

Analytical Chemistry

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 performed 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 disappear 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 affect 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 be doubled. Pure water boils at 100°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°C , while the presence of sugar for example it freezes at -1.86°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).

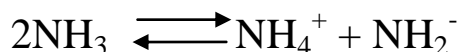
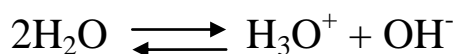
Table 1.1 Classification of electrolytes

Strong electrolytes	Weak electrolytes
1- Inorganic acids HNO ₃ , HClO ₄ , H ₂ SO ₄ , HCl, HI, HBr, HClO ₃ , HBrO ₃	1- Many inorganic acids such as H ₂ CO ₃ , H ₃ PO ₄ , H ₂ S, H ₂ SO ₃ , H ₃ BO 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:



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

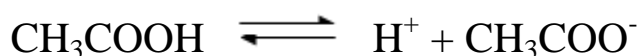
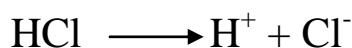
electron pairs of the oxygen. Higher hydrates such as H_5O_2^+ and H_7O_3^+ are also present, but their stabilities are significantly less than that of H_3O^+ . As a matter of convenience, chemists use the term H^+ instead of H_3O^+ .

1.5 Acids and Bases

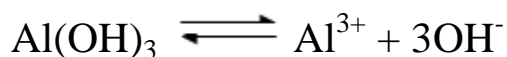
The classification of substances as acids or bases was founded upon several characteristic properties that these compounds impart to an aqueous solution. Typical properties include the red and blue colors that are associated with the reaction of acids and bases with litmus, the sharp taste of a dilute 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:



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



The relative strengths of acids and bases could be compared by measuring the degree of dissociation in aqueous solution. A

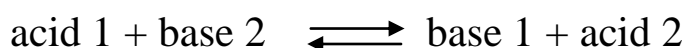
completely ionized acid called strong acid, like HCl, and a partially ionized acid called weak acid, like CH₃COOH. The same rule applied for strong and weak bases.

*** *Bronsted and Lowry acids and bases***

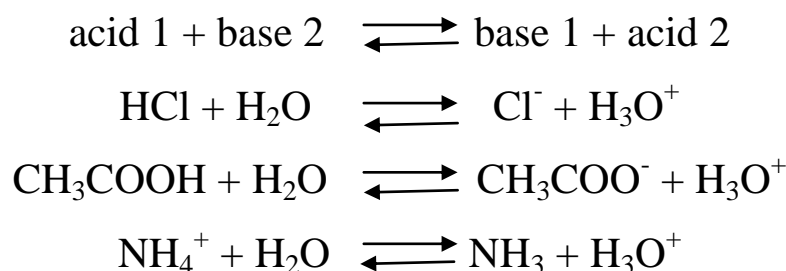
Bronsted and Lowry proposed independently in 1932 that an acid is any substance that is capable of donating a proton: a base is any substance that can accept a proton. The loss of a proton by an acid gives rise to an entity that is a potential proton acceptor and thus a base; it is called the conjugated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

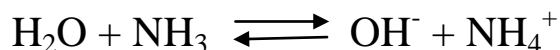


It is important to recognize that the acidic character of a substance will be observed only in the presence of a proton acceptor; similarly basic behavior requires the presence of a proton donor. Neutralization in the Bronsted-Lowry sense, can be expressed as:



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:

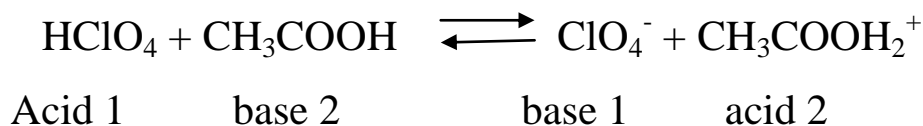




Note that acids can be anionic, cationic, or electrically neutral. It is also seen that water acts as a proton acceptor (a base) with respect to the first three solutes and as a proton donor or acid with respect to the last one; solvents that possess both acidic and basic properties are called amphiprotic.

Acids and bases differ in the extent to which they react with solvents. To illustrate 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 substances 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:



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

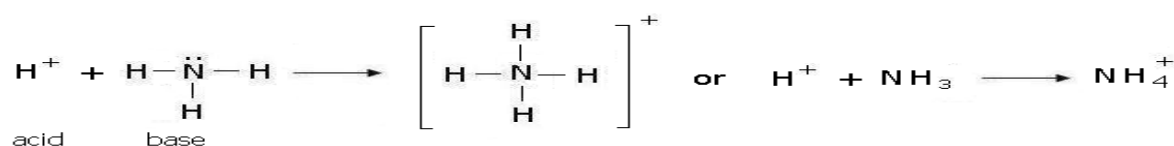
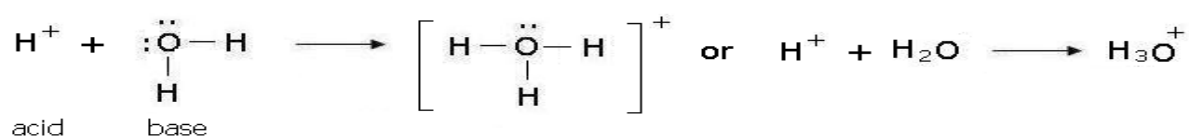
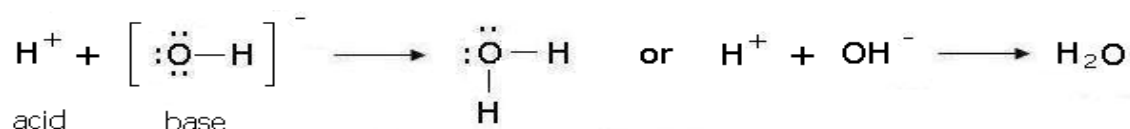
A consequence of the Bronsted theory is that the most effective proton donors (that is the strongest acids) give rise, upon loss of their protons to the least effective proton acceptors (the weakest conjugate bases).

