of the reaction the concentration of HI was 2.08 *M*, then become 1.68 *M* in the equilibrium state, so the disappeared quantity is:

$$2.08 - 1.68 = 0.40\ M$$

If we go back to the balanced equation we find that the disappearance of 2 mole from HI gives 1 mole from H_2 and 1 mole from I_2, then the concentration of H_2 and I_2 at the equilibrium 0.40/2 = 0.2, so:

$$K_c = \frac{[H_2][I_2]}{[HI]^2}$$

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

the concentration at the beginning	2.08	0	0
the concentration at the equilibrium	1.68	0.20	0.20

$$K_c = \frac{(0.20)(0.20)}{(1.68)^2} = 0.014 = 1.4 \text{ x } 10^{-2}$$

4.3 Dissociation of Water

Water is weak electrolyte, and the aqueous solutions contain small concentrations of hydronium H_3O^+, and hydroxide OH^- ions as a consequence of the dissociation reaction:

$$2H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

or $$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

The equilibrium constant of this reaction is:

$$K_{eq} = \frac{[H^+][OH^-]}{[H_2O]}$$

The concentration of water in dilute aqueous solutions is enormous when compared with the concentration of hydrogen and hydroxide ions. As a consequence, $[H_2O]$ in the equation can be taken as constant:

$$K_{eq}\,[H_2O] = K_w = [H^+][OH^-]$$

Where K_w is the *ion-product constant* for water.

At 25°C, the ion-product constant for water is 1.00×10^{-14}, so:

$[H_3O^+] = 1.0 \times 10^{-7}\ M$

$[OH^-]\ \ = 1.0 \times 10^{-7}\ M$

Example 3

If the concentration of OH^- ion in an ammonia solution was 0.0025 *M*, calculate the concentration of H^+ ion.

$$K_w = [H^+][OH^-]$$

$$[H^+] = \frac{K_w}{[OH^-]}$$

$$[H^+] = \frac{1.0 \times 10^{-14}}{0.0025} = 4.0 \text{ x } 10^{-12}\ M$$

Example 4

In a 1.0×10^{-4} *M* HCl solution, the concentration of hydrogen ions $[H^+]$ was 1.0×10^{-4}, calculate the hydroxide ions concentration. The ionization constant of water at 25°C is 1.0×10^{-14}.

$$K_w = [H^+][OH^-]$$

$$1.0 \text{ x } 10^{-14} = (1.0 \text{ x } 10^{-4})\ [OH^-]$$

$$[OH^-] = \frac{1.0 \text{ x } 10^{-14}}{1.0 \text{ x } 10^{-4}} = 1.0 \text{ x } 10^{-10}\ M$$

4.4 pH Concept

Because the concentrations of H^+ and OH^- ions in aqueous solutions are very small, scientists invented the pH concept which is the negative logarithm of hydrogen ion concentration in mole/liter. The negative logarithm gives positive number for the pH.

$$pH = \log\left[\frac{1}{H^+}\right]$$

$$pH = -\log [H^+]$$

The pH is a measure of hydrogen ion concentration, so we can identify the solutions of acids and bases at 25°C by knowing the pH:

acidic solutions: $[H^+] > 1.0 \times 10^{-7}\ M$, $pH < 7.00$

basic solutions: $[H^+] < 1.0 \times 10^{-7}\ M$, $pH > 7.00$

neutral solutions: $[H^+] = 1.0 \times 10^{-7}\ M$, $pH = 7.00$

The pOH is the negative logarithm of hydroxide ion concentration in the solution:

$$pOH = -\log [OH^-]$$

$$[H^+][OH^-] = K_w = 1.0 \times 10^{-14}$$

If we take the negative logarithm for both sides of the equation, we get:

$$-(\log [H^+] + \log [OH^-]) = -\log (1.0 \times 10^{-14})$$

$$-\log [H^+] - \log [OH^-] = 14.00$$

From the definition of pH and pOH we get:

$$pH + pOH = 14$$

In neutral solution pH + pOH = 7

Example 5

The concentration of the hydrogen ion H^+ in a solution was 3.2×10^{-4}, calculate the pH of the solution.

$$pH = -\log [H^+]$$

$$= -\log (3.2 \text{ x } 10^{-4}) = 3.49$$

Example 6

The pH of a solution of acidic rain was 4.82. Calculate the concentration of H^+ ion for this solution.

$$pH = -\log [H^+]$$

$$4.82 = -\log [H^+]$$

$$[H^+] = 1.5 \text{ x } 10^{-5}\ M$$

Example 7

Calculate the pH of a 0.10 *M* NaOH solution.

NaOH is a strong electrolyte, so the value of OH^- comes from the strong electrolyte.

$$[OH^-] = 0.10\ M$$

$$K_w = [H^+][OH^-]$$

$$[H^+] = \frac{K_w}{[OH^-]}$$

$$[H^+] = \frac{1.0 \text{ x } 10^{-14}}{0.10} = 1.0 \text{ x } 10^{-13}\ M$$

$$\text{pH} = -\log [H^+]$$

$$= -\log (1.0 \text{ x } 10^{-13}) = 13$$

Example 8

In a solution of NaOH, the concentration of OH^- ion was 2.9×10^{-4} *M*. Calculate the pH of the solution.

$$\text{pOH} = -\log [OH^-]$$

$$= -\log (2.9 \text{ x } 10^{-4})$$

$$= 3.54$$

$$\text{pH} + \text{pOH} = 14.00$$

$$\text{pH} = 14 - \text{pOH}$$

$$= 14 - 3.54 = 10.46$$

4.5 Dissociation of Weak Acids and Bases

When a weak acid or a weak base is dissolved in water, partial dissociation occurs. Thus if we assume that a weak acid HA dissociates according to the equation:

$$HA_{(aq)} + H_2O_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

or in a simpler way:

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$$

the equilibrium constant is:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

where K_a is the *acid-dissociation constant*. The stronger the acid the higher the value of K_a. Only weak acids have dissociation constant. Because the values of dissociation constants are very small, we use its logarithm, we call it mathematically pK_a.

$$pK_a = - \log K_a$$

Table 4-1 contains values of K_a for some weak acids.

Table 4-1 Values of K_a for some Weak Acids

K_a Value	**Acid**
4.5×10^{-4}	$HNO_2 \rightleftharpoons H^+ + NO_2^-$ Nitrous acid
1.7×10^{-4}	$HCOOH \rightleftharpoons H^+ + HCOO^-$ Formic acid
6.5×10^{-5}	$C_6H_5COOH \rightleftharpoons H^+ + C_6H_5COO^-$ Benzoic acid
1.8×10^{-5}	$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$ Acetic acid
6.2×10^{-10}	$HCN \rightleftharpoons H^+ + CN^-$ Hydrocyanic acid

Weak polyprotic acids dissociate on steps, and each step has its own dissociation constant. Carbonic acid H_2CO_3 for example dissociates on two steps:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

In an analogous way bases dissociate, and if a weak base dissolved in aqueous solution, it dissociates for small degree then reaches equilibrium:

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

The dissociation constant is:

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Note that a concentration term for water ($[H_2O]$) does not appear in the denominator of either equation because it small and can be considered constant.

Example 9

Calculate K_a for acetic acid if premier concentration was 0.1 mol/L and the percentage of dissociation is 1.34%.

percentage of dissociation is 1.34, this means:
in every 100 mole, 1.34 mole dissociate
in every 0.1 mole X mole dissociate

$$X = \frac{1.34 \text{ x } 0.1}{100} = 0.00134$$

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

concentration at the beginning 0.10 0 0
concentration at the equilibrium 0.1- 0.00134 0.00134 0.00134

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$= \frac{(0.00134)(0.00134)}{0.10 - 0.00134}$$

$$= 1.82 \text{ x } 10^{-5}$$

Example 10

If the K_a for acetic acid is 1.8×10^{-5}, calculate the molar concentration for hydrogen ions $[H^+]$, and the dissociation percentage for 0.50 *M* acetic acid.

suppose x is the number of dissociated moles of acid per liter, so:

x = number of H^+ and CH_3COO^- moles produced per each liter, and $(0.50 - x)$ = number of undissociated CH_3COOH moles per liter.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

concentration at the beginning	0.50	0	0
concentration at the equilibrium	$0.50 - x$	x	x

$$K_a = 1.8 \text{ x } 10^{-5} = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$= \frac{(x)(x)}{0.50 - x}$$

The dissociation of weak acetic acid is very small, so the concentration of x is very small in contrast with the concentration of undissociated acid. In this example the value $(0.50 - x)$ probably is very near to 0.50, so we can use a simple way and avoid using the quadratic equation:

$$1.8 \times 10^{-5} \approx \frac{(x)(x)}{0.50}$$

$$x^2 \approx 0.90 \times 10^{-5} = 9.0 \times 10^{-6}$$

$$x \approx \sqrt{9.0} \times \sqrt{10^{-6}}$$

$$x \approx 3.0 \times 10^{-3}\ M = [H^+]$$

it is also equal to the number of dissociated moles of acetic acid per liter.

$$\text{percentage of dissociated acid} = \frac{\text{number of dissociated moles}}{\text{number of moles at the start}} \times 100$$

$$= \frac{3.0 \times 10^{-3}}{0.50} = 0.60\%$$

4.6 Complex Formation Constant

An analytically important class of reactions involves the formation of soluble complex ion. Example is:

$$Fe^{3+} + SCN^- \rightleftharpoons Fe(SCN)^{2+} \qquad K_f = \frac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^-]}$$

where K_f is called the formation constant for the complex.

4.7 Oxidation-Reduction Equilibrium Constant

Equilibrium constant for oxidation-reduction reactions can be formulated in the usual way. For example:

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H_3O^+ \rightleftharpoons 6Fe^{3+} + 2Cr^{3+} + 21H_2O$$

$$K = \frac{[Fe^{3+}]^6[Cr^{3+}]^2}{[Fe^{2+}]^6[Cr_2O_7^{2-}][H_3O^+]^{14}}$$

The concentration of water does not appear in the equilibrium since it is constant.

4.8 Le Chatelier's Principle

There is a general rule that helps us to predict the direction in which an equilibrium reaction will move when a change in concentration, pressure, volume, or temperature occurs. The rule, known as ***Le Chatelier's principle***, state that *if an external stress is applied to a system at equilibrium, the system adjusts in such a way that the stress is partially offset as the system reaches a new equilibrium position*. The word stress here means a change in concentration, pressure, volume, or temperature that removes a system from the equilibrium state.

4.9 Factors Affect Chemical Equilibrium

1- Effect of pressure

Changes in pressure ordinary do not affect the concentrations of reacting species in condensed phases (say, in an aqueous solution) because liquids and solids are virtually incompressible. On the other hand, concentrations of gases are greatly affected by changes in pressure.

Suppose that the equilibrium system,

$$N_2O_{4\,(g)} \rightleftharpoons 2NO_{2(g)}$$

is in a cylinder fitted with a movable piston. What happens if we increase the pressure on the gases by pushing down on the piston at constant temperature? Since the volume decreases, the concentration of both NO_2 and N_2O_4 increase. Because the concentration of NO_2 is squared in the equilibrium constant expression, the increase in pressure increases the numerator more than the denominator. The system is no longer at equilibrium.

2- Effect of temperature

The values of equilibrium are measured at certain temperature. Any change in temperature will change the equilibrium constant. For example, the formation of NO_2 from N_2O_4 is an endothermic process, and the reverse reaction is exothermic:

$$N_2O_{4\,(g)} \rightarrow 2NO_{2(g)}$$

At equilibrium the net heat effect is zero because there is no net reaction. If the system is heated at constant volume more N_2O_4 will dissociate to NO_2, and that shift the reaction to the right. In opposite, if the temperature is decreased, the reaction will shift to the left.

3- Effect of concentration

If we consider the equilibrium:

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

Any increase in H_3O^+ or CH_3COO^- concentration shifts the equilibrium to the left, and any increase in CH_3COOH concentration shifts the equilibrium to the right, but K remains constant.

4- Effect of catalyst

In an equilibrium system, a catalyst increases the speed of both forward and reverse reactions to the same extent. A catalyst does not change the relative amounts present at equilibrium; the value of the equilibrium constant is not changed. The catalyst dose change the time required for reaching the equilibrium. Reactions that require days or weeks to come to equilibrium may reach it in a matter of minutes in the presence of a catalyst.

4.10 Buffer Solutions

A solution that contains a weak acid plus a salt of that acid, or a weak base plus a salt of that base, has the ability to react with both strong acids and strong bases. Such a system is referred to as a buffer solution, because small additions of either strong acids or strong bases produce little change in the pH.

A simple buffer solution can be prepared by adding comparable molar amounts of acetic acid (CH_3COOH) and its salt sodium acetate (CH_3COONa) to water. This has the ability to neutralize either added acid or added base. Sodium acetate, a strong electrolyte, dissociate completely in water:

$$CH_3COONa_{(s)} \rightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

If an acid is added, the H^+ ions will be consumed by the conjugate base in the buffer, CH_3COO^-, according to the equation:

$$CH_3COO^-_{(aq)} + H^+_{(aq)} \rightarrow CH_3COOH_{(aq)}$$

If a base is added to the buffer system, the OH^- ions will be neutralized by the acid in the buffer:

$$CH_3COOH_{(aq)} + OH^-_{(aq)} \rightarrow CH_3COO^-_{(aq)} + H_2O_{(l)}$$

In general, a buffer system can be represented as salt-acid or conjugate base-acid. Thus the sodium acetate-acetic acid buffer system can be written as CH_3COONa/CH_3COOH or simply CH_3COO^-/CH_3COOH.

4.11 Calculation of the pH of Buffer Solutions

A general buffer equation can be derived by considering the following reactions for a weak acid, HA, and the salt of its conjugate weak base, NaA.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad \ldots\ldots\ldots\ldots1)$$

$$A^- + H_2O \rightleftharpoons OH^- + HA \qquad K_b = \frac{[OH^-][HA]}{[A^-]} = \frac{K_w}{K_a} \qquad \ldots\ldots2)$$

To find the pH of a solution containing both an acid, HA, and its conjugate base, NaA, we need to express the equilibrium concentrations of HA and NaA in terms of their analytical concentrations. C_{HA} and C_{NaA}. An examination of the two equilibria reveals that the first reaction decreases the concentration of HA by an amount equal to

$[H_3O^+]$, whereas the second increases the HA concentration by an amount equal to $[OH^-]$. Thus, the species concentration of HA is related to its analytical concentration by the equation:

$$[HA] = C_{HA} - [H_3O^+] + [OH^-] \text{ …….3)}$$

Similarly, the first equilibrium will increase the concentration of A^- by an amount equal to $[H_3O^+]$, and the second will decrease this concentration by the amount $[OH^-]$. Thus, the equilibrium concentration is given by a second equation similar to Equation 3.

$$[A^-] = C_{NaA} + [H_3O^+] - [OH^-] \text{ …….4)}$$

Because of the inverse relationship between $[H_3O^+]$ and $[OH^-]$, it is always possible to eliminate one or the other from Equations 3 and 4. Moreover, the difference in concentration between these two species is usually so small relative to the molar concentrations of acid and conjugated base that Equations 3 and 4 simplify to:

$$[HA] \approx C_{HA} \text{ ………5)}$$

$$[A^-] \approx C_{NaA} \text{ ………6)}$$

Substitution of Equations 5 and 6 into the dissociation-constant expression and rearrangement yields:

$$[H_3O^+] = K_a \frac{C_{HA}}{C_{NaA}} \text{ …………..7)}$$

The assumption leading to Equations 5 and 6 sometimes breaks down with acids or bases that have dissociation constants greater than about 10^{-3} or when the molar concentration of either the acid or its conjugate base (or both) is very small. In these circumstances, either $[OH^-]$ or $[H_3O^+]$ must be retained in Equations 3 and 4, depending on whether the solution is acidic or basic. In any case, Equations 5 and 6 should always be used initially. The provisional values for [H_3O^+] and [OH^-] can then be used to test the assumptions.

* *The Henderson-Hasselbalch Equation*

The Henderson-Hasselbalch equation, which is used to calculate the pH of buffer solutions, is frequently encountered in the biological literature and biochemical texts. It is obtained by expressing each term in Equation 7 in the form of its negative logarithm and inverting the concentration ratio to keep all signs positive:

$$-\log [H_3O^+] = -\log K_a + \log \frac{C_{\text{NaA}}}{C_{\text{HA}}}$$

Therefore,

$$\text{pH} = \text{p}K_a + \log \frac{C_{\text{NaA}}}{C_{\text{HA}}} \quad \ldots\ldots 8)$$

Example 11

What is the pH of a solution that is 0.400 M in formic acid and 1.00 M in sodium formate?

The pH of this solution will be affected by the Kw of formic acid and the K_b of formate ion.

$$HCOOH + H_2O \rightleftharpoons H_3O^+ + HCOO^- \qquad K_a = 1.80 \times 10^{-4}$$

$$HCOO^- + H_2O \rightleftharpoons HCOOH + OH^- \qquad K_b = \frac{K_w}{K_a} = 5.56 \times 10^{-11}$$

Since the K_a for formic acid is orders of magnitude larger than the K_b for formate, the solution will be acidic and K_a will determine the H_3O^+ concentration. We can thus write:

$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]} = 1.80 \times 10^{-4}$$

$$[HCOO^-] \approx C_{HCOO^-} = 1.00\ M$$

$$[HCOOH] \approx C_{HCOOH} = 0.400\ M$$

Substitution into Equation 7 gives, with rearrangement:

$$[H_3O^+] = 1.8 \times 10^{-4} \times \frac{0.400}{1.00} = 7.20 \times 10^{-5}\ M$$

Note that the assumption that $[H_3O^+] << C_{HCOOH}$ and that $[H_3O^+] << C_{HCOO^-}$ is valid. Thus:

$$pH = -\log(7.20 \times 10^{-5}) = 4.14$$

4.12 Buffer Capacity

The buffer capacity of a solution is defined as the number of equivalents of strong acid or strong base needed to cause 1.00 liter of the buffer to undergo a 1.00-unit change in pH. The buffer capacity is dependent upon the concentration of the conjugated acid-base pair. It is also dependent upon their concentration ratio, and reaches maximum when this ratio is unity.

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Chapter 5

Introduction to Volumetric Methods of Analysis

5.1 Introduction

A quantitative analysis based upon the measurement of volume is called a volumetric or titrimetric method. Volumetric methods are much widely used than gravimetric methods because they are usually more rapid and convenient; in addition, they are often as accurate.

5.2 Definition of Some Terms

Titration is the process by which the quantity of analyte in a solution is determined from the amount of a standard reagent it consumes. Ordinarily, a titration is performed by carefully adding the reagent of known concentration until reaction with the analyte is judged to be complete; the volume of standard reagent is then measured. Occasionally, it is convenient or necessary to add an excess of the reagent and then determine the excess by back-titration with a second reagent of known concentration.

The reagent of exactly known concentration that is used in a titration is called a standard solution. The accuracy with which its concentration is known sets a define limit upon the accuracy of the method; for this reason, much care is taken in the preparation of standard solutions. The concentration of a standard solution is established either directly or indirectly:

1- by dissolving a carefully weighed quantity of the pure reagent and dilution to an exactly known volume.

2- by titrating a solution containing a weighed quantity of a pure compound with the reagent solution.

In either method, a highly purified chemical compound called a primary standard is required as the reference material. The process whereby the concentration of a standard solution is determined by titration of a primary standard is called standardization.

The goal of every titration is the addition of standard solution in an amount that is chemically equivalent to the substance with which it reacts. This condition is achieved at the *equivalence point*. For example, the equivalence point in the titration of sodium chloride with silver nitrate is attained when exactly one formula weight of silver ion has been introduced for each formula weight of chloride ion present in the sample. In the titration of sulfuric acid with sodium hydroxide, the equivalence point occurs when two formula weights of the latter have been introduced for each formula weight of the former.

The equivalence point in a titration is a theoretical concept; in actual fact, its position can be estimated only by observing physical changes associated with equivalence. These changes manifest themselves at the *end point* of the titration. It is to be hoped that any volume difference between the end point and the equivalence point will be small. Differences do exist, however, owing to inadequacies in the physical changes and our ability to observe them; a titration error is the result.

A common method of end-point detection in volumetric analysis involves the use of a supplementary chemical compound that exhibits a change in color as a result of concentration changes occurring near the equivalence point. Such a substance is called an indicator.

5.3 Reactions and Reagents Used in Volumetric Analysis

It is convenient to classify volumetric methods according to four reaction types, specifically, precipitation, complex formation, neutralization (acid-base), and oxidation-reduction. Each reaction type is unique in such matters as nature of equilibria involved; the indicators, reagents, and primary standard available; and the definition of equivalent weight.

** Primary standards*

The accuracy of a volumetric analysis is critically dependent upon the primary standard used to establish, directly or indirectly, the concentration of the standard solution. Important requirements for a substance to serve as a good primary standard include the following:

1- **Highest purity.** Moreover, established methods should be available for confirming its purity.

2- **Stability.** It should not be attacked by constituents of the atmosphere.

3- **Absence of hydrate water.** If the substance were hygroscopic or efflorescent, drying and weighing would be difficult.

4- **Ready availability at reasonable cost.**

5- **Reasonably high equivalent weight**. The weight of a compound required to standardize or prepare a solution of a given concentration increases directly with its equivalent weight. Since the relative error in weighing decreases with increasing weight, a high equivalent weight will tend to minimize weighing errors.

Few substances meet or even approach these requirements. As a result, the number of primary-standard substances available to the chemist is limited.

In some instances, it is necessary to use less pure substances in lieu of a primary standard. The assay (that is, the percent purity) of such a secondary standard must be established by careful analysis.

5.4 Standard Solution

An ideal standard solution for titrimetric analysis would have the following properties:

1- Its concentration should remain constant for months or years after preparation to eliminate the need for restandardization.

2- Its reaction with the analyte should be rapid in order that the waiting period after each addition of reagent does not become excessive.

3- The reaction between the reagent and the analyte should be reasonably complete.

4- The reaction of the reagent with the analyte must be such that it can be described by a balanced chemical equation; otherwise, the weight of the analyte cannot be calculated directly from the volumetric data. This requirement implies the absence of side reactions between the reagent and the unknown or with other constituents of the solution.

5- A method must exist for detecting the equivalence point between the reagent and the analyte; that is, a satisfactory end point is required.

Few volumetric reagents currently in use meet all of these requirements perfectly.

5.5 End Point in Volumetric Methods

End points are based upon a physical property which changes in a characteristic way at or near the equivalence point in the titration. The most common end point involves a color change due to the reagent, the analyte, or an indicator substance. Other physical properties, such as electrical potential, conductivity, temperature, and refractive index, have also been employed to locate the equivalence point in titration.

5.6 Theory of Neutralization Titration for Simple Systems

End-point detection in a neutralization titration is ordinary based upon the sharp change in pH that occurs near the equivalence point. The pH range with which such a change occurs varies from titration to titration and is determined both by the nature and the concentration of the analyte as well as the titrant. The selection of an appropriate indicator and the estimation of the titration error require knowledge of the pH changes which occur throughout the titration. Thus, we need to know how neutralization titration curves are derived.

5.7 Standard Solutions for Neutralization Titrations

The standard solutions employed for neutralization titrations are always strong acids or strong bases because these react more completely than their weaker counterparts, and they therefore provide sharper end point. Standard solutions of acids are prepared by diluting concentrated acids.

Standard solutions of bases are ordinarily prepared from solid bases.

5.8 Acid-Base Indicators

An acid-base indicator is a weak organic acids or a weak organic base whose undissociated form differ in color from its conjugate base or its conjugate acid form.

For example, the behavior of an acid-type indicator, HIn, is described by the equilibrium:

$$\underset{\text{acid color}}{HIn + H_2O} \rightleftharpoons \underset{\text{base color}}{In^- + H_3O^+}$$

Here, internal structure changes accompany dissociation and cause the color change. The equilibrium for a base-type indicator, In, is:

$$\underset{\text{base color}}{In + H_2O} \rightleftharpoons \underset{\text{acid color}}{InH^+ + OH^-}$$

The equilibrium-constant expression for the dissociation of acid-type indicator takes the form:

$$K_a = \frac{[H_3O^+][In^-]}{[HIn]}$$

$$[H_3O^+]K_a = \frac{[HIn]}{[HI^-]}$$

We then see that the hydronium ion concentration determines the ratio of the acid to the conjugate base from the indicator, which in turn controls the color of the solution.

The human eye is not very sensitive to color differences in a solution containing a mixture of HIn and In^-, particularly when the ratio $[HIn]/[In^-]$ is greater than about 10 or smaller than about 0.1. Consequently, the color change detected by an average observer occurs within a limited range of concentration ratios from about 10 to about 0.1. At greater or smaller ratios, the color appears essentially constant to the eye and is independent of the ratio. As a result, we can write that the average indicator, HIn, exhibits its pure acid color when:

$$\frac{[HIn]}{[In^-]} \geq \frac{10}{1}$$

and its base color when:

$$\frac{[HIn]}{[In^-]} \leq \frac{1}{10}$$

The color appears to be intermediate for ratios between these two values.

5.9 The Common Acid-Base Indicators

The list of acid-base indicators is large and includes a number of organic compounds. An indicator covering almost any desired pH range can ordinarily be found. A few common indicators are given in Table 5-1.

Table 5-1 Some Important Acid-Base Indicators

Common Name	**Transition Range, pH**	**Color Change**		**Indicator Type**
		Acid	**Base**	
Thymol blue	1.2-2.8 8.0-9.6	red yellow	yellow blue	1
Methyl yellow	2.9-4.0	red	yellow	2
Methyl orange	3.1-4.4	red	orange	2
Bromocresol green	3.8-5.4	yellow	blue	1
Methyl red	4.2-6.3	red	yellow	2
Bromocresol purple	5.2-6.8	yellow	purple	1
Bromothymol blue	6.2-7.6	yellow	blue	1
Phenol red	6.8-8.4	yellow	red	1
Cresol purple	7.6-9.2	yellow	purple	1
Phenolphthalein	8.3-10.0	colorless	red	1
Thymolphthalein	9.3-10.5	colorless	blue	1
Alizarin yellow GG	10-12	colorless	yellow	2
(1) Acid type $HIn + H_2O \rightleftharpoons H_3O^+ + In^-$ (2) Base type $In + H_2O \rightleftharpoons InH^+ + OH^-$				

5.10 Titration of a Strong Acid with a Strong Base

Strong acids and strong bases are completely ionized in their solutions, examples HCl and NaOH.

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

At the equivalence point, the hydronium and hydroxide ions are present in equal concentrations. The solution containing NaCl salt does not undergo hydrolysis, and the pH of the solution is 7.00.

If the values of pH are plotted against the volumes of NaOH added, we obtain curve as shown in Figure 5-1, called titration curve for a strong acid with strong base.

** The effect of concentration*

The effect of reagent and analyte concentrations on the neutralization titration curves for strong acids are shown by the plots in Figure 5-1. Note that with 0.1 M NaOH as the titrant, the change in pH in the equivalence-point region is large. With 0.001 M NaOH, the change is markedly less but still pronounced.

** Choosing an indicator*

Figure 5-1 shows that the selection of an indicator is not critical when the reagent concentration is approximately 0.1 M.

Here, the volume differences in titrations with the three indicators shown are of the same magnitude as the uncertainties associated with reading the buret; therefore, they are negligible. Note, however, that bromocresol green is unsuited for a titration involving the 0.001 M reagent because the color change occurs over a 5-mL range well before the equivalence point. The use of phenolphthalein is subject to similar objections. Of the three indicators, then, only bromothymol blue provides a satisfactory end point with a minimal systematic error in the titration of the more dilute solution.

Titration curves for strong bases are derived in an analogous way to those for strong acids. The solution is neutral at the equivalence point.

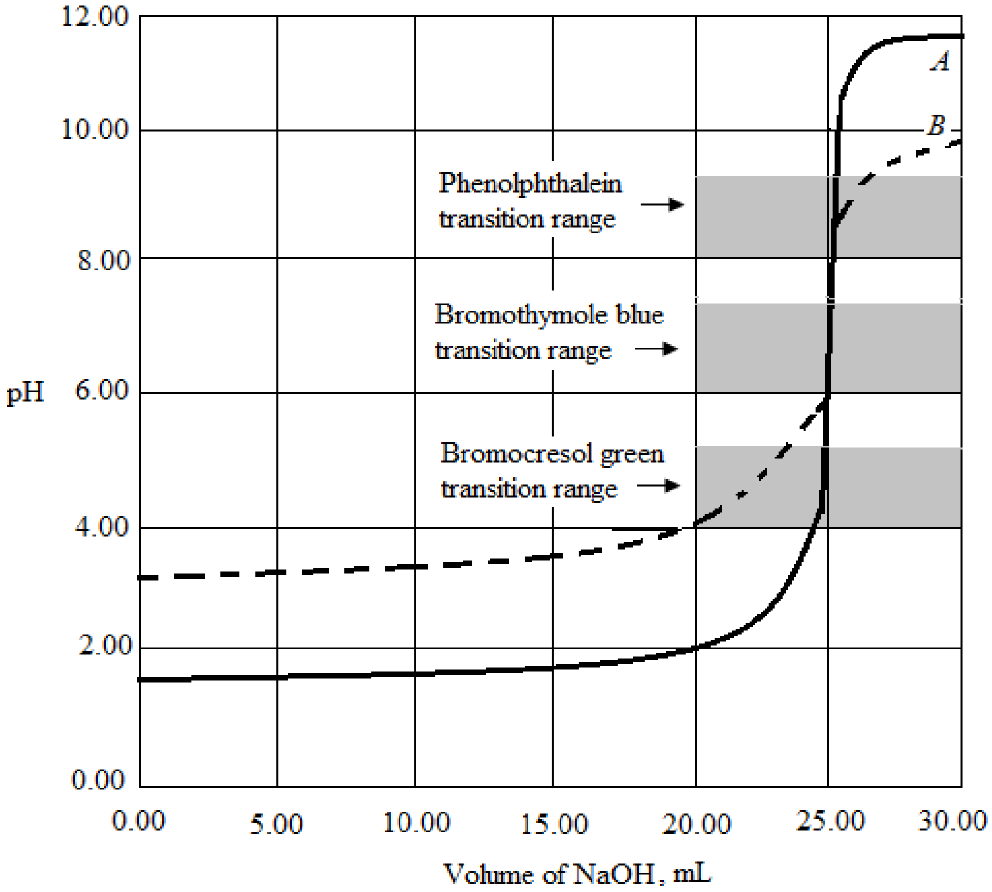

Figure 5-1 Titration Curves for HCl with NaOH. Curve *A*: 50.00 mL of 0.0500 M HCl with 0.1000 M NaOH. Curve *B*: 50.00 mL of 0.000500 M HCl with 0.001000 M NaOH.

5.11 Titration of a weak Acid with a Strong Base

Weak acid, like acetic acid, does not ionize in the solution completely. The equation for the reaction is:

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

At the beginning, the solution contains only a weak acid or weak base, and the pH is calculated from the concentration of the solute and its dissociation constant.

At the equivalence point, the solution contains only the salt, and the pH is calculated from the concentration of this product. The solution containing CH_3COONa salt, undergoes hydrolysis as shown in the equation:

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$$

which increases the hydroxide ions concentration over the concentration of hydrogen ions, because NaOH ionizes completely and the CH_3COOH ionizes partially. The pH of the solution is 8.72. The titration curve is shown in Figure 5-2.

**** The effect of concentration***

The initial pH values are higher and the equivalence-point pH is lower for the more dilute solution (curve B).

**** Choosing an indicator***

Figure 5-2 shows that the choice of indicator is more limited for the titration of a weak acid than for the titration of a strong acid. The bromocresol green is totally unsuited for titration of 0.1000 M acetic acid. Bromothymol blue does not work either because its full color change occurs over a range of titrant volume from about 47 mL to 50 mL of 0.1000 M base. An indicator exhibiting a color change in the basic region, such as phenolphthalein, however, should provide a sharp end point with a minimal titration error.