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.

The theory is particularly useful with respect to these latter systems. Here an acid is any substance that either contains, or reacts with the solvent to produce, the cation that is characteristic of the solvent, similarly a base is any substance that directly or indirectly yields the anion characteristic of the solvent.

*** Lewis acids and bases**

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

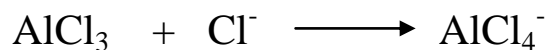




acid base



acid base



acid base

Salts *

Salts are formed by the reactions of cations and anions. Some of the salts are anhydrous like NaCl, KCl, KMnO₄ and K₂Cr₂O₇. Other salts are hydrous such as CaCl₂.2H₂O, CuSO₄.5H₂O and ZnSO₄.7H₂O. 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).

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

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.

1.7 Chemical Formula, Formula Weight and Molecular Weight

An empirical formula expresses the simplest combination of atoms in a substance. It also serves as the chemical formula unless experimental evidence exists to indicate that the fundamental aggregate is actually some multiple of the empirical formula. For example, the chemical formula for hydrogen is H_2 because the gas exists as diatomic molecules under ordinary conditions. In contrast, Ne serves adequately to describe the composition of neon, which is observed to be monatomic.

The entity expressed by the chemical formula may or may not actually exist. For example, no evidence has been found for sodium chloride molecules, as such in the solid state or in aqueous solution. Rather, this substance consists of sodium ions and chloride ions, no one of which can be shown to be in simple combination with any other single ion. Nevertheless, the formula NaCl is convenient for stoichiometric accounting and is so used. It is also necessary to note that the chemical formula is frequently that of the principal species only. Thus, for example, water in the liquid state contains small amounts of such entities as H_3O^+ , OH^- , H_4O_2 (and undoubtedly others), in addition to H_2O . Here the

chemical formula of H₂O is that for the predominant species and is perfectly satisfactory for chemical accounting; it is, however only an approximation of the actual composition of the real substance.

The gram formula weight (gfw) is the summation of atomic weights in grams, of all the atoms in the chemical formula of a substance. Thus, the gram formula weight for H₂ is 2.016 (2×1.008) g, for NaCl is 58.44 (35.45 + 22.99) g. The definition for the gram formula weight carries with it no inference concerning the existence or nonexistence of the substance for which it has been calculated.

We shall employ the term gram molecular weight (gmw) rather than gram formula weight when we are concerned with a real chemical species. Thus, the gram molecular weight of H₂ is its gram formula weight 2.016 g. If we are dealing with the substance NaCl in water, we will not assign to it a gram molecular weight because this species is not found in aqueous media. It is perfectly proper to assign gram molecular weight to Na⁺ (23.00 g) and Cl⁻ (35.45 g) since these are real chemical entities (strictly, these should be called gram ionic weight rather than gram molecular weights, although this terminology is seldom encountered).

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 H₂ contains:

$$\frac{25.0 \text{ g}}{2.016 \text{ g/mole}} = 12.4 \text{ moles of H}_2$$

$$12.4 \text{ moles} \times \frac{6.02 \times 10^{23} \text{ molecules}}{\text{Mole}} = 7.47 \times 10^{24} \text{ molecules H}_2$$

The same weight of NaCl contains:

$$\frac{25.0 \text{ g}}{58.44 \text{ g/fw}} = 0.428 \text{ fw NaCl}$$

which corresponds to 0.428 mole Na⁺ and 0.428 mole Cl⁻

1.8 Equivalent Weight

For acids:

It is the weight of acid that contains 1g ion of alternative hydrogen.

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

Example 2

Calculate the equivalent weights for the following acids: HCl, H₂SO₄, H₃PO₄. Atomic weights for H = 1, O = 16, Cl = 35.5, S = 32, P = 31.

$$\begin{aligned} \text{equivalent weight for HCl} &= \frac{\text{molar mass}}{\text{no. of alternative hydrogen ions}} \\ &= \frac{1 + 35.5}{1} = 36.5 \text{ gram/equivalent} \\ \text{for H}_2\text{SO}_4 &= \frac{(2 \times 1) + 32 + (16 \times 4)}{2} = 49 \\ \text{for H}_3\text{PO}_4 &= \frac{(3 \times 1) + 31 + (16 \times 4)}{3} = 32.67 \end{aligned}$$

For bases:

It is the weight of base that contains 1g ion of alternative hydroxide.