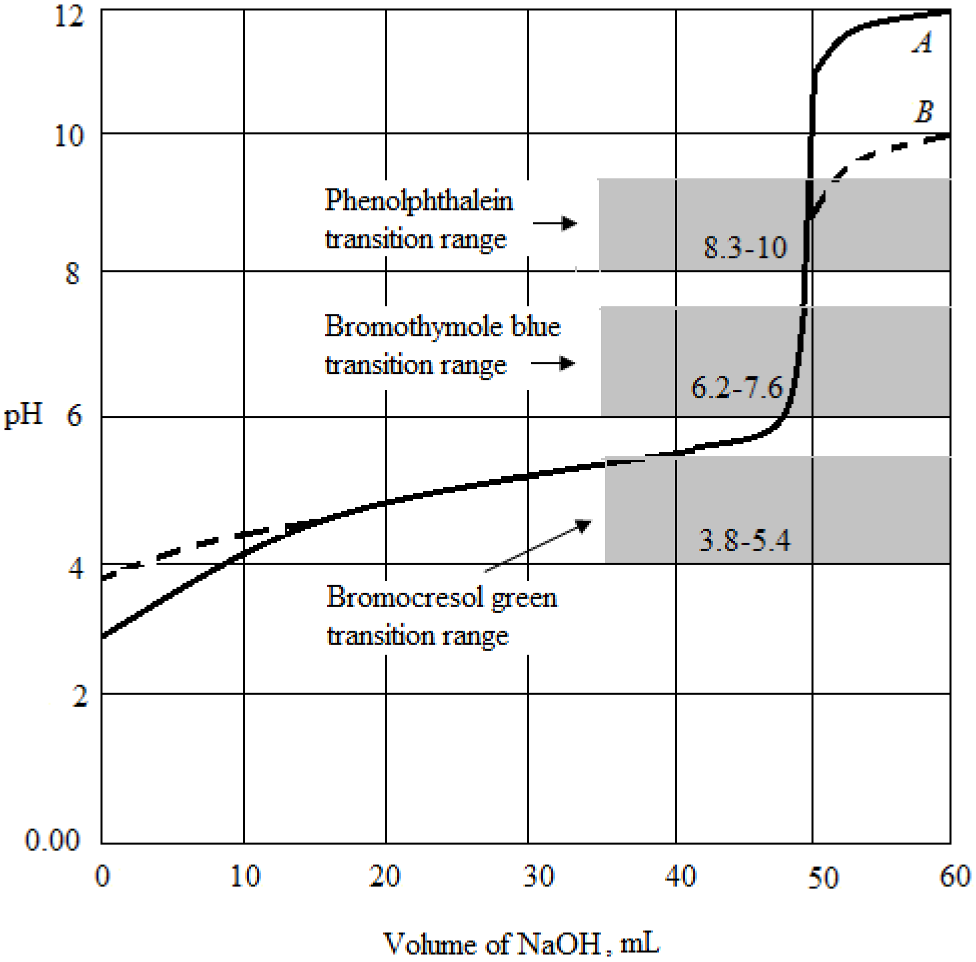

Figure 5-2 Titration Curves for CH_3COOH with NaOH. Curve *A*: 0.1000 M acid with of 0.1000 M base. Curve *B*: 0.001000 M acid with 0.001000 M base.

The end-point pH associated with the titration of 0.001000 M acetic acid (curve B) is so small that a significant titration error is likely to be introduced regardless of indicator. Use of an indicator with a transition range between that of phenolphthalein and that of bromothymol blue in conjunction with a suitable color comparison standard, however, makes it possible to establish the end point in this titration with decent precision.

5.12 Titration of a Strong Acid with a Weak Base

The calculations needed to draw the titration curve for a weak base are analogous to those for a weak acid.

Consider the titration of HCl, (a strong acid) and ammonium hydroxide (a weak base). The equation for the reaction is:

$$HCl + NH_4OH \rightleftharpoons NH_4Cl + H_2O$$

The pH at the equivalence point, is less than 7.00 (5.28), due to the hydrolysis of the ammonium chloride, and formation of HCl, which is more ionized than NH_4OH.

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$$

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Chapter 6

Titration Curves for Complex Acid-Base Systems

6.1 Introduction

Complex systems are defined as solutions made up of:

(1) two acids or two bases of different strength.

(2) an acid or a base that has two or more acidic or basic functional groups.

(3) an amphiprotic substance, which is capable of acting as both an acid and a base.

Polyfunctional acids and bases play important roles in many chemical and biological systems. The human body contains a complicated system of buffers within cells and within bodily fluids, such as human blood. The pH of human blood is controlled to be within the range of 7.35 to 7.45 primarily by the carbonic acid/bicarbonate buffer system.

6.2 Mixture of Strong and Weak Acids or Strong and weak Bases

It is possible to determine each of the components in a mixture containing a strong acid and a weak acid (or a strong base and a weak base) provided that the concentrations of the two are the same order of magnitude and that the dissociation constant for the weak acid or base is somewhat less than about 10^{-4}. To demonstrate that this statement is true, let us show how a titration curve can be constructed for a solution containing roughly equal concentrations of HCl and HA, where HA is a weak acid with dissociation constant of 10^{-4}.

When the amount of base added is equivalent to the amount of hydrochloric acid originally present, the solution is identical in all respects to one prepared by dissolving appropriate quantities of the weak acid and sodium chloride in a suitable volume of water. The sodium chloride, however, has no effect on the pH (neglecting the influence of increased ionic strength); thus, the reminder of the titration curve is identical to that for a dilute solution of HA.

The shape of the curve for a mixture of weak and strong acids, and hence the information obtainable from it, depends in large measure on the strength of the weak acid. Figure 6-1 depicts the pH change that occurs during the titration of mixtures containing hydrochloric acid and several weak acids.

Note that the rise in pH at the first equivalence point is small or essentially nonexistent when the weak acid has a relatively large dissociation constant (curve *A* and *B*). For titrations such as these, only the total number of millimoles of weak and strong acid can be determined accurately. Conversely, when the weak acid has a very small dissociation constant, only the strong acid content can be determined. For weak acids of intermediate strength (K_a somewhat less than 10^{-4} but greater than 10^{-8}), there are usually two useful end points.

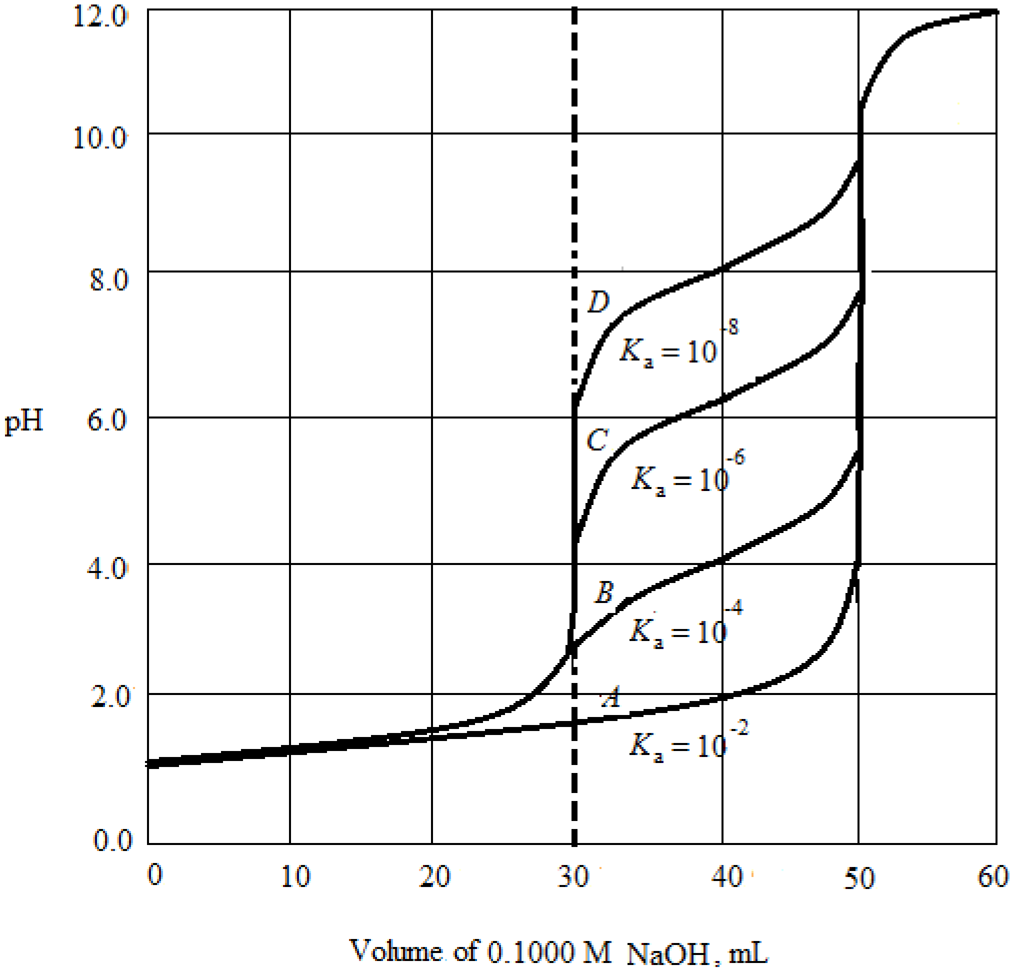

Figure 6-1 Curves for the Titration of Strong Acid/Weak Acid Mixtures with 0.1000 M NaOH. Each titration is on 25.00 mL of a solution that is 0.1200 M in HCl and 0.0800 M in HA.

Determination of the amount of each component in a mixture that contains a strong base and a weak base is also possible, subject to the constraints just described for the strong acid/weak acid system. The computation of a curve for such a titration is analogous to that for a mixture of acids.

6.3 Polyfunctional Acids and Bases

Several species are encountered in analytical chemistry that have two or more acidic functional groups. Generally, the two groups differ in strength and, as a consequence, exhibit two or more end points in a neutralization titration.

**** The phosphoric acid system***

Phosphoric acid is a typical polyfunctional acid. In aqueous solution, it undergoes the following three dissociation reactions:

$$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+ \quad K_{a1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = 7.11 \times 10^{-3}$$

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+ \quad K_{a2} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.32 \times 10^{-8}$$

$$HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^+ \quad K_{a3} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.5 \times 10^{-13}$$

With this acid, as with other polyprotic acids, $K_{a1} > K_{a2} > K_{a3}$.

When we add two adjacent stepwise equilibria, we multiply the two equilibrium constant to obtain the equilibrium constant for the resulting overall reaction. Thus, for the first two dissociation equilibria for H_3PO_4, we write:

$$K_{a1}K_{a2} = \frac{[H_3O^+]^2[HPO_4^{2-}]}{[H_3PO_4]}$$

$$= 7.11 \times 10^{-3} \times 6.32 \times 10^{-8} = 4.49 \times 10^{-10}$$

Similarly, for the reaction:

$$H_3PO_4 \rightleftharpoons 3H_3O^+ + PO_4^{3-}$$

we may write:

$$K_{a1}K_{a2}K_{a3} = \frac{[H_3O^+]^3[PO_4^{3-}]}{[H_3PO_4]}$$

$$= 7.11 \times 10^{-3} \times 6.32 \times 10^{-8} \times 4.5 \times 10^{-13} = 2.0 \times 10^{-22}$$

**** The carbon dioxide carbonic acid system***

When carbon dioxide is dissolved in water, a dibasic acid system is formed by the following reaction:

$$CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_3 \qquad K_{hyd} = \frac{[H_2CO_3]}{[CO_{2(aq)}]} = 2.8 \times 10^{-3}$$

$$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^- \quad K_1 = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = 1.5 \times 10^{-4}$$

$$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-} \quad K_2 = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11}$$

The first reaction describes the hydration of aqueous CO_2 to form carbonic acid. Note that the magnitude of K_{hyd} indicates that the concentration of $CO_{2(aq)}$ is much larger than the concentration of H_2CO_3 (that is, $[H_2CO_3]$ is only about 0.3% that of $[CO_{2(aq)}]$. Thus, a more useful way of discussing the acidity of solutions of carbon dioxide is to combine the first and the second equations to give:

$$CO_{2(aq)} + 2H_2O \rightleftharpoons H_3O^+ + HCO_3^- \quad K_{a1} = \frac{[H_3O^+][HCO_3^-]}{[CO_{2(aq)}]}$$

$$= 2.8 \times 10^{-3} \times 1.5 \times 10^{-4}$$

$$= 4.2 \times 10^{-7}$$

$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$ $K_{a2} = 4.69 \times 10^{-11}$

6.4 Titration Curves for Polyfunctional Acids

Compounds with two or more acid functional groups yield multiple end points in a titration provided that the functional groups differ sufficiently in strength as acids.

Figure 6-2 shows the titration curve for diprotic acid H_2A with dissociation constant of $K_{a1} = 1.00 \times 10^{-3}$ and $K_{a2} = 1.00 \times 10^{-7}$.

We can calculate each equivalence point for reaction like this.

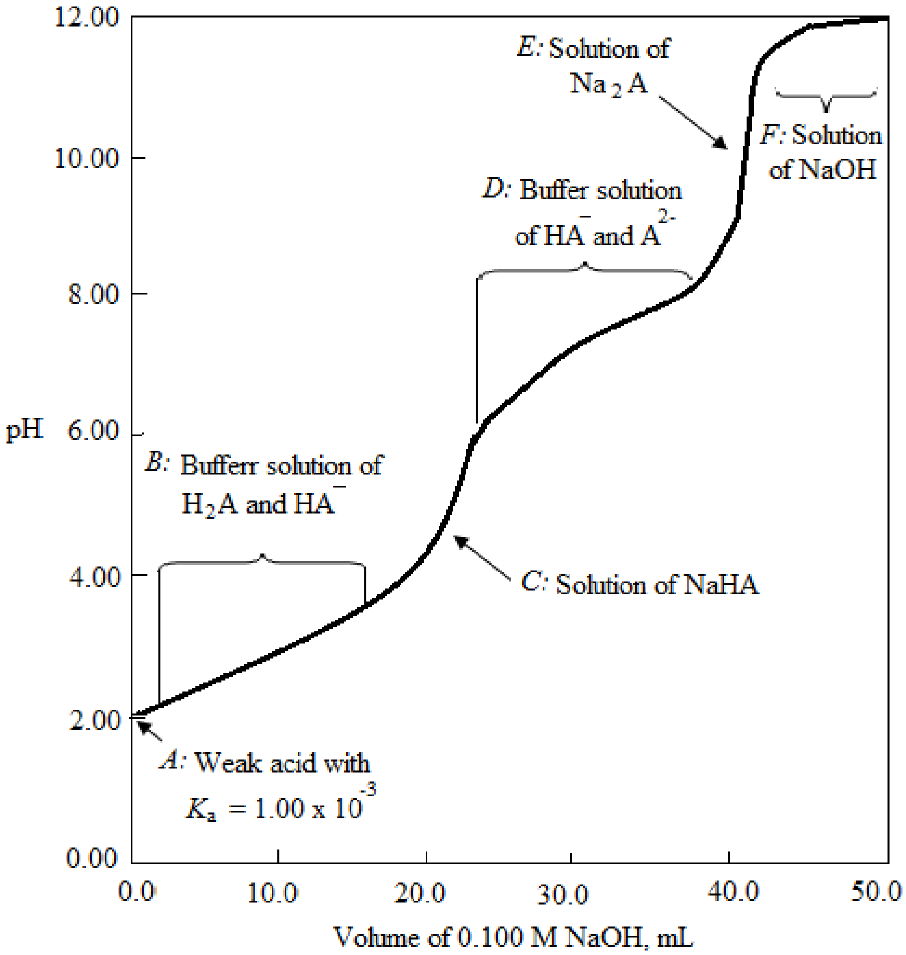

Figure 6-2 Titration of 20.00 mL of 0.1000 M H_2A with 0.1000 M NaOH. For H_2A, $K_{a1} = 1.00 \times 10^{-3}$ and $K_{a2} = 1.00 \times 10^{-7}$. The method of pH calculation is shown for several points regions on the titration curve.