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

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.

$$\begin{aligned} \text{equivalent weight for NaOH} &= \frac{\text{molar mass}}{\text{no. of alternative hydroxide ions}} \\ &= \frac{23 + 16 + 1}{1} = 40 \text{ gram/equivalent} \end{aligned}$$

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

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

For salts:

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

$$\begin{aligned} \text{equivalent weight for salt} &= \frac{\text{molar mass}}{\text{no. of metal ions} \times \text{oxidation no.}} \\ &= \frac{\text{molar mass}}{\text{no. of acidic radical ions} \times \text{oxidation no.}} \end{aligned}$$

Example 4

Calculate the equivalent weights for the following salts: Na₂O, Na₂CO₃, Al₂(SO₄)₃. Atomic weights for O = 16, C = 12, Na = 23, S = 32, Al = 26.98.

$$\begin{aligned} \text{equivalent weight for Na}_2\text{O} &= \frac{\text{molar mass}}{\text{no. of metal ions} \times \text{oxidation no.}} \\ &= \frac{(23 \times 2) + 16}{2 \times 1} = 31 \text{ gram/equivalent} \end{aligned}$$

$$\text{for Na}_2\text{CO}_3 = \frac{(23 \times 2) + 12 + (16 \times 3)}{2 \times 1} = 53$$

$$\text{for Al}_2(\text{SO}_4)_3 = \frac{(26.98 \times 2) + [32 + (16 \times 4)] 3}{2 \times 3} = 56.99$$

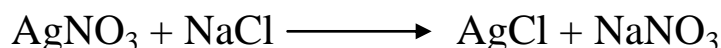
For salts in precipitation reactions:

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.



$$\text{equivalent weight for AgNO}_3 = \frac{\text{molar mass for AgNO}_3}{\text{oxidation number of Ag}}$$

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

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

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

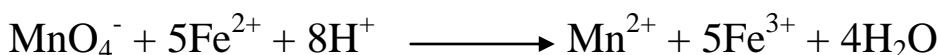
For oxidation-reduction agents:

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

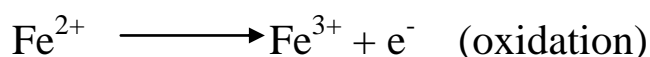
$$\text{equivalent weight for oxidation or reduction agent} = \frac{\text{molar mass}}{\text{the difference between oxidation numbers}}$$

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.



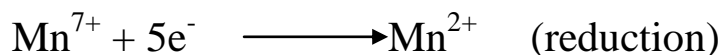
The ferrous oxidized to ferric:



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

$$\begin{aligned} \text{equivalent weight for FeSO}_4 &= \frac{\text{molar mass for FeSO}_4}{1} \\ &= \frac{152}{1} = 152 \text{ gram/equivalent} \end{aligned}$$

the manganese gain 5 electrons:



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

$$\begin{aligned} \text{equivalent weight for KMnO}_4 &= \frac{\text{molar mass for KMnO}_4}{5} \\ &= \frac{158}{5} = 31.6 \end{aligned}$$

1.9 Concentration Units

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

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

Example 7

Calculate the mass percentage for a solution prepared by dissolving 15 g of AgNO₃ in 100 cm³ water. The density of water is 1 g/cm³.

$$\begin{aligned} \text{weight of solvent} &= \text{volume} \times \text{density} \\ &= 100 \text{ cm}^3 \times 1 \text{ g/cm}^3 \\ &= 100 \text{ g} \end{aligned}$$

$$\begin{aligned} \text{weight of solution} &= 100 \text{ g solvent} + 15 \text{ g solute} \\ &= 115 \text{ g} \end{aligned}$$

$$\begin{aligned} \text{mass percentage w/w\%} &= \frac{\text{g solute}}{\text{g solution}} \times 100 \\ &= \frac{15}{115} \times 100 \\ &= 13.04\% \end{aligned}$$

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

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 8

10 g of organic solvent (density 1.5 g/cm³) was added to 90 g water, the density of the solution become 1.1 g/cm³. Calculate the v/v% and the w/w% concentrations of the organic substance in the solution.

$$\text{weight of solution} = 90 \text{ g} + 10 \text{ g} = 100 \text{ g}$$

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

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

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

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

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

It is the weight of the solute in 100 ml solution, this means:

$$\text{weight of solute (g)} = \text{percentage} \left(\frac{\text{g}}{100 \text{ ml}} \right) \times \text{volume (ml)}$$

Example 9

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

$$\text{weight of solute (g)} = \text{percentage} \left(\frac{\text{g}}{100 \text{ ml}} \right) \times \text{volume (ml)}$$

$$\begin{aligned} &= \left(\frac{0.85 \text{ g}}{100 \text{ ml}} \right) \times 500 \text{ ml} \\ &= 4.25 \text{ g} \end{aligned}$$

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

and there are:

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

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

5- Molar concentration (M)

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

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

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

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

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

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

Example 10

Calculate the molar concentration (M) of a solution prepared by dissolving 29.35 g of NaCl in 200 ml water. Atomic weights for Na = 23.99, Cl = 35.45.

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

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

6- Normal concentration (N)

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

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

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

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

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

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

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

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

Example 11

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

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

$$0.25 = M \times 3, \text{ so } M = 0.0833 \text{ Molar}$$

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 12

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.

$$\begin{aligned} \text{Molal concentration (m)} &= \frac{\text{weight of substance in g} \times 1000}{\text{molecular weight} \times \text{weight of solvent in g}} \\ &= \frac{92.9 \times 1000}{46.1 \times 500} = 4 \text{ m} \end{aligned}$$

*** 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 13

Calculate the mole fraction for ethanol $\text{C}_2\text{H}_5\text{OH}$ 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:

$$\begin{aligned} \text{mole fraction for water} &= 1 - \text{mole fraction for ethanol} \\ &= 1 - 0.167 = 0.833 \end{aligned}$$

*** Solutions Normality**

$$N = \frac{D \times \% \times 1000}{\text{equivalent weight} \times 100}$$

D = density.

To dilute a solution we use the law:

$$\begin{array}{ccc} N_1 \times V_1 & = & N_2 \times V_2 \\ \text{before dilution} & & \text{after dilution} \end{array}$$

For solutions:

no. of milliequivalents (meq) = V of solution \times Normality (N)

For solids:

$$\text{no. of milliequivalents} = \frac{\text{wt. of solids (g)}}{\text{equivalent weight}} \times 1000$$

Chapter 2

Gravimetric Analysis

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. In *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. In *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. We shall concern ourselves principally with precipitation methods because these are more frequently encountered than methods involving volatilization.

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:

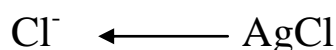
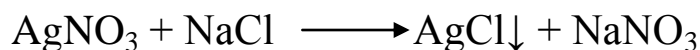
$$\% A = \frac{\text{weight of A}}{\text{weight of sample}} \times 100 \quad (3-1)$$

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:



$$35.45 \equiv 143.3$$

$$x \quad \quad \quad 0.204$$

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

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 $\text{Ag} = 107.86$, $\text{Cl} = 35.45$, $\text{Al} = 26.98$. We know that each AlCl_3 yield three AgCl . Therefore,

$$\begin{array}{rcl} \text{AlCl}_3 & \equiv & 3\text{AgCl} \\ 133.3 & \equiv & 3 \times 143.3 \\ x & & 0.204 \\ & & \frac{133.3}{3 \times 143.3} \\ x = 0.204 \times & & = 0.0633 \text{ g} \end{array}$$

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.

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. More often than not, 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. The student should clearly understand that contamination of a precipitate by a second substance whose solubility product has been exceeded does not constitute coprecipitation.

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. At the one extreme are 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. At the other extreme are particles with dimensions on the order of several tenths of a millimeter. The temporary 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 comprising the solid phase increase from colloidal to those typical of crystals. Indeed, some precipitates possess characteristics intermediate between these defined extremes. The majority of precipitates, however, are easily recognizable as being predominately colloidal or predominately crystalline. Thus, while imperfect, this classification can be usefully applied to most solid phases.

Although the phenomenon of precipitation has long been attracted the attention of chemists, fundamental information regarding the mechanism of the process remains incompletely understood. It is certain, however, that the particle size of the solid that forms is influenced in part by such 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 effect of these variables can be accounted for, at least qualitatively, by assuming that the particle size is related to a single property of the system called its relative supersaturation, where:

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

Here 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 presumably causes the solution to be momentarily supersaturated (that is $Q > S$). Under most circumstances, this unstable condition is relieved, 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.

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. 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 exponentially with relative supersaturation, whereas the rate of particle growth bears an approximately linear relationship to this parameter. That is,

$$\text{rate of nucleation} = k_1 \left(\frac{Q - S}{S} \right)^n$$

where n is thought to be about 4, and

$$\text{rate of growth} = k_2 \left(\frac{Q - S}{S} \right)$$

Normally, k_2 is greater than k_1 ; thus, at low relative supersaturations, growth predominates. When the supersaturation is great, the exponential nature of nucleation may cause this process to occur to the near exclusion of particle growth. These effects are illustrated in Figure 3-1.

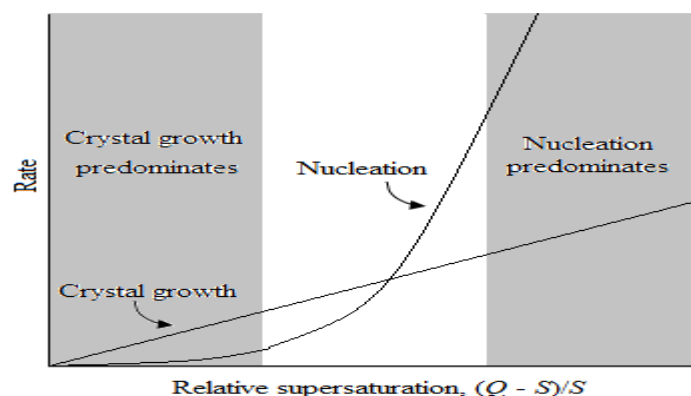


Figure 3-1 Effect of Relative Supersaturation on Precipitation Processes

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), and slow addition of the precipitating agent with 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.

A crystalline solid is much easier to manipulate than a colloidal suspension. For this reason, particle growth is usually to be preferred over further nucleation during the formation of a precipitate. If, however, the solubility S of a precipitate is very small, it is essentially impossible to avoid a momentarily large relative supersaturation as solutions are mixed; as a consequence, colloidal suspensions often cannot be avoided. For example, under conditions feasible for an analysis, the hydrous oxide of iron(III), aluminum, and chromium(III) and the sulfides of most

heavy metal ions can be formed only as colloids because of their very low solubilities. The same is true for the halide precipitates of silver ion.

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 hasten the coagulation process, namely, 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. The presence of this charge is readily demonstrated experimentally by observing the migration of the particles under the influence of an electric field.

Adsorption of ions upon an ionic solid has, as its origin, the normal bonding forces that are responsible for crystal growth. Thus, a silver ion at the surface of a silver chloride particle has a partially unsatisfied bonding capacity by virtue of its surface

location. 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.