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Chapter 7

Precipitation Titration

7.1 Introduction

Precipitation titrimetry, which is based on reactions that yield compounds of limited solubility, is one of the oldest analytical techniques, dating back to the mid-1800s. Because of the slow rate of formation of most precipitates, however, there are only a few precipitating agents that can be used in titrimetry. The most important precipitating reagent is silver nitrate, which is used for the determination of the halides, the halide-like anions (SCN^-, CN^-, CNO^-), mercaptans, fatty acids, and several divalent and trivalent inorganic anions. Titrimetric methods based on silver nitrate are sometimes called **argentometric methods**.

7.2 Precipitation Titration Curves Involving Silver Ion

The most common method of determining the halide ion concentration of aqueous solutions is titration with a standard solution of silver nitrate. The reaction product is solid silver halide. A titration curve for this method usually consists of a plot pAg versus the volume of silver nitrate added. To construct titration curves, three types of calculations are required, each of which corresponds to a distinct stage in the reaction: (1) preequivalence, (2) equivalence, and (3) postequivalence.

7.3 The Effect of Concentration on Titration Curves

The effect of reagent and analyte concentrations on titration curves was shown by the two titration curves in Figure 7-1. With 0.1 M $AgNO_3$ (Curve *A*), the change in pAg in the equivalence-point region is large. With the 0.01 M reagent, the change is markedly less but still pronounced. Thus, an indicator for Ag^+ that produces a signal in the 4.0 to 6.0 pAg range should give a minimum error for the stronger solution. For the more dilute chloride solution, the change in pAg in the equivalence-point region would be too small to be detected precisely with a visual indicator.

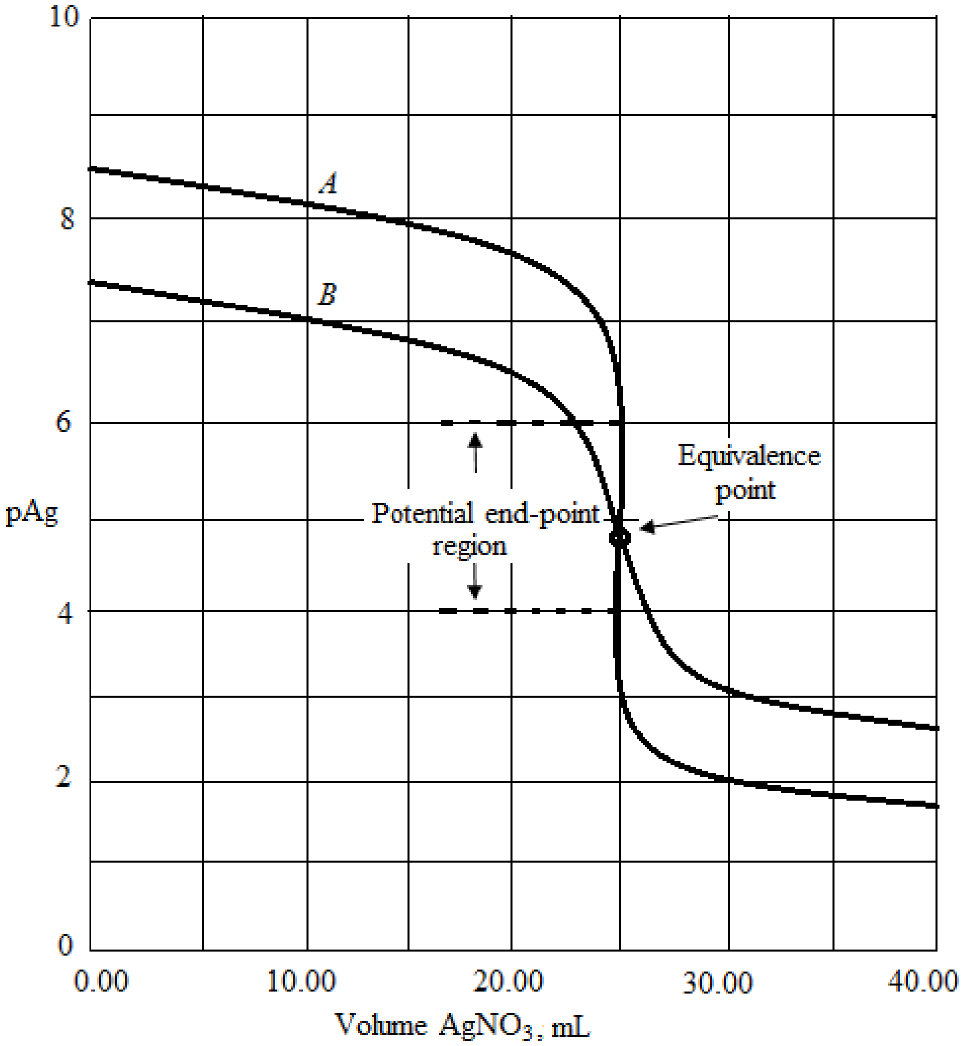

Figure 7-1 Titration Curve for *A*, 50.00 mL of 0.0500 M NaCl with 0.1000 M $AgNO_3$, and *B*, 50.00 mL of 0.00500 M NaCl with 0.0100 M $AgNO_3$.

7.4 Indicators for Argentometric Titrations

Three types of end points are encountered in titrations with silver nitrate: (1) chemical, (2) potentiometric, and (3) amperometric. Potentiometric end points are obtained by measuring the potential between a silver electrode and a reference electrode whose potential is constant and independent of the added reagent. To obtain an amperometric end point, the current generated between a pair of silver microelectrodes in the solution of the analyte is measured and plotted as a function of reagent volume.

The end point produced by a chemical indicator usually consists of a color change or, occasionally, the appearance or disappearance of turbidity in the solution being titrated. The requirements for an indicator for a precipitation titration are that (1) the color change should occur over a limited range in p-function of the titrant or the analyte and (2) the color change should take place within the steep portion of the titration curve for the analyte.

7.5 Mohr's Method

Mohr's method for chloride determination depends on the titration reaction:

$$Ag^+ + Cl^- \rightleftharpoons AgCl_{(s)} \quad \text{white ppt.}$$

When all Cl^- ions react with Ag^+ ions, the first extra drop of Ag^+ will react with $CrO4^{2-}$ ions of the indicator forming red precipitate, and that is the end point of the reaction.

$$2Ag^+ + CrO_4^{2-} \rightleftharpoons Ag_2CrO_{4(s)} \quad \text{red ppt.}$$

Sodium chromate can serve as an indicator for argentometric determination of chloride, bromide, and cyanide ions by reacting with silver ion to form a brick-red silver chromate (Ag_2CrO_4) precipitate in the equivalence-point region.

Silver chromate do not precipitate at the beginning, although its solubility constant is smaller than that of silver chloride, and that is because the required amount of silver ions to precipitate the chloride ions is 1.82×10^{-7} mol/L, which is much less than the amount of silver ions required for precipitation of chromate ions (3.3×10^{-5} mol/L). Consequently, chromates precipitate after precipitation of chloride ions.

The concentration of chromate ions has an important role in determining the end point. From the calibration curve for silver nitrate with chloride we see that the equivalence point located at pAg = 4.87, that is, the concentration of silver ion is equal to 1.35×10^{-5} mol/L, accordingly, the chromate ions concentration required to initiate the precipitation of silver chromate is equal to 6.0×10^{-3} mol/L. In principle, this amount of chromate ions is required to start the formation of the red brick precipitate of silver chromate. This is by simply adding a slight access of the silver solution after the equivalence point. But, since the chromate gives a bright yellow color at this concentration, which makes it impossible to see the red color of silver chromate easily, it is preferable and necessary to add a concentration less than 6.0×10^{-3} mol/L. This, of course, requires a greater concentration of the silver needed to form the red brick precipitate. This results in adding an excess amount of silver nitrate, especially in dilute solutions, so that the precipitate can be seen clearly. In both cases, there will be some error in the calibration. To overcome this difficulty, the volume taken must be corrected by titrating a volume approximately equal to the volume of the total solution at the equivalence point containing calcium carbonate and equivalent amount of the indicator then subtracting the volume of silver nitrate needed to form silver chromate precipitate, from the volume of silver reacted with the chloride.

The Mohr titration must be carried out at pH of 7 to 10 because chromate ion is the conjugate base of the weak chromic acid, react with hydrogen:

$$CrO_4^{2-} + H^+ \rightleftharpoons HCrO_4^-$$

$$2HCrO_4^- \rightleftharpoons H_2O + Cr_2O_7^{-2}$$

In a strong alkaline solution, the silver ions precipitate as silver oxide:

$$2Ag^+ + 2OH^- \rightleftharpoons 2AgOH \rightleftharpoons Ag_2O + H_2O$$

Normally, a suitable pH is achieved by saturating the analyte solution with sodium hydrogen carbonate.

7.6 Fajan’s Method

Fagan’s method also called adsorption indicator, this indicator is an organic compound that tends to be adsorbed onto the surface of the solid in a precipitation titration. Ideally, the adsorption (or desorption) occurs near the equivalence point and results not only in a color change but also in a transfer of color from the solution to the solid (or the reverse).

Fluorescein is a typical adsorption indicator that is useful for the titration of chloride ion with silver nitrate. In aqueous solution, fluorescein partially dissociates into hydronium ions and negatively charged fluoresceinate ions that are yellow-green.

The fluoresceinate ion forms an intensely red silver salt. Whenever this dye is used as an indicator, however, its concentration is never large enough to precipitate as silver fluoresceinate.

In the early stage of the titration of chloride ion with silver nitrate, the colloidal silver chloride particles are negatively charged because of adsorption of excess chloride ions (Figure 7.2). The dye anions are repelled from this surface by electrostatic repulsion and impart a yellow-green color to the solution.

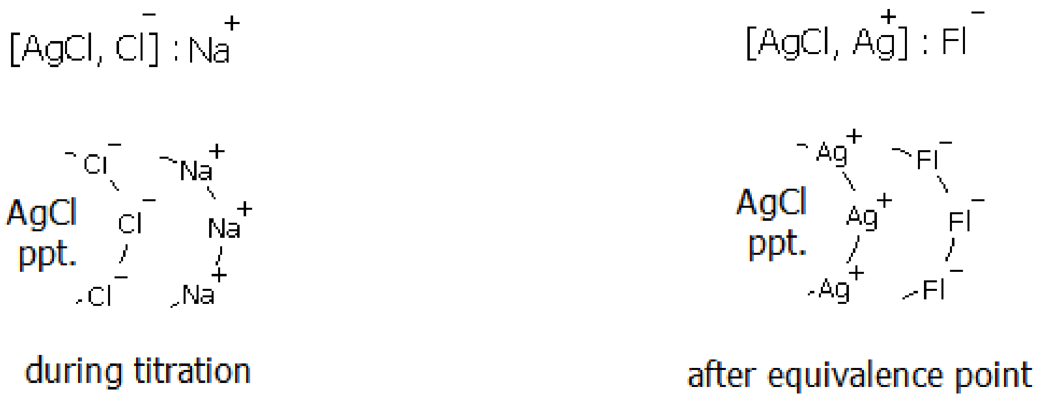

Figure 7-2 Fajan’s Method for the Titration of Chloride

Beyond the equivalence point, however, the silver chloride particles strongly adsorb silver ions and thereby have a positive charge. Fluoresceinate anions are now attracted into the counter-ion layer that surrounds each colloidal silver chloride particle. The net result is the appearance of the red color of silver fluoresceinate in the surface layer of the solution surrounding the solid. It is important to emphasize that the color change is an adsorption (not a precipitation) process, because the solubility product of silver fluoresceinate is never exceeded. The adsorption is reversible, the dye being desorbed on back-titration with chloride ion.

Titrations involving adsorption indicators are rapid, accurate, and reliable, but their application is limited to the relatively few precipitation reactions in which a colloidal precipitate is formed rapidly.

7.7 Volhard's Method

The most important application of the Volhard's method is the indirect determination of halide ions. A measured excess of standard silver nitrate solution is added to the sample, and the excess silver is determined by back-titration with a standard thiocyanate solution.

At the beginning the following reaction takes place:

$$Ag^+ + Cl^- \rightleftharpoons AgCl_{(s)}\downarrow$$

Then the excess Ag^+ ions are determined by titration with standard solution of KSCN.

$$Ag^+ + SCN^- \rightleftharpoons AgSCN_{(s)}$$

When all the Ag^+ ions are reacted SCN^- ions, the first excess drop of SCN^- will react with iron(III) ions of the indicator forming red complex indicating the end point of the reaction.

$$Fe^{3+} + SCN^- \rightleftharpoons \underset{\text{red}}{[Fe(SCN)]^{2+}} \qquad K_f = 1.05 \times 10^3 = \frac{[Fe(SCN)]^{2+}}{[Fe^{3+}][SCN^-]}$$

The titration must be carried out in acidic solution to prevent precipitation of iron(III) as the hydrated oxide.

The strong acidic environment required for the Volhard procedure represents a distinct advantage over other titrimetric methods of halide analysis because such ions as carbonate, oxalate, and arsenate (which form slightly soluble silver salts in neutral media but not in acidic media) do not interfere.

Silver chloride is more soluble than silver thiocyanate. As a consequence, in chloride determinations by the Volhard method, the reaction:

$$AgCl_{(s)} + SCN^- \rightleftharpoons AgSCN_{(s)} + Cl^-$$

occurs to a significant extent near the end of the back-titration of the excess silver ion. This reaction causes the end point to fade and results in an overconsumption of thiocyanate ion, which in turn leads to low values for the chloride analysis. This error can be circumvented by filtering the silver chloride before undertaking the back-titration. Filtration is not required in the determination of other halides because they all from silver salts that are less soluble than silver thiocyanate. We can also heat the solution containing the precipitate to collect the particles together, or adding some organic solvent such as nitrobenzene or chloroform, which covers the AgCl precipitate in the bottom of conical flask and shields it from the aqueous medium which contains the excess Ag^+.

Another application for Volhard’s method is to determine $AgNO_3$ concentration by direct titration with thiocyanate using iron(III) ions as indicator.

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Analytical Chemistry

College of Pharmacy - Universty of Anbar / First Year 2021 - 2022

Dr. Jasim H. Hassen

Chapter 8

Complex-Formation Titration

8.1 Introduction

Most metal ions react with electron-pair donors to form coordination compounds or complexes. The donor species, or ***ligand***, must have at least one pair of unshared electrons available for bond formation. Water, ammonia, and halide ions are common inorganic ligands. In fact, most metal ions in aqueous solution actually exist as aquo complexes. Copper(II) in aqueous solution, for example, is readily complexed by water molecules to form species such as $Cu(H_2O)_4^{2+}$. We often simplify such complexes in chemical equations by writing the metal ion as if it were uncomplexed Cu^{2+}. Remember that such ions are actually aquo complexes in aqueous solution.

The number of covalent bonds that a cation tends to form with electron donors is its ***coordination number***. Typical values for coordination number are 2, 4, and 6. The species formed as a result of coordination can be electrically positive, neutral, or negative. For example, copper(II), which has a coordination number of 4, forms a cationic ammine complex, $Cu(NH_3)_4^{2+}$; a neutral complex with glycine, $Cu(NH_2CH_2COO)_2$; and an anionic complex with chloride ion, $CuCl_4^{2-}$.

Titrimetric methods based on complex formation, sometimes called ***complexometric*** methods, have been used for more than a century. The truly remarkable growth in their analytical application, based on a particular class of coordination compounds called ***chelates***. A chelate is produced when a metal ion coordinates with two or more donor groups of a single ligand to form a five- or six-member heterocyclic ring. The copper complex of glycine mentioned is an example. Here, the copper bonds to both the oxygen of the carboxyl group and the nitrogen of the amine group.

A ligand that has a single donor group, such as ammonia, is called ***unidentate*** (single-toothed), whereas one such as glycine, which has two groups available for covalent bonding, is called ***bidentate***. Tridentate, tetradentate, pentadentate, and hexadentate chelating agents are also known.