The nature and magnitude of the charge on particles of a colloidal suspension depend, in a complex way, on a number of variables. For the colloidal suspensions of interest in analysis, however, the species adsorbed, and thus the charge on the particles, can be readily predicted from the empirical observation that lattice ions are generally more strongly adsorbed than any others. Thus, a silver chloride particle will be positively charged in a solution containing an excess of silver ions, owing to the preferential adsorption of these ions. It will have a negative charge in the presence of excess chloride ion for the same reason. It is of interest to note that the silver chloride particles formed in a gravimetric chloride analysis initially carry a negative charge but become positive as an excess of the precipitating agent is added.

The extent of adsorption increases rapidly with increases in concentration of the adsorbed ion. Ultimately, however, the surface of each particle becomes saturated; under these circumstances, further increases in concentration have little or no effect.

Figure 3-2 depicts 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.

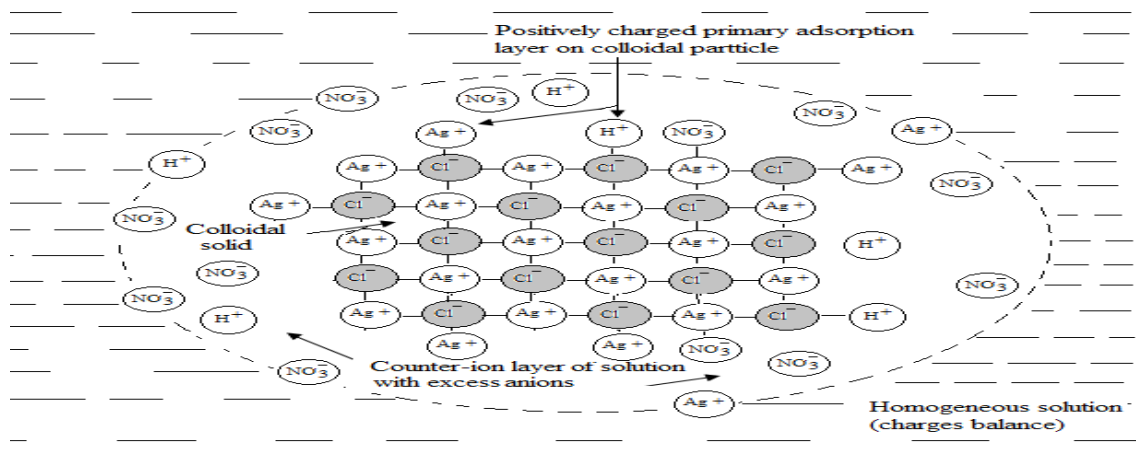


Figure Colloidal AgCl Particle Suspended in a Solution of $AgNO_3$

Considered together, the primarily adsorbed ions and their counter ions in solution constitute an electrical double layer which imparts a degree of stability to a colloidal suspension. These layers cause a colloidal particle to shear away as it approaches another; the forces that would otherwise permit cohesion between the particles are insufficient to overcome the repulsions due to the electrical double layer. In order to coagulate a colloid, then, these repulsive forces must be minimized.

The effect of the charged double layer on stabilization of a colloid is readily seen in the precipitation of chloride ion with silver ion. With initial addition of silver nitrate, silver chloride is

formed in an environment having a high chloride ion concentration. The negative charge for silver chloride particles is therefore high; the volume of the positive counter-ion layer surrounding each particle must also be relatively large to contain enough positive ions (hydronium or sodium ions, for example) to neutralize the negative charge of the particles. Coagulation under these circumstances does not occur. As more silver ions are added, the charge per particle decreases because the chloride ion concentration is decreased, and the number of particles is increased; the repulsive effect of the double layer is thus decreased. As chemical equivalence is approached, a sudden appearance of the coagulated colloid is observed. Here the number of adsorbed chloride ions per particle becomes small, and the double layer shrinks to a point where individual particles can approach one another closely enough to permit agglomeration. It is of interest that the agglomeration process can be reversed by addition of a large excess of silver ions; here, of course, the charge of the double layer is reversed with the counter-ion layer being negative.

Coagulation is often brought about by a short period of heating, especially if accompanied by stirring. The increased temperature reduces adsorption and thus the net charge on a particle; in addition, the particles acquire kinetic energies sufficient to overcome the barrier to close approach.

An even more effective method of coagulation is to increase the electrolyte concentration of the solution by addition of a suitable ionic compound. Under these circumstances, the volume of solution that contains enough ions of opposite charge to neutralize the charge on the particle is lessened. Thus, the introduction of an electrolyte has the effect of shrinking the counter-ion layer, with the result that the surface charge on the particles is more completely neutralized. With their effective charge decreased, the particles can approach one another more closely.

*** *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 (in the film of liquid surrounding the particle) through the processes of coagulation and

filtration. The net effect of surface adsorption is the carrying down of an otherwise soluble species as a surface contaminant.

*** *Peptization of colloids***

Peptization refers to the process whereby a coagulated colloid reverts to its original dispersed state. Peptization frequently occurs when pure water is used to wash such a precipitate. Washing is not particularly effective in dislodging adsorbed contaminants; it does tend, however, 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.

The chemist is thus faced with a dilemma in handling coagulated colloids. He would like to free the precipitate of contaminants, but in so doing he runs the risk of losses from peptization. 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.

*** *Practical treatment of colloidal precipitates***

In general, colloids are precipitated from hot, stirred solutions to which sufficient electrolyte has been added to assure coagulation. With many colloids, the physical characteristics of the coagulated mass be improved by permitting the solid to stand in contact with the hot solution from which it was formed. During this process, which is known as *digestion*, weakly bound water appears to be lost from the precipitate; the result is a denser mass that is easier to filter.

A dilute solution of a volatile electrolyte is used to wash the filtered precipitate. Washing does not appreciably affect primarily adsorbed ions because the attraction between these species and solid is too strong. Some exchange may occur between the existing counter ions and one of the ions in the wash solution. Under any circumstances, it must be expected that the precipitate will still be contaminated to some degree, even after extensive washing. The error introduced into the analysis from this source can range from 1 or 2 ppt (as in the coprecipitation of silver nitrate on silver chloride) to an intolerable level (as in the coprecipitation of heavy metal hydroxides upon the hydrous oxides of trivalent iron or aluminum).

A drastic way to minimize the effects of adsorption is reprecipitation. Here the filtered solid is redissolved and again precipitated. The first precipitate normally carries down only a

small fraction of the total contaminant present in the original solvent. Thus, the solution containing the redissolved precipitate will have a significantly lower contaminant concentration than the original. When precipitation is again carried out, less adsorption is to be expected. Reprecipitation adds substantially to the time required for an analysis; nevertheless, it is a near necessity for such precipitates as the hydrous oxides of iron(III) and aluminum, which possess extraordinary tendencies to adsorb the hydroxides of zinc, cadmium, and manganese.

Crystalline Precipitates

In general, crystalline precipitates are more easily handled than coagulated colloids. Here the size of individual particles can be varied to a degree. As a consequence, the physical properties and purity of the solid are determined by experimental variables over which the chemist has a measure of control.

**** Methods of improving particle size and filterability***

Generally, 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 tends to reduce the momentary local supersaturation in the solution. Ordinarily, S can

be increased by precipitating from hot solution. Quite noticeable gains in particle size can be obtained with these simple measures.

*** *Purity of crystalline precipitates***

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.

Two types of coprecipitation, *inclusion* and *occlusion*, are associated with crystalline precipitates. The two differ in the manner in which the contaminant is distributed throughout the interior of the solid. Included impurities are randomly distributed, in the form of individual ions or molecules, throughout the crystal. Occlusion, on the other hand, involves a nonhomogeneous distribution of impurities, consisting of numerous ions or molecules of the contaminant, within imperfections in the crystal lattice.

Occlusion occur 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 a 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 undoubtedly 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. The fact that little improvement in filtering characteristics is obtained if the mixture is stirred during digestion tends to confirm this view.

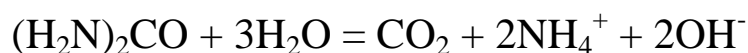
Direction of Coprecipitation Errors

Coprecipitated impurities may cause the results of an analysis to 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 weight than the barium sulfate that would have formed had no coprecipitation occurred. If barium chloride were the contaminant, however, a negative error would arise because its formula weight is less than that of the sulfate salt.

Precipitation from Homogeneous Solution In precipitation from homogeneous solution, the precipitating agent is chemically generated in the solution at a sufficiently slow rate so that the relative supersaturation is always low. Local reagent excesses do not occur because the precipitating agent appears homogeneously throughout the entire solution. In general, homogeneously formed precipitates, both colloidal and crystalline, are better suited for analysis than precipitates formed by direct addition of a reagent.

Urea is often employed for the homogeneous generation of hydroxide ion. The reaction can be expressed by the equation:



This reaction proceeds slowly at temperatures just below boiling; typically one to two hours are needed to produce sufficient reagent to complete a precipitation. The method is particularly valuable for the precipitation of hydrous oxide or basic salts. For

example, the hydrous oxide of iron(III) and aluminum, when formed by direct addition of base, are bulky, gelatinous masses that are heavily contaminated and difficult to filter. In contrast, when produced by the homogeneous generation of hydroxide ion, these same products are dense, readily filtered, and have considerable higher purity. Homogeneous precipitation of crystalline precipitates also results in marked increases in crystal size; enhanced purity often accompanies this crystal growth.

Drying and Ignition of Precipitates

After filtration, a gravimetric precipitate is heated until its weight becomes constant. Heating serves the purpose of removing the solvent and volatile electrolytes carried down with the precipitate; in addition, this treatment may induce chemical decomposition to give a product of known composition.

The temperature required to produce a suitable product varies from precipitate to precipitate.

Time Required for a Gravimetric Analysis

In considering the time required to perform an analysis, it is necessary to differentiate between elapsed time and operator time. The first refers to the clock hours or minutes between the start of the analysis and the report of the result. Operator time, on the other hand, represents the actual time the chemist or technician must spend in performing the various manipulations required to complete the analysis and calculate the result. A characteristic of

the gravimetric method is that the difference between elapsed time and operator time is large, when compared with other methods, because the most time-consuming steps in the analysis do not require the constant attention of the analyst. For example, drying of crucibles, evaporation of solutions, digestion of precipitates, and ignition of products frequently take several hours to complete but require, at the most, a few minutes of the analyst's time, thus leaving him free to perform other tasks.