Another important type of complex is formed between metal ions and cyclic organic compounds, known as ***macrocycles***. These molecules contain nine or more atoms in the cycle and include at least three heteroatoms, usually oxygen, nitrogen, or sulfur.

8.2 Complexation Equilibria

Complexation reactions involve a metal ion M reacting with a ligand L to form a complex ML, as shown in the equation:

$$M + L \rightleftharpoons ML \qquad \ldots\ldots\ldots 1)$$

Where the charges on the ions are omitted so as to be general. Complexation reactions occur in a stepwise fashion; the reaction in equation 1 is often followed by additional reactions:

$$ML + L \rightleftharpoons ML_2 \qquad \ldots\ldots\ldots 2)$$

$$ML_2 + L \rightleftharpoons ML_3 \qquad \ldots\ldots\ldots 3)$$

$$ML_{n-1} + L \rightleftharpoons ML_n \qquad \ldots\ldots\ldots 4)$$

Unidentate ligands invariably add in a series of steps, as shown here. With multidentate ligands, the maximum coordination number of the cation may be satisfied with only one ligand or a few added ligands. For example, Cu(II), with a maximum coordination number of 4, can form complexes with ammonia that have formulas $Cu(NH_3)^{2+}$, $Cu(NH_3)_2^{2+}$, $Cu(NH_3)_3^{2+}$, and $Cu(NH_3)_4^{2+}$. With the bidentate ligand glycine (gly), the only complexes that form are $Cu(gly)^{2+}$ and $Cu(gly)_2^{2+}$.

The equilibrium constants for complex formation reactions are generally written as formation constants. Thus, each of the reactions 1 through 4 is associated with a stepwise formation constant K_1 through K_4. For example, $K_1 = [ML]/[M][L]$, $K_2 = [ML_2]/[ML][L]$, and so on. We can also write the equilibria as the sum of individual steps. These have overall formation constants designated by the symbol β_n. Thus,

$$M + L \rightleftharpoons ML \qquad \beta_1 = \frac{[ML]}{[M][L]} = K_1 \quad \ldots\ldots\ldots\ldots5)$$

$$M + 2L \rightleftharpoons ML_2 \qquad \beta_2 = \frac{[ML_2]}{[M][L]^2} = K_1\, K_2 \quad \ldots\ldots\ldots6)$$

$$M + 3L \rightleftharpoons ML_3 \qquad \beta_3 = \frac{[ML_3]}{[M][L]^3} = K_1\, K_2\, K_3 \quad \ldots\ldots7)$$

$$M + nL \rightleftharpoons ML_n \qquad \beta_n = \frac{[ML_n]}{[M][L]^n} = K_1\, K_2 \ldots\ldots K_n \;\ldots8)$$

Except for the first step, the overall formation constants are products of the stepwise formation constants for the individual steps leading to the product.

8.3 Titrations with Inorganic Complexing Agents

Complexation reactions have many uses in analytical chemistry, but their classical application is in ***complexometric titrations***. Here, a metal ion reacts with a suitable ligand to form a complex, and the equivalence point is determined by an indicator or an appropriate instrumental method. The formation of soluble inorganic complexes is not widely used for titrations, but the formation of precipitates, particularly with silver nitrate as the titrant, is the basis for many important determinations.

The progress of a complexometric titration is generally illustrated by the titration curve, which is usually a plot of pM = -log [M] as a function of the volume of titrant added. Most often, in complexometric titration the ligand is the titrant and the metal ion the analyte, although occasionally the reverse is true. Most simple inorganic ligands are unidentate, which can lead to low complex stability and indistinct titration end points. As titrants, multidentate ligands, particularly those having four or six donor groups, have two advantageous over their unidentate counterparts. First, they generally react more completely with cations and thus provide sharper end points.

Second, they ordinarily react with metal ions in a single-step process, whereas complex formation with unidentate ligands involves two or more intermediate species.

The advantage of a single-step reaction is illustrated by the titration curves shown in Figure 8-1. Each of the titrations involves a reaction that has an overall equilibrium constant of 10^{20}. Curve *A* is derived for a reaction in which a metal ion M having a coordination number of 4 reacts with a tetradentate ligand D to form the complex of MD. (We have again omitted the charges on the two reactants for convenience). Curve *B* is for the reaction of M with a hypothetical bidentate ligand B to give MB_2 in two steps. The formation constant for the first step is 10^{12} and for the second 10^8. Curve *C* involves a unidentate ligand A that forms MA_4 in four steps with successive formation constant of 10^8, 10^6, 10^4, and 10^2. These curves demonstrate that a much sharper end point is obtained with a reaction that takes place in a single step. For this reason, multidentate ligands are ordinarily preferred for complexometric titration.

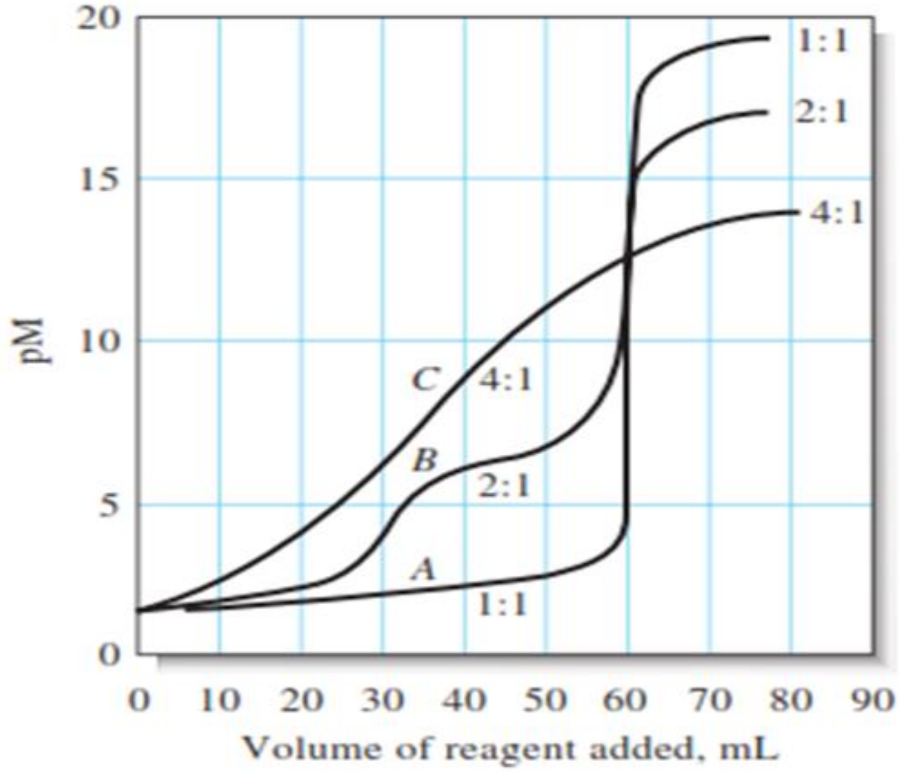


Figure 8-1 Titration Curves for Complexometric Titrations. Titration of 60.0 mL of a solution that is 0.020 M in metal M with (A) a 0.020 M solution of the tetradentate ligand D to give MD as the product; (B) a 0.040 M solution of the bidentate ligand B to give MB_2; and (C) a 0.080 M solution of the unidentate ligand A to give MA_4. The overall formation constant for each product is 10^{20}.

The most widely used complexometric titration employing a unidentate ligand is the titration of cyanide with silver nitrate. This method involves the formation of the soluble $Ag(CN)_2^-$. Other titrant are $Hg(NO_3)_2$ for analyte Br^-, Cl^-, SCN^-, CN^-, thiourea, and $NiSO_4$ for CN^-, and KCN for Cu^{2+}, Hg^{2+}, Ni^{2+}.

8.4 Organic Complexing Agents

Many different organic complexing agents have become important in analytical chemistry because of their inherent sensitivity and potential selectivity in reacting with metal ions. Such reagents are particularly useful in precipitating metals, in binding metals to prevent interferences, in extracting metals from one solvent to another, and in forming complexes that absorb light for spectrophotometric determinations. The most useful organic reagents form chelate complexes with metal ions.

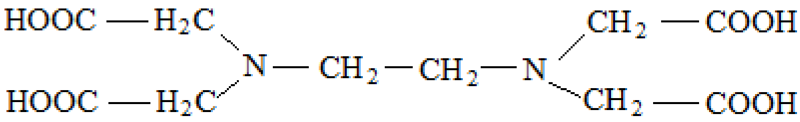
Many organic reagents are used to convert metal ions into forms that can be readily extracted from water into an immiscible organic phase as shown in Table 8-1.

Table 8-1 Organic Reagents for Extracting Metals

Reagent	**Metal Ions Extracted**	**Solvents**
8-Hydroxyquinoline	Zn^{2+}, Cu^{2+}, Ni^{2+}, Al^{3+}	Water → $CHCl_3$
Diphenylthiocarbazone	Cd^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}	Water → $CHCl_3$, or CCl_4
Acetylacetone	Fe^{3+}, Cu^{2+}, Zn^{2+}, U(VI)	Water → $CHCl_3$, CCl_4,or C_6H_6
Ammonium pyrrolidine dithiocarbamate	Transition metals	Water→ Methyl isobutyl ketone

** Ethylenediaminetetraacetic acid (EDTA)*

It is the most widely used complexometric titrant. EDTA has the structural formula:



The EDTA molecule has six potential sites for bonding a metal ion: the four carboxylic groups and the two amino groups, each of the latter with an unshared pair of electrons. Thus, EDTA is a hexadentate ligand.

The dissociation constants for the acidic groups in EDTA are $K_1 = 1.02 \times 10^{-2}$, $K_2 = 2.14 \times 10^{-3}$, $K_3 = 6.92 \times 10^{-7}$, and $K_4 = 5.50 \times 10^{-11}$. It is of interest that the first two constants are of the same order of magnitude, which suggests that the two protons involved dissociate from opposite ends of the rather long molecule. As a consequence of their physical separation, the negative charge created by the first dissociation does not greatly affect the removal of the second proton. The same cannot be said for the dissociation of the other two protons, however, which are much closer to the negatively charged carboxylate ions created by the initial dissociations.

The various EDTA species are often abbreviated H_4Y, H_3Y^-, H_2Y^{2-}, HY^{3-}, and Y^{4-}.

*** Reagents for EDTA titration***

The free acid H_4Y and the dihydrate of the sodium salt, $Na_2H_2Y.2H_2O$, are commercially available in reagent quality. The former can serve as a primary standard after it has been dried for several hours at 130°C to 145°C. It is then dissolved in the minimum amount of base required for complete solution.

*** Complexes of EDTA and metal ions***

Solutions of EDTA are particularly valuable as titrants because the reagent combines with metal ion in a 1:1 ratio regardless of the charge on the cation. For example, the silver and aluminum complexes are formed by the reactions:

$$Ag^+ + Y^{4-} \rightleftharpoons AgY^{3-}$$

$$Al^{3+} + Y^{4-} \rightleftharpoons AlY^-$$

EDTA is a remarkable reagent not only because it forms chelates with all cations except alkali metals but also because most of these chelates are sufficiently stable for titrations. This great stability result from the several complexing sites within the molecule that give rise to a cage-like structure, in which the cation is surrounded by and isolated from solvent molecules.

*** Effect of other complexing agents on EDTA**

Many EDTA titrations are complicated by the tendency on the part of the ion being titrated to precipitate as a basic oxide or hydroxide at the pH required for satisfactory titration. In order to keep the metal ion in solution, particularly in the early stage of the titration, it is necessary to include an auxiliary complexing agent. Thus, for example, the titration of zinc(II) is ordinary performed in the presence of high concentrations of ammonia and ammonium chloride. These species buffer the solution to an acceptable pH. In addition, the ammonia prevents precipitation of zinc hydroxide by forming ammine complexes. The titration reaction with EDTA is thus best represented as:

$$Zn(NH_3)_4^{2+} + HY^{3-} \rightleftharpoons ZnY^{2-} + 3NH_3 + NH_4^+$$

The solution also contains such other zinc/ammonia species as $Zn(NH_3)_3^{2+}$, $Zn(NH_3)_2^{2+}$, and $Zn(NH_3)^{2+}$. Calculation of pZn in a solution that contains ammonia must take these species into account. Qualitatively, complexation of a cation by an auxiliary complexing reagent causes preequivalence pM values to be larger than in a comparable solution with no such reagent.

*** Indicators for EDTA titrations**

Nearly 200 organic compounds have been investigated as indicators for metal ions in EDTA titrations. In general these indicators are organic dyes that form colored chelate with metal ions in a pM range that is characteristic of the particular cation dye. The complexes are often intensely colored and are discernible to the eye at concentrations in the range of 10^{-6} to 10^{-7} M.

Eriochrome Black T is a typical metal ion indicator that is used in the titration of several common cations. Its behavior as a weak acid is described by the equations:

$$H_2O + \underset{\text{red}}{H_2In^-} \rightleftharpoons \underset{\text{blue}}{HIn^{2-}} + H_3O^+ \qquad K_1 = 5 \times 10^{-7}$$

$$H_2O + \underset{\text{blue}}{HIn^{2-}} \rightleftharpoons \underset{\text{orange}}{In^{3-}} + H_3O^+ \qquad K_2 = 2.8 \times 10^{-12}$$

Note that the acids and their conjugate bases have different colors. Thus, Eriochrome Black T behaves as an acid-base indicator as well as a metal ion indicator.

The metal complexes of Eriochrome Black T are generally red, as is H_2In^-. Thus, for metal ion detection, it is necessary to adjust the pH to 7 or above so that the blue form of the species, HIn^{2-}, predominates in the absence of a metal ion. Until the equivalence point in a titration, the indicator complexes the excess metal ion so that the solution is red. With the first slight excess of EDTA, the solution turns blue as a consequence of the reaction:

$$\underset{\text{red}}{MIn^-} + HY^{3-} \rightleftharpoons \underset{\text{blue}}{HIn^{2-}} + MY^{2-}$$

Eriochrome Black T forms red complexes with more than two dozen metal ions, but the formation constant of only a few are appropriate for end point detection.

8.5 The Scope of EDTA Titrations

Complexometric titrations with EDTA have been applied to the determination of virtually every metal cation, with the exception of the alkali metal ions. Because EDTA complexes most cations, the reagent might appear at first glance to be totally lacking in selectivity. In fact, however, considerable control over interferences can be realized by pH regulation. For example, trivalent cations can usually be titrated without interference from divalent species by maintaining the solution at a pH of about 1. At this pH, the less stable divalent chelates do not form to any significant extent, but the trivalent ions are quantitatively complexed.

Similarly, ions such as cadmium and zinc, which form more stable EDTA chelate than does magnesium, can be determined in the presence of the latter ion by buffering the mixture to a pH of 7 before titration. Eriochrome Black T serves as an indicator for the cadmium or zinc end points without interference from magnesium because the indicator chelate with magnesium is not formed at this pH.

Finally, interference from a particular cation can sometimes be eliminated by adding a suitable masking agent, an auxiliary ligand that preferentially forms highly stable complexes with the potential interfering ion. Thus, cyanide ion is often employed as a masking agent to permit the titration of magnesium and calcium ions in the presence of ions such as cadmium, cobalt, copper, nickel, zinc, and palladium. All of the latter form sufficiently stable cyanide complexes to prevent reaction with EDTA

8.6 The Determination of Water Hardness

Water hardness was defined in terms of the capacity of cations in the water to replace the sodium or potassium ions in soaps and to form sparingly soluble products that cause scum in the sink or bathtub. Most multiply charged cations share this undesirable property. In natural waters, the concentrations of calcium and magnesium ions generally far exceed those of any other metal ion. Consequently, hardness is now expressed in terms of the concentration of calcium carbonate that is equivalent to the total concentration of all the multivalent cations in the sample.

The determination of hardness is a useful analytical test that provides a measure of the quality of water for household and industrial uses. The test is important to industry because hard water, on being heated, precipitates calcium carbonate, which clogs boilers and pipes.