If methods for a given analysis are compared on the basis of operator time, the gravimetric approach often proves to be the most efficient, particularly where only one or two samples are to be analyzed, because no time is expended in calibration or standardization. On the other hand, as the number of samples to be analyzed increases, the time required for calibration in a nongravimetric procedure becomes smaller on a per sample basis and often become negligible when eight or ten samples are involved (assuming of course, that a single calibration will suffice for all of the samples), washing, and weighing may become larger than the equivalent operations in a nongravimetric procedure. Often, but not always, a gravimetric approach becomes less advantageous when a large number of samples is involved.

Sensitivity of the Gravimetric Method

In contrast to many analytical methods, a gravimetric analysis is seldom, if ever, limited in sensitivity (or accuracy) by the tool

employed for measurement. Thus with a suitable types of balance it is perfectly feasible to obtain the weight of a few micrograms of material to within a few parts per thousand of its true value; for larger masses, the weighing uncertainty can be decreased to a few parts per million.

The sensitivity of a gravimetric analysis is more likely to be limited by the difficulties encountered in attempting to separate a small amount of precipitate from a relatively large volume of solution that contains high concentrations of other constituents from the sample. In some situations solubility losses may be troublesome; in others, the precipitation rate may be so slow as to make the process impractical. For colloidal precipitates, coagulation often becomes difficult or impossible when the amounts of material are low. Finally, mechanical losses of a significant fraction of the solid become inevitable during filtration of a minute amount of solid suspended in a large volume of solution.

Because of these problems, the chemist is wise to discard the idea of employing a gravimetric analysis for a constituent if its concentration is likely to be below 0.1%; the method is best applied where the concentration is greater than 1%.

Accuracy of Gravimetric Methods

It is difficult to generalize about the accuracy of gravimetric methods because each is subject in varying degree to uncertainties

from such sources as solubility, coprecipitation, and variation in the chemical composition of the final product. Each of these factors is dependent upon the composition of the sample. For example, the iron content of a sample containing no other heavy metal ions is readily determined gravimetrically to within a few parts per thousand. On the other hand, in the presence of divalent cations such as zinc, nickel, and copper, errors of several percent must be expected unless an inordinate amount of time is expected in overcoming the effects of coprecipitation by these ions. Solubility losses are also affected by sample composition. With multicomponent samples, the likelihood of complex formation between the analyte and a constituent of the sample is enhanced; in addition, purification of the precipitate may require a large volume of wash water and a concomitant increase in loss by solubility.

For simple samples containing more than 1% of analyte, the accuracy of gravimetric analysis is seldom surpassed by other methods; here errors may often be decreased to a part or two in 1000. With increasing sample complexity, larger errors are inevitable unless a great deal of time is expended in circumventing them. Here the accuracy of the gravimetric method may be no better than, and sometimes poorer than, other analytical methods.

Specificity of Gravimetric Methods

With a few notable exceptions, gravimetric reagents are not very specific; instead, virtually all are selective in the sense that they tend to form precipitates with groups of ions. Each ion within any group will then interfere with the analysis of any other ion in the group unless a preliminary separation is performed.

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.

Table 3-1 Some Inorganic Precipitating Agents

Precipitating Agent	Element Precipitated
NH ₃ (aq)	Be (BeO), Al (Al ₂ O ₃), Fe (Fe ₂ O ₃), Sn (SnO ₂)
H ₂ S	Cu (CuO), Zn (ZnO), Ge (GeO ₂), Sn (SnO ₂)
(NH ₄) ₂ S	Hg (HgS), Co (Co ₃ O ₄)
H ₂ SO ₄	Li, Mn, Sr, Cd, Pb, Ba (all as sulfates)
HCl	Ag (AgCl), Hg (Hg ₂ Cl ₂), Na (NaCl), Si (SiO ₂)
AgNO ₃	Cl (AgCl), Br (AgBr), I (AgI)
NH ₄ SCN	Cu (Cu ₂ (SCN) ₂)
HNO ₃	Sn (SnO ₂)

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.

*** *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 ₂ NOH	Te
H ₂ NOH	Se
H ₂ C ₂ O 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

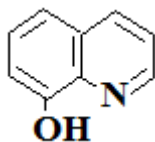
reagents tend to be more selective in their reactions than many of the inorganic reagents listed in Table 3.1.

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.

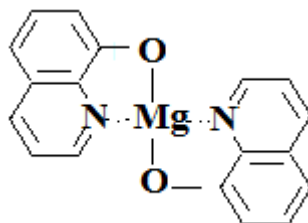
Organic reagents which yield sparingly soluble coordination compounds typically contain at least two functional groups, each of which is capable of bonding with the cation by donation of a pair of electrons. The functional groups are located in the molecule in such a way that a five- or six-membered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

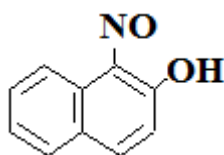


Typical of these is the product with magnesium:



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:

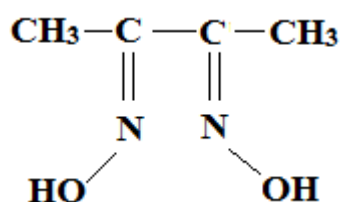


The reagent reacts with cobalt(II) to give a neutral cobalt(III) chelate having the structure CoA_3 , where A^- is the conjugate base of the reagent. Note that formation of the product involves both oxidation and precipitation of the cobalt by the reagent; the precipitate is contaminated by reduction products of the reagent

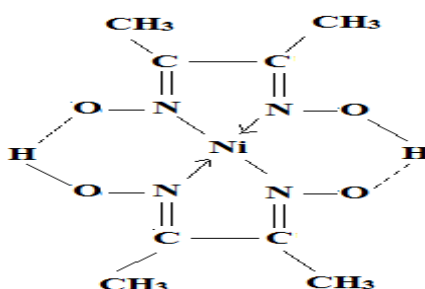
as a consequence. Therefore, it is common practice to ignite the chelate in oxygen to produce Co_3O_4 ; alternatively, the ignition is performed in a hydrogen atmosphere to produce the element as the weighed form.