Water hardness is ordinarily determined by EDTA titration after the sample has been buffered to pH 10. Magnesium, which forms the least stable EDTA complex of all of the common multivalent cations in typical water samples, is not titrated until enough reagent has been added to complex all of the other cations in the sample. Therefore, a magnesium ion indicator, such as Calmagite or Eriochrome Black T, can serve as indicator in water hardness titrations. Often, a small concentration of the magnesium-EDTA chelate is incorporated into the buffer or the titrant to ensure sufficient magnesium ions for satisfactory indicator action.

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Dr. Jasim H. Hassen

Chapter 9

Oxidation-Reduction Titration

9.1 Equilibria in Oxidation-Reduction system

Oxidation-reduction, or redox, processes involve the transfer of electrons from one reactant to another. Volumetric methods based upon electron transfer are more numerous and more varied than those for any other reaction type.

Oxidation involves the loss of electrons by a substance and reduction the gain of electrons. In any oxidation-reduction reaction, the molar ratio between the substance oxidized and the substance reduced is such that the number of electrons lost by one species is equal to the number gained by the other. This fact must always be taken into account when balancing equations for oxidation-reduction reactions.

Oxidizing agents or oxidants possess a strong affinity for electrons and cause other substances to be oxidized by abstracting electrons from them. In the process, the oxidizing agent accepts electrons and is thereby reduced. Reducing agents or reductants have little affinity for electrons and, in fact, readily give up electrons thereby causing some other species to be reduced. A consequence of this electrons transfer is the oxidation of the reducing agent.

Separation of an oxidation-reduction reaction into its component parts (that is, into half-reactions) is a convenient way of indicating clearly the species that gains electrons and the one that losses them. Thus, the overall reaction:

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightleftharpoons 5Fe^{3+} + Mn^{2+} + 4H_2O$$

is obtained by combining the half-reaction for the oxidation of iron(II):

$$5Fe^{2+} \rightleftharpoons 5Fe^{3+} + 5e^-$$

with that for the reduction of permanganate:

$$MnO_4^- + 5e^- + 8H^+ \rightleftharpoons Mn^{2+} + 4H_2O$$

Note that it was necessary to multiply the first half-reaction through by 5 to eliminate the electrons from the overall equation.

9.2 Balancing of Redox Equations

The redox equations can be balanced by two methods:

* *The change in oxidation numbers method*

By this method we follow the rules:

1- Determine the oxidation numbers for all the elements involved in the reaction.

2- From the oxidation numbers determine the oxidizing and reducing agents.

3- Count the difference in the oxidation numbers from the oxidizing and reducing agents, and according to it chose the numbers for alternate multiplication, in order to equalize the number of lost and gained electrons.

4- Balance the other ions that did not change.

Example 1

Balance the following equation:

$$KMnO_4 + NH_3 \longrightarrow KNO_3 + MnO_2 + KOH + H_2O$$

We determine the oxidation numbers:

$$KMnO_4 + NH_3 \longrightarrow KNO_3 + MnO_2 + KOH + H_2O$$

+1 +7 (-2)4 -3 (+1)3 +1 +5 (-2)3 +4 (-2)2 +1 -2 +1 (+1)2 -2

Note the change in the manganese and nitrogen oxidation numbers.

$$\begin{tikzcd}
Mn^{7+} \arrow[r] & Mn^{4+} & \text{the change } (-3) \arrow[ddl] \\
& & \text{(alternate multiplication)} \\
N^{3-} \arrow[r] & N^{5+} & \text{the change } (+8) \arrow[uul]
\end{tikzcd}$$

To maintain the total number of oxidation numbers, we need 8 manganese atoms for each 3 nitrogen atoms.

$$8KMnO_4 + 3NH_3 \longrightarrow 3KNO_3 + 8MnO_2 + KOH + H_2O$$

The oxidation number of potassium did not change, so we balance it and also we balance the oxygen and hydrogen atoms.

$8KMnO_4 + 3NH_3 \longrightarrow 3KNO_3 + 8MnO_2 + 5KOH + 2H_2O$

**** The ion-electron method***

To use this method we follow the rules:

1- Divide the reaction to oxidation reaction and reduction reaction, and write it in ionic form.

2- Balance the number of atoms for each half-reaction.

3- Balance each half-reaction electrically by the addition of a suitable number of electrons to the more electropositive side.

4 - The number of electrons in each half-reaction must be equal, if not use the alternate multiplication.

5- Add the two balanced half reactions to each other.

6- The molecular equation can be obtained from the ionic equation by addition of ions with the reactants and distribute it over the products.

7- We may need to add water molecules or its ions (H^+, OH^-) to balance the equation.

Example 2

Balance the following equation:

$K_2Cr_2O_7 + FeCl_2 + HCl \longrightarrow CrCl_3 + FeCl_3 + H_2O + KCl$

The equation in the ionic form is:

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

The reduction half-reaction is:

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

To balance the number of atoms we multiply Cr^{3+} by 2, water by 7, and hydrogen by 14, the equation becomes:

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

Now we balance the electrons on each side of the reaction. The number of positive charges in the reactants is 12 and in the products is 6 only, and to reduce 12 positive charges to 6 we need to add 6 electrons to the reaction:

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

The number of atoms and charges in this half reaction is balanced.

The oxidation half-reaction is:

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

The number of atoms is equal, but the number of charges is not, and to balance it we add 1 electron to the more electropositive side.

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

and to make the number of electrons equal we multiply the last equation by 6, then add the two equations:

$$\begin{array}{l} Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \\ 6Fe^{2+} \longrightarrow 6Fe^{3+} + 6e^- \\ \hline Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \end{array} \quad \text{addition}$$

To obtain the molecular equation, we add the other ions and distribute it over the products:

$$K_2Cr_2O_7 + 6FeCl_2 + 14HCl \longrightarrow 2CrCl_3 + 6FeCl_3 + 7H_2O + 2KCl$$

9.3 Auxiliary Oxidizing and Reducing Reagents

The analyte in an oxidation-reduction titration must be in a single oxidation state at the outset. Often, the steps that precede the titration, such as dissolving the sample and separating interferences, convert the analyte to a mixture of oxidation states. For example, when a sample containing iron is dissolved, the resulting solution usually contains a mixture of iron(II) and iron(III) ions. If we choose to use a standard oxidant to determine iron, we must first treat the sample solution with an auxiliary reducing agent to convert all of the iron to iron(II). If we plan to titrate with a standard reductant, however, pretreatment with an auxiliary oxidizing reagent is needed.

To be useful as a preoxidant or a prereductant, a reagent must react quantitatively with the analyte. In addition, any reagent excess must be easily removable because the excess reagent usually interferes with the titration by reacting with the standard solution.

9.4 Auxiliary Reducing Reagents

A number of metals are good reducing agents and have been used for the preredution of analytes. Included among these are zinc, aluminum, cadmium, lead, nickel, copper, and silver (in the presence of chloride ion). Sticks or coil of the metal can be immersed directly in the analyte solution. After reduction is judged complete, the solid is removed manually and rinsed with water. The analyte solution must be filtered to remove granular or powdered forms of the metal. An alternative to filtration is the use of a redactor, such as Jones redactor, which has a diameter of about 2 cm and holds a 40 to 50 cm column of amalgamated zinc.

Zinc can be amalgamated by allowing its granules to stand briefly in a solution of mercury(II) chloride, where the following reaction occurs:

$$2Zn_{(s)} + Hg^{2+} \longrightarrow Zn^{2+} + Zn(Hg)_{(s)}$$

Zinc amalgam is nearly as effective for reduction as the pure metal and has the important virtue of inhibiting the reduction of hydrogen ions by zinc. This side reaction needlessly uses up the reducing agent and also contaminates the sample solution with a large amount of zinc(II) ions. Solutions that are quite acidic can be passed through a redactor without significant hydrogen formation.

9.5 Auxiliary Oxidizing Reagents

** Sodium Bismuthate*

Sodium bismuthate is a powerful oxidizing agent capable, for example, of converting manganese(II) quantitatively to permanganate ion. This bismuth salt is a sparingly soluble solid with a formula that is usually written as $NaBiO_3$, although its exact composition is somewhat uncertain. Oxidations are performed by suspending the bismuthate in the analyte solution and boiling for brief period. The unused reagent is then removed by filtration. The half-reaction for the reduction of sodium bismuthate can be written as:

$$NaBiO_{3(s)} + 4H^+ + 2e^- \rightleftharpoons BiO^+ + Na^+ + 2H_2O$$

** Ammonium Peroxydisulfate*

Ammonium peroxydisulfate, $(NH_4)_2S_2O_8$, is also a powerful oxidizing agent. In acidic solution, it convert chromium(III) to dichromate, cerium(III) to cerium(IV), and manganese(II) to permanganate. The half-reaction is:

$$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$$

The oxidations are catalyzed by trace of silver ion. The excess reagent is easily decomposed by a brief period of boiling:

$$2S_2O_8^{2-} + 2H_2O \rightleftharpoons 4SO_4^{2-} + O_{2(g)} + 4H^+$$

** Sodium Peroxide and Hydrogen Peroxide*

Peroxide is a convenient oxidizing agent either as the sodium salt or as a dilute solution of the acid. The half-reaction for hydrogen peroxide in acidic solution is:

$$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$$

After oxidation is complete, the solution is freed of excess reagent by boiling:

$$2H_2O_2 \longrightarrow 2H_2O + O_{2(g)}$$

9.6 Applying Standard Reducing Agents

Standard solutions of most reductants tend to react with atmospheric oxygen. For this reason, reductants are seldom used for direct titration of oxidizing analytes; indirect methods are used instead. The two most common reductants are iron(II) and thiosulfate ions.

** Iron(II) solutions*

Solutions of iron(II) are easily prepared from iron(II) ammonium sulfate, $Fe(NH_4)_2(SO_4)_2.6H_2O$ (Mohr's salt), or from the closely related iron(II) ethylenediamine sulfate $FeC_2H_4(NH_3)_2(SO_4)_2.4H_2O$ (Oesper's salt). Air oxidation of iron(II) takes place rapidly in neutral solutions but is inhibited in the presence of acids, with most stable preparations being about 0.5 M in H_2SO_4. Such solutions are stable for no more than one day. Numerous oxidizing agents are conveniently determined by treatment of the analyte solution with a measured excess of standard iron(II) followed by immediate titration of the excess with a standard solution of potassium dichromate or cerium(IV). Just before or just after the analyte is titrated, the volumetric ratio between the standard oxidant and the iron(II) solution is established by titrating two or three aliquots of the latter with former.

This procedure has been applied to the determination of organic peroxides; hydroxylamine; chromium(VI); cerium(IV); molybdenum(VI); nitrate, chlorate, and perchlorate ions; and numerous other oxidants.

** Sodium Thiosulfate*

Thiosulfate ion ($S_2O_3^{2-}$) is a moderately strong reducing agent that has been widely used to determine oxidizing agents by an indirect procedure that involves iodine as an intermediate. With iodine, thiosulfate ion is oxidized quantitatively to tetrathionate ion ($S_4O_6^{2-}$) according to half-reaction:

$$2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e^-$$

The quantitative reaction with iodine is unique. Other oxidants can oxidize the tetrathionate ion to sulfate ion.

The scheme used to determine oxidizing agents involves adding an unmeasured excess of potassium iodide to a slightly acidic solution of the analyte. Reduction of the analyte produces a stoichiometrically equivalent amount of iodine. The liberated iodine is then titrated with a standard solution of sodium thiosulfate, $Na_2S_2O_3$, one of the few reducing agents that is stable toward air oxidation. An example of this procedure is the determination of sodium hypochlorite in bleaches. The reactions are:

$$OCl^- + 2I^- + 2H^+ \longrightarrow Cl^- + I_2 + H_2O \quad \text{(unmeasured excess KI)}$$

$$I_2 + S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

The quantitative conversion of thiosulfate ion to tetrathionate ion requires a pH smaller than 7. If strongly acidic solution must be titrated, air oxidation of the excess iodide must be prevented by blanking the solution with an inert gas, such as carbon dioxide or nitrogen.

****Detecting end points in iodine-thiosulfate titration***

A solution that is about 5×10^{-6} M in I_2 has a discernible color, which corresponds to less than one drop of a 0.05 M iodine solution in 100 mL. Thus, provided that the analyte solution is colorless, the disappearance of the iodine color can serve as the indicator in titrations with sodium thiosulfate.

More commonly, titrations involving iodine are performed with a suspension of starch as an indicator. The deep blue color that develops in the presence of iodine is believed to rise from the absorption of iodine into the helical chain of β-amylose, a macromolecular component of most starches. The closely related α-amylose forms a red adduct with iodine. This reaction is not easily reversible and is thus undesirable. In commercially available soluble starch, the alpha fraction has been removed to leave principally β-amylose; indicator solutions are easily prepared from this product.

Aqueous starch suspensions decompose within a few days, primarily because of bacterial action. The decomposition products tend to interfere with the indicator properties of the preparation and may also be oxidized by iodine. The rate of decomposition can be inhibited by preparing and storing the indicator under sterile conditions and by adding mercury(II) iodide or chloroform as a bacteriostat.

Standardizing thiosulfate solution

Potassium iodate is an excellent primary standard for thiosulfate solutions. In this application, weighed amounts of primary-standard grade reagent are dissolved in water containing an excess of potassium iodide. When this mixture is acidified with a strong acid, the following reaction occurs instantaneously:

$$IO_3^- + 5I^- + 6H^+ \rightleftharpoons 3I_2 + 2H_2O$$

The liberated iodine is then titrated with the thiosulfate solution. The stoichiometry of the reaction is:

$$1 \text{ mol } IO_3^- = 3 \text{ mol } I_2 = 6 \text{ mol } S_2O_3^{2-}$$

Other primary standards for sodium thiosulfate are potassium dichromate, potassium bromate, potassium hydrogen iodate, potassium hexacyanoferrate(III), and metallic copper. All these compounds liberate stoichiometric amounts of iodine when treated with excess potassium iodide.

9.7 Applying Standard Oxidizing Agents

The choice among oxidizing agents depends on the strength of the analyte as a reducing agent, the rate of reaction between oxidant and analyte, the stability of the standard oxidant solutions, the cost, and the availability of a satisfactory indicator.

** The strong oxidants–potassium permanganate and cerium(IV)*

Solutions of permanganate ion and cerium(IV) ion are strong oxidizing reagents whose applications closely parallel one another. Half-reactions for the two are:

$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O \quad E^o = 1.51$ V

$Ce^{4+} + e^- \rightleftharpoons Ce^{3+} \qquad E^o = 1.44$ V (1 M H_2SO_4)

The formal potential shown for the reaction of cerium(IV) is for solutions that are 1 M in sulfuric acid. In 1 M perchloric acid and 1 M nitric acid, the potentials are 1.70 V and 1.61 V, respectively. Solutions of cerium(IV) in the latter two acids are not very stable and thus find limited application.

The half-reaction shown for permanganate ion occurs only in solutions that are 0.1 M or greater in strong acid. In less acidic media, the product may be Mn(III), Mn(IV), or Mn(VI), depending on conditions.

Despite some advantages of cerium solutions, like stability, over permanganate solutions, the latter are more widely used. One reason is the color of permanganate solutions, which is intense enough to serve as an indicator in titrations. A second reason for the popularity of permanganate solutions is their modest cost.

Detecting the end points

A useful property of a potassium permanganate solution is its intense purple color, which is sufficient to serve as an indicator for most titrations. If you add as little as 0.01 to 0.02 mL of a 0.02 M solution of permanganate to 100 mL of water, you can perceive the purple color of the resulting solution. If the solution is very dilute, diphenylamine sulfonic acid or the 1,10-phenanthroline complex of iron(II) provides a sharper end point.

The permanganate end point is not permanent because excess permanganate ions react slowly with the relatively larger concentration of manganese(II) ions present at the end point, according to the reaction:

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightleftharpoons 5MnO_{2(s)} + 4H^+$$

The equilibrium constant for this reaction is about 10^{47}, which indicates that the equilibrium concentration of permanganate ion is incredibly small even in highly acidic media. Fortunately, the rate at which this equilibrium is approached is so slow that the end point fades only gradually over a period of perhaps 30 seconds.

Solutions of cerium(IV) are yellow-orange, but the color is not intense enough to act as an indicator in titrations. Several oxidation-reduction indicators are available for titrations with standard solutions of cerium(IV). The most widely used of these is the iron(II) complex of 1,10-phenanthroline or one of its substituted derivatives.

*The preparation and stability of standard solutions

Aqueous solutions of permanganate are not entirely stable because of water oxidation:

$$4MnO_4^- + 2H_2O \longrightarrow 4MnO_{2(s)} + 3O_{2(g)} + 4OH^-$$

Although the equilibrium constant for this reaction indicates that the products are favored, permanganate solutions, when properly prepared, are reasonably stable because the decomposition reaction is slow. It is catalyzed by light, heat, acids, bases, manganese(II), and manganese dioxide.

Moderately stable solutions of permanganate ion can be prepared if the effects of these catalyst, particularly manganese dioxide, are minimized. Manganese dioxide is a contaminant in even the best grade of solid potassium permanganate. Removal of manganese dioxide by filtration before standardization markedly improves the stability of standard permanganate solutions. Before filtration, the reagent solution is allowed to stand for about 24 hours or is heated for a brief period to hasten oxidation of the organic species generally present in small amounts in distilled and deionized water. Paper cannot be used for filtration because permanganate ion reacts with it to form additional manganese dioxide.

Standardized permanganate solutions should be stored in the dark. Filtration and restandardization are required if any solid is detected in the solution or on the walls of the storage bottle. In any event, restandardization every 1 or 2 weeks is a good precautionary measure.

The most widely used compounds for the preparation of solution of cerium(IV) are cerium(IV) ammonium nitrate $Ce(NO_3)_4.2NH_4NO_3$, cerium(IV) ammonium sulfate $Ce(SO_4)_2.2(NH_4)_2SO_4.2H_2O$, cerium(IV) hydroxide $Ce(OH)_4$, Ce(IV) hydrogen sulfate $Ce(HSO_4)_4$. Primary-standard cerium ammonium nitrate is available commercially and can be used to prepare standard solutions of the cation directly by weigh. More commonly, less expensive reagent-grade cerium(IV) ammonium nitrate or ceric hydroxide is used to prepare solutions that are subsequently standardized. In either case, the reagent is dissolved in a solution that is at least 0.1 M in sulfuric acid to prevent the precipitation of basic salts.

Sulfuric acid solutions of cerium(IV) are remarkably stable and can be stored for months or heated at 100°C for prolonged periods without a change in concentration.

Standardizing permanganate and cerium(IV) solutions

Sodium oxalate is a widely used primary standard. In acidic solutions, the oxalate ion is converted to the undissociated acid. Thus, its reaction with permanganate can be described by:

$$2MnO_4^- + 5H_2C_2O_4 + 6H^+ \longrightarrow 2Mn^{2+} + 10CO_{2(g)} + 8H_2O$$

The reaction between permanganate ion and oxalic acid is complex and proceeds slowly even at elevated temperature unless manganese(II) is present as a catalyst. Thus, when the first few milliliters of standard permanganate are added to a hot solution of oxalic acid, several seconds are required before the color of the permanganate ion disappears. As the concentration of manganese(II) builds up, however, the reaction proceeds more and more rapidly as a result of autocatalysis.

Sodium oxalate is also widely used to standardize Ce(IV) solutions. The reaction between Ce^{4+} and $H_2C_2O_4$ is:

$$2Ce^{4+} + H_2C_2O_4 \longrightarrow 2Ce^{3+} + 2CO_{2(g)} + 2H^+$$

Cerium(IV) standardization against sodium oxalate are usually performed at 50°C in a hydrochloric acid solution containing iodine monochloride as a catalyst.

**** Potassium dichromate***

In its analytical applications, dichromate ion is reduced to green chromium(III) ion:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O \qquad E^o = 1.33\ V$$

Dichromate titrations are generally carried out in solutions that are about 1 M in hydrochloric or sulfuric acid. In these media, the formal potential for the half-reaction is 1.0 to 1.1 V.

Potassium dichromate solutions are indefinitely stable, can be boiled without decomposition, and do not react with hydrochloric acid. Moreover, primary standard reagent is available commercially and at modest coast.

****Preparing dichromate Solution***

For most purposes, reagent-grade potassium dichromate is sufficiently pure to permit the direct preparation of standard solutions; the solid is simply dried at 150°C to 200^0C before being weighed.

The orange color of a dichromate solution is not intense enough for use in end point detection. Diphenylamine sulfonic acid is an excellent indicator for titrations with this reagent, however. The oxidized form of the indicator is violet, and its reduced form is essentially colorless; thus, the color change observed in a direct titration is from the green of chromium(III) to violet.

****Applying potassium dichromate solutions***

The principal use of dichromate is the volumetric titration of iron(II) based on the reaction:

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

Often, this titration is performed in the presence of moderate concentration of hydrochloric acid.

The reaction of dichromate with iron(II) has been widely used for the indirect determination of a variety of oxidizing agents. In these applications, a measured excess of an iron(II) solution is added to an acidic solution of the analyte. The excess iron(II) is then back-titrated with standard potassium dichromate. Standardization of the iron(II) solution by titration with the dichromate is performed concurrently with the determination because solution of iron(II) tend to be air oxidized. This method has been applied to the determination of nitrate, chlorite, permanganate, and dichromate ions as well as organic peroxides and several other oxidizing agents.

**** Iodine***

Iodine is a weak oxidizing agent used primarily for the determination of strong reductants. The most accurate description of the half-reaction for iodine in these applications is:

$$I_3^- + 2e^- \rightleftharpoons 3I^- \quad E^o = 0.536\text{ V}$$

where I_3^- is the triiodide ion.

Standard iodine solutions have relatively limited application compared with the other oxidants we have described because of their significantly smaller electrode potential. Occasionally, however, this low potential is advantageous because it imparts a degree of selectivity that makes the determination of strong reducing agents in the presence of weak ones. Iodine solution lack stability, however, and must be restandardized regularly.

****Standardizing and applying iodine solution***

Iodine solutions can be standardized against anhydrous sodium thiosulfate or barium thiosulfate monohydrate, both of which are available commercially. Often, solutions of iodine are standardized against solutions of sodium thiosulfate that have in turn been standardized against potassium iodate or potassium dichromate.

Analytical Chemistry

College of Pharmacy - Universty of Anbar / First Year 2021 - 2022

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Chapter 10

Spectrophotometric Analysis

10.1 Introduction

Measurement based on light and other forms of electromagnetic radiation are widely used throughout analytical chemistry. The interaction of radiation and matter are the subject of the science called ***spectroscopy***. Spectroscopic analytical methods are based on measuring the amount of radiation produced or absorbed by molecular or atomic species of interest.

We can classify spectroscopic methods according to the region of the electromagnetic spectrum involved in the measurement. The regions of the spectrum that have been used include γ-ray, X-ray, ultraviolet (UV), visible, infrared (IR), microwave, and radio-frequency (RF). Indeed, current usage extends the meaning of spectroscopy further to include techniques that do not even involve electromagnetic radiation, such as acoustic, mass, and electron spectroscopy.

10.2 Electromagnetic Radiation

Electromagnetic radiation, or light, is a form of energy whose behavior is described by the properties of both waves and particles. The optical properties of electromagnetic radiation, such as diffraction, are explained best by describing light as a wave. Many of the interactions between electromagnetic radiation and matter, such as absorption and emission, however, are better described by treating light as a particle, or photon. Nevertheless, the dual models of wave and particle behavior provide a useful description for electromagnetic radiation.

10.3 Wave Properties

In dealing with phenomena such as reflection, refraction, interference, and diffraction, electromagnetic radiation is conveniently modeled as wave consisting of perpendicularly oscillating electric and magnetic fields. The electric field for a single-frequency wave oscillates sinusoidally in space and time, as shown in Figure 10-1. The electric field is represented as a vector whose length is proportional to the field strength.

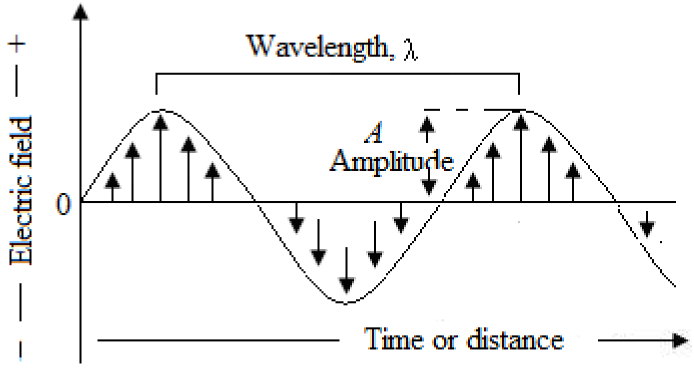

Figure 10-1 Radiation of Wavelength λ and Amplitude A. The arrows represent the electric vector of the radiation.

The *x*-axis in this plot is either time as the radiation passes a fixed point in space or distance at a fixed time. Note that the direction in which the field oscillates is perpendicular to the direction in which the radiation propagates.

10.4 Wave Characteristics

In Figure 10-1, the amplitude of the sine wave is shown, and the wavelength is defined. The time in seconds required for the passage of successive maxima or minima through a fixed point in space is called the ***period***, *p*, of the radiation. The frequency, υ, is the number of oscillations of the electric field vector per unit time and is equal to 1/*p*.

The frequency of a light wave, or any wave of electromagnetic radiation, is determined by the source that emits it and remains constant regardless of the medium traversed. In contrast, the velocity, *v*, of the wave front through a medium depends on both the medium and the frequency. The ***wavelength***, *λ*, is the linear distance between successive maxima or minima of a wave, as shown in Figure 10-1. Multiplication of the frequency (in waves per unit time) by the wavelength (in distance per wave) gives the velocity of the wave, in distance per unit time (cm s^{-1} or m s^{-1}), as shown in the equation:

$$v = \upsilon \lambda \quad \ldots\ldots\ldots 1)$$

Table 10-1 gives the wavelength units for several spectral regions.

Table 10-1 Wavelength Units for Various Regions

Region	Unit	Definition
X-ray	Angstrom, A°	10^{-10} m
Ultraviolet/visible	Nanometer, nm	10^{-9} m
Infrared	Micrometer, µm	10^{-6} m

10.5 The Speed of Light

In a vacuum, light travels at its maximum velocity. This velocity, which is given the special symbol *c*, is 2.99792×10^8 m s^{-1}. The velocity of light in air is only about 0.03% less than its velocity in a vacuum. Thus, for a vacuum or for air, Equation 1 conveniently gives the velocity of light.

$$c = \upsilon \lambda \text{ ....2)}$$

$$= 3.00 \times 10^8 \text{ m s}^{-1} = 3.00 \times 10^{10} \text{ cm s}^{-1}$$

In the medium containing matter, light travels, with a velocity less than *c* because of interaction between the electromagnetic field and electrons in the atoms or molecules of the medium. Since the frequency of the radiation is constant, the wavelength must decrease as the light passes from a vacuum to a medium containing matter.

The wavenumber $\bar{\upsilon}$ is another way to describe electromagnetic radiation. It is defined as the number of waves per centimeter and is equal to $1/\lambda$. By definition, $\bar{\upsilon}$ has the units of cm^{-1}.

10.6 Radiant Power and Intensity

The ***radiant power*** *p* in watts (W) is the energy of a beam that reaches a given area per unit time. The ***intensity*** is the radiant power-per-unit solid angle (Solid angle is the three dimensional spread at the vertex of a cone measured as the area intercepted by the cone on a unit sphere whose center is at the vertex). Both quantities are proportional to the square of the amplitude of the electric field. Although it is not strictly correct, radiation power and intensity are frequently used interchangeably.

10.7 The Particle Nature of Light: Photons

In many radiation/matter interactions, it is most useful to consider light as consisting of photons or quanta. We can relate the energy of a photon to its wavelength, frequency, and wavenumber by:

$$E = h\upsilon = \frac{hc}{\lambda} = hc\bar{\upsilon} \quad \text{.........3)}$$

where *h* is Planck's constant (6.63 × 10^{-34} J s). Note that the wavenumber and frequency, in contrast to the wavelength, are directly proportional to the photon energy. Wavelength is inversely proportional to energy. The radiant power of a beam of radiation is directly proportional to the number of photon per second.

***Example* 1**

Calculate the wavenumber of a beam of infrared radiation with a wavelength of 5.00 µm.

$$\bar{\upsilon} = \frac{1}{5.00\ \mu\text{m} \times 10^{-4}\ \text{cm}/\mu\text{m}} = 2000\ \text{cm}^{-1}$$

Example 2

Calculate the energy in joules of one photon of the radiation, if the wavenumber is 2000 cm^{-1}.

$$\begin{aligned} E &= hc\bar{\upsilon} \\ &= 6.63 \times 10^{-34}\ \text{J.s} \times 3.00 \times 10^{10}\ \text{cm/s} \times 2000\ \text{cm}^{-1} \\ &= 3.98 \times 10^{-20}\ \text{J} \end{aligned}$$

10.8 Interaction of Radiation and Matter

The most interesting types of interactions in spectroscopy involve transitions between different energy levels of chemical species. Other types of interactions, such as reflection, refraction, elastic scattering, interference, and diffraction, are often related to the bulk properties of materials rather than to energy levels of specific molecules or atoms. Although these bulk interactions are also of interest in spectroscopy, we limit our discussion here to those interactions that involve energy-level transitions. The specific types of interactions that we observe depend strongly on the energy of the radiation used and the mode of direction.

10.9 The Electromagnetic Spectrum

The electromagnetic spectrum covers an enormous range of energies (frequencies) and thus wavelengths (Table 10-2). Useful frequencies vary from >10^{19} Hz (γ-ray) to 10^3 Hz (radio waves). An X-ray photon ($\upsilon \approx 3 \times 10^{18}$ Hz, $\lambda \approx 10^{-10}$ m), for example, is approximately 10,000 times as energy as a photon emitted by an ordinary light bulb ($\upsilon \approx 3 \times 10^{14}$ Hz, $\lambda \approx 10^{-6}$ m) and 10^{15} times as energetic as a radio-frequency photon ($\upsilon \approx 3 \times 10^3$ Hz, $\lambda \approx 10^5$m).

The visible portion, to which our eyes respond, is only a minute portion of the entire spectrum. Such different types of radiation as gamma (γ) rays or radio waves differ from visible light in the energy (frequency) of their photons.

Table 10-2 Regions of the UV, Visible, and IR Spectrum

Region	Wavelength Range
UV	180-380 nm
Visible	380-780 nm
Near-IR	0.78-2.5 µm
Mid-IR	2.5-50 µm

Figure10-2 shows the regions of the electromagnetic spectrum that are used for spectroscopic analysis. Also shown are the types of atomic and molecular transition that result from the interactions of the radiation with sample. Note that the low-energy radiation used in nuclear magnetic resonance (NMR) and electron spin resonance (ESR) spectroscopy causes subtle changes, such as changes in spin; the high-energy radiation used in γ-ray spectroscopy can produce much more dramatic effects, such as nuclear configuration changes.

Note that spectrochemical methods that use not only visible but also ultraviolet and infrared radiation are often called optical methods in spite of the fact that the human eye is sensitive to neither of the latter two types of radiation.

10.10 Spectroscopic Measurements

Spectroscopists use the interactions of radiation with matter to obtain information about a sample. Several of the chemical elements were discovered by spectroscopy. The sample is usually stimulated in some way by applying energy in the form of heat, electrical energy, light, particles or a chemical reaction. Prior to applying the stimulus, the analyte is predominantly in its lowest energy state, or ***ground state***. The stimulus then causes some of the analyte species to undergo a transition to a higher energy or ***excited state***. We acquire information about the analyte by measuring the electromagnetic radiation emitted as it returns to the ground state or by measuring the amount of electromagnetic radiation absorbed as a result of excitation.

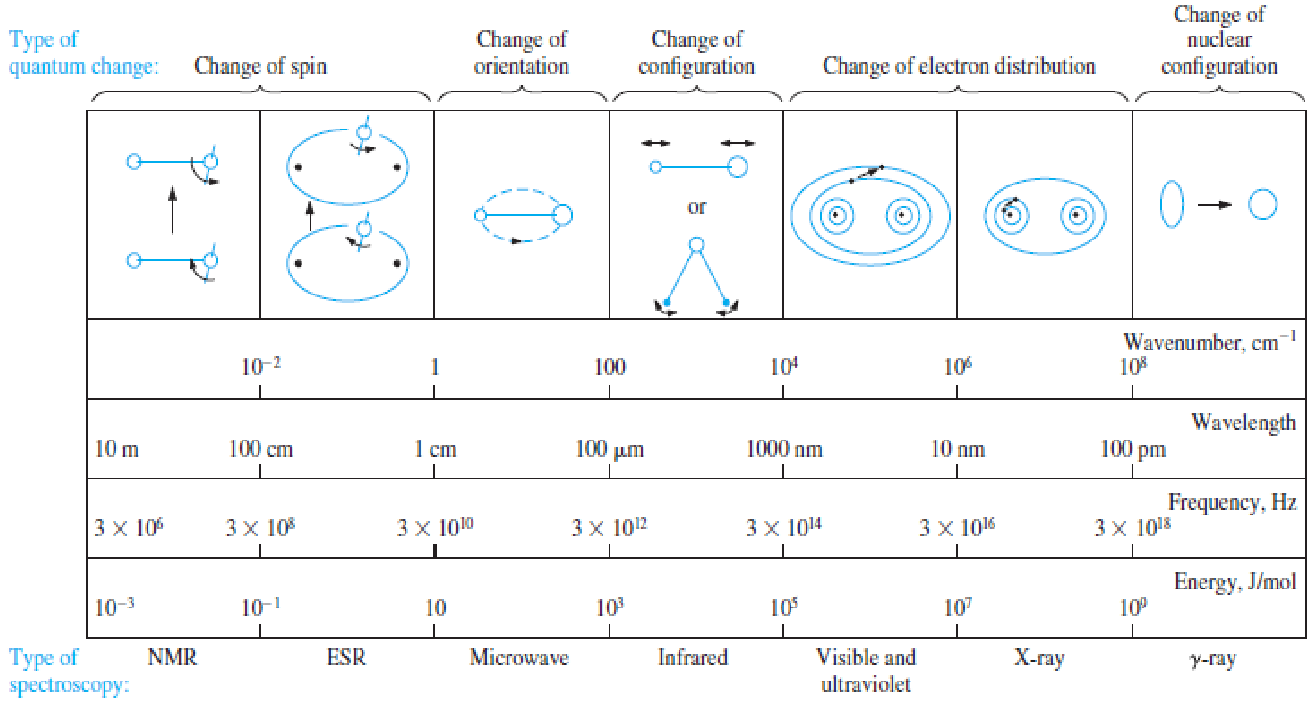

Figure 10-2 The Regions of the Electromagnetic Spectrum. Interaction of an analyte with electromagnetic radiation can result in the types of changes shown.

Figure 10-3 illustrates the processes involved in emission and chemiluminescence spectroscopy. Here, the analyte is stimulated by heat or electrical energy or by a chemical reaction. ***Emission spectroscopy*** involves methods in which the stimulus is heated or electrical energy, while ***chemiluminescence spectroscopy*** refers to excitation of the analyte by a chemical reaction. In both cases, measurement of the radiant power emitted as the analyte returns to the ground state can give information about its identity and concentration. The results of such a measurement are often expressed graphically by a ***spectrum***, which is a plot of the emitted radiation as a function of frequency or wavelength.

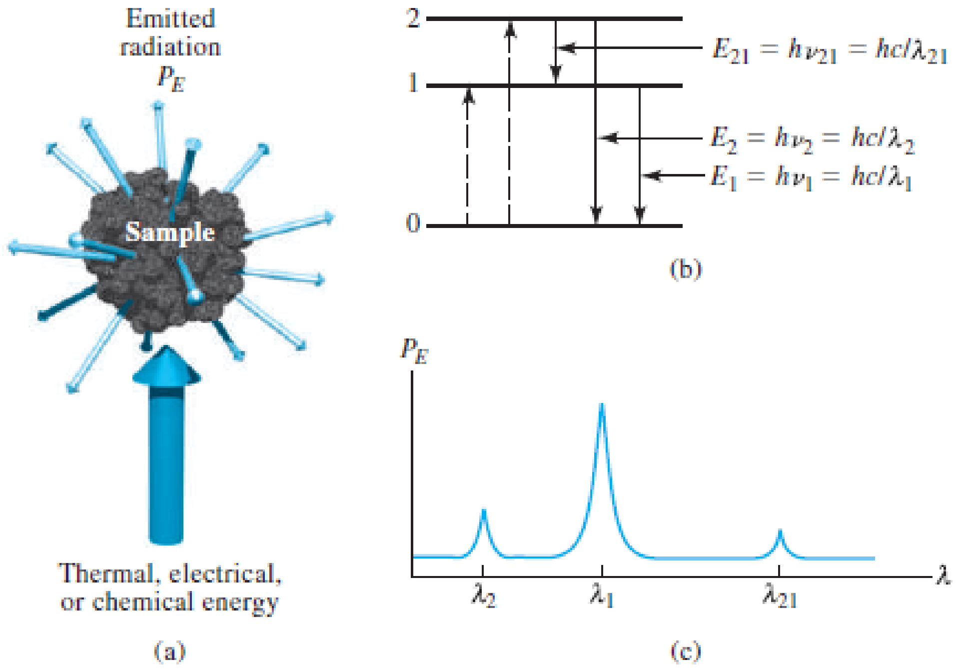

Figure 10-3 Emission or Chemiluminescence Processes. In (a), the sample is excited by the application of thermal, electrical, or chemical energy. These processes do not involve radiant energy and are hence called nonradiative processes. In the energy-level diagram (b), the dashed lines with upward pointing arrows symbolize these nonradiative excitation processes, while the solid lines with downward pointing arrows indicate that the analyte losses its energy by emission of a photon. In (c), the resulting spectrum is shown as a measurement of the radiant power emitted P_E as a function of wavelength, λ.

When the sample is stimulated by application of an external electromagnetic radiation source, several processes are possible. For example, the radiation can be scattered or reflected. What is important to us is that some of the incident radiation can be absorbed and thus promote some of the analyte species to an excited state, as shown in Figure 10-4.

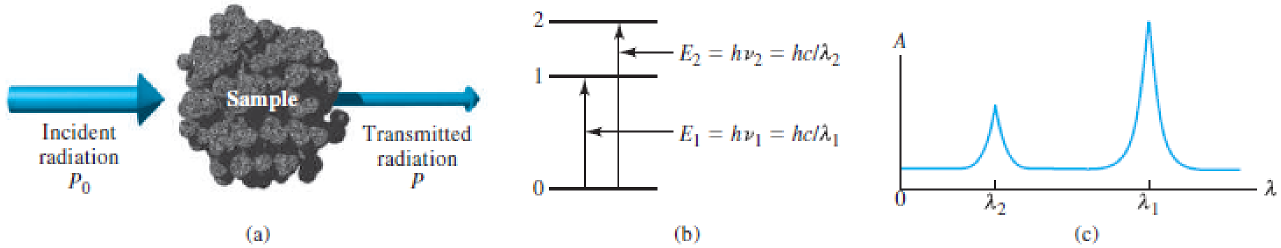

Figure 10-4 Absorption Methods. In (a) radiation of incident radiant power P_0 can be absorbed by the analyte, resulting in a transmitted beam of lower radiant power P. For absorption to occur, the energy of the incident beam must correspond to one of the energy differences shown in (b).The resulting absorption spectrum is shown in (c).

In ***absorption spectroscopy***, we measure the amount of light absorbed as a function of wavelength. In ***photoluminescence spectroscopy*** (Figure 10-5), the emission of photon is measured after absorption. The most important forms of photoluminescence for analytical chemistry purposes are ***fluorescence*** and ***phosphorescence spectroscopy***.

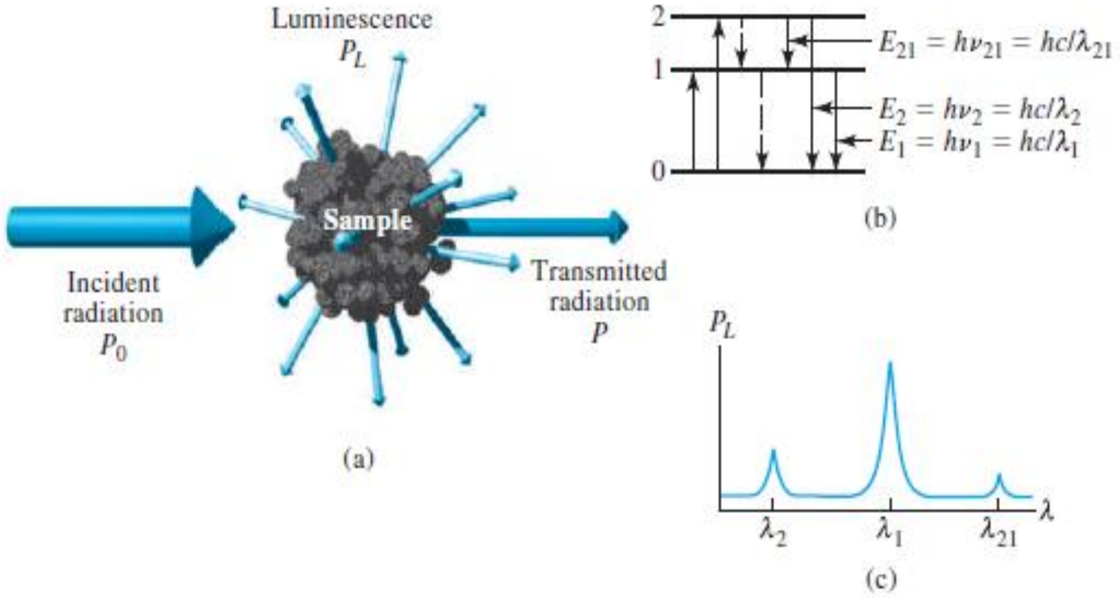

Figure 10-5 Photoluminescence Methods (Fluorescence and Phosphorescence). They result from absorption of electromagnetic radiation and then dissipation of the energy by emission of radiation (a). In (b), the absorption can cause excitation of the analyte to state 1 or state 2. Once excited, the excess energy can be lost by emission of a photon (luminescence, shown as solid line) or by nonradiative processes (dashed lines). The emission occurs over all angles, and the wavelengths emitted (c) correspond to energy differences between levels. The major distinction between fluorescence and phosphorescence is the time scale of emission, with fluorescence being prompt and phosphorescence being delayed.

10.11 The Absorption of Radiation

The absorption law, also known as the ***Beer-Lambert law*** or just ***Beer's law***, tells us quantitatively how the amount of attenuation depends on the concentration of the absorbing molecules and the path length over which absorption occurs. As light traverses a medium containing an absorbing analyte, decreases in intensity occur as the analyte becomes excited. For an analyte solution of a given concentration, the longer the length of the medium through which the light passes (path length of light), the more absorbers are in the path, and the greater the attenuation. Also, for a given path length of the light, the higher the concentration of absorbers, the stronger the attenuation.

Figure 10-6 depicts the attenuation of a parallel beam of ***monochromatic radiation*** as it passes through an absorbing solution of thickness b centimeters and concentration c moles per liter. Because of interaction between the photons and absorbing particles, the radiant power of the beam decreases from P_o to P. The ***transmittance*** T of the solution is the fraction of incident radiation transmitted by the solution. Transmittance is often expressed as a percentage called the percent transmittance.

$$T = P / P_o \quad \ldots\ldots\ldots\ldots.4)$$

The ***absorbance*** A of a solution is related to the transmittance in a logarithmic manner as shown in Equation 5. Notice that as the absorbance of a solution increases, the transmittance decreases.

$$A = - \log T = \log \frac{P_0}{P} \quad \ldots\ldots\ldots.5)$$

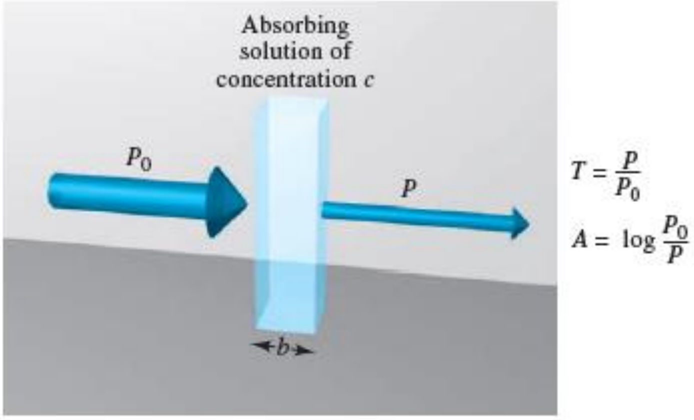

Figure 10-6 Attenuation of a Beam of Radiation by an Absorbing Solution. The larger arrow on the incident beam signifies a higher radiant power than is transmitted by the solution. The path length of the absorbing solution is *b*, and the concentration is *c*.

10.12 Measuring Transmittance and Absorbance

Ordinarily, transmittance and absorbance, as defined by equations 4 and 5, cannot be measured because the solution to be studied must be held in some sort of container (cell or cuvette). Reflection and scattering losses can occur at the cell walls. These losses can be substantial. For example, about 8.5% of the beam of yellow light is lost by reflection when it passes through a glass cell. Light can also be scattered in all directions from the surface of large molecules or particles (such as dust) in the solvent and this scattering can cause further attenuation of the beam as it passes through the solution.

The compensate for these effects, the power of the beam transmitted through a cell containing the analyte solution is compared with one that traverses either an identical cell containing only the solvent or a reagent blank. An experimental absorbance that closely approximates the true absorbance for the solution is thus obtained; that is:

$$A = \log \frac{P_0}{P} \approx \log \frac{P_{\mathrm{solvent}}}{P_{solution}} \quad \ldots\ldots\ldots 6)$$

The term P_0 and P will henceforth refer to the power of a beam that has passed through cells containing the blank (solvent) and the analyte, respectively.

10.13 Beer's Law

According to Beer's law, absorbance is directly proportional to the concentration of the absorbing species c and to the path length b of the absorbing medium, as expressed by Equation 7.

$$A = \log (P_0/P) = abc \quad \ldots\ldots\ldots\ldots 7)$$

Here, a is a proportionality constant called the ***absorptivity***. Because absorbance is a unitless quantity, the absorptivity must have units that cancel the units of b and c. If, for example, c has the units of g L^{-1} and b has the units of cm, absorptivity has the units of L g^{-1} cm^{-1}.

When we express the concentration in Equation 7 in moles per liter and b in centimeters, the proportionality constant is called the ***molar absorptivity*** and is given the special symbol, ε. Thus:

$$A = \varepsilon bc$$

where ε has the units of L mol^{-1} cm^{-1}.

10.14 Absorption Spectra

An absorption spectrum is a plot of absorbance versus wavelength. Absorbance could also be plotted against wavenumber or frequency. Most modern scanning spectrophotometers produce such an absorption spectrum directly.

10.15 Atomic Absorption

When a beam of polychromic ultraviolet or visible radiation passes medium containing gaseous atoms, only a few frequencies are attenuated by absorption. When recorded on a very high resolution spectrometer, the spectrum consists of a number of very narrow absorption lines.

10.16 Emission Spectra

Atoms, ions, and molecules can be excited to one or more higher energy levels by any of several processes, including bombardment with electron or other elementary particles; exposure to a high-temperature plasma, flame or electric arc; or exposure to a source of electromagnetic radiation.

Radiation from a source is conveniently characterized by means of an emission spectrum, which usually takes the form of a plot of the relative power of the emitted radiation as a function of wavelength or frequency.

Reference

Douglas A. Skoog, Donald M. West, F. Holler, Stanley R. Crouch, Fundamentals of Analytical Chemistry, Eighth Edition, Brooks/Cole-Thomson Learning. U. S. A. 2004.