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.



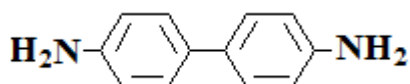
Its coordination compound with palladium is the only one that is sparingly soluble in acid solution. Similarly, only the nickel compound precipitates from a weakly alkaline environment. Nickel dimethylglyoxime is bright red and has the structure:



This precipitate is so bulky that only small amounts of nickel can be handled conveniently; it also has an exasperating tendency to creep as it filtered and washed. The solid is readily dried at 110°C and has the composition indicated by its formula.

Sodium Tetrphenylboron. Sodium tetrphenylboron, $(C_6H_5)_4B^- Na^+$, 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 $C_{12}H_{12}N_2 \cdot H_2SO_4$. 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.

3.18 Gravimetric Organic Functional Group Analysis

Several reagents have been developed which react selectively with certain organic functional groups, and thus permit the determination of most compound containing these groups.

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 definite 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 abrupt change in pH that occurs in the vicinity of 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.

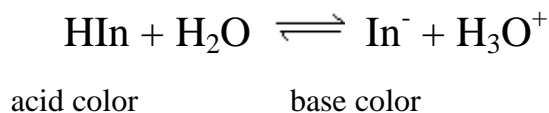
5.7 Standard Solutions for Neutralization Titrations

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.

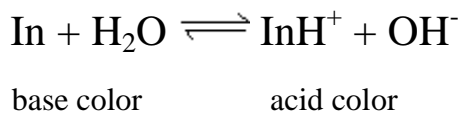
Standard solutions of bases are ordinarily prepared from solid bases.

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:



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



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

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]}$$

$$[\text{H}_3\text{O}^+]K_a = \frac{[\text{In}^-]}{[\text{HIn}]}$$

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:

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

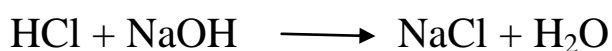
and its base color when:

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

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

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.



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.

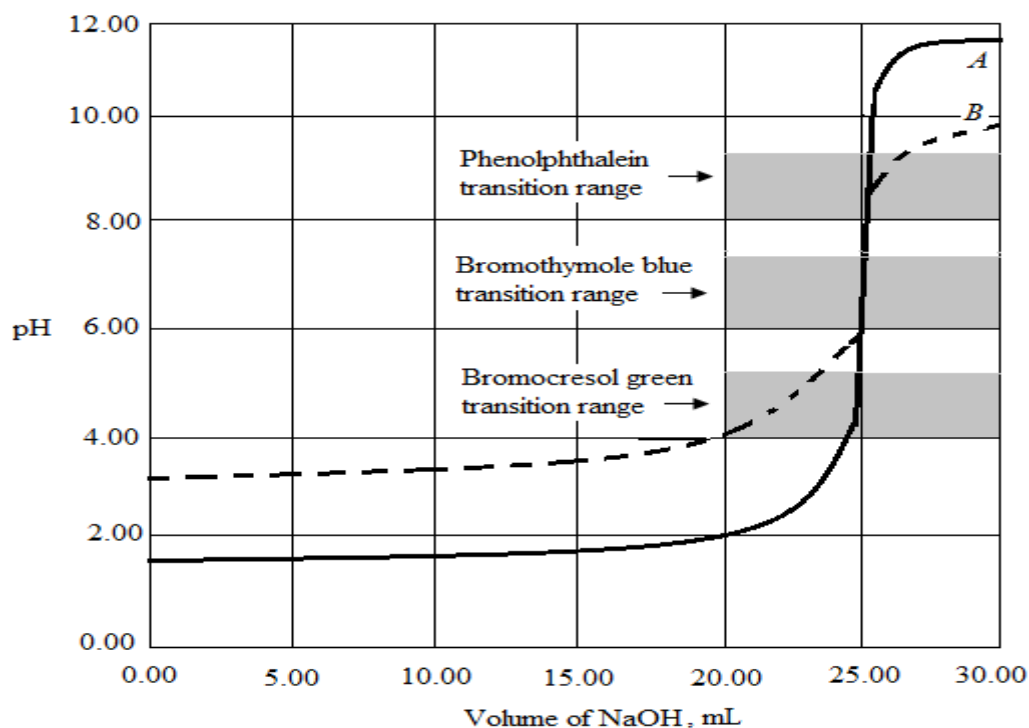


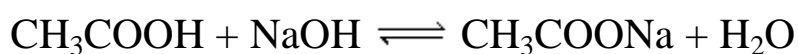
Figure 5-1 Titration Curves for HCl with NaOH. Curve A: 50.00 mL of 0.0500 M HCl with 0.1000 M NaOH. Curve B: 50.00 mL of 0.000500 M HCl with 0.001000 M NaOH.

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.

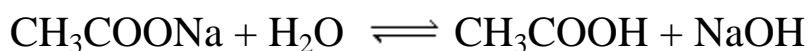
5.11 Titration of a weak Acid with a Strong Base

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



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:



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).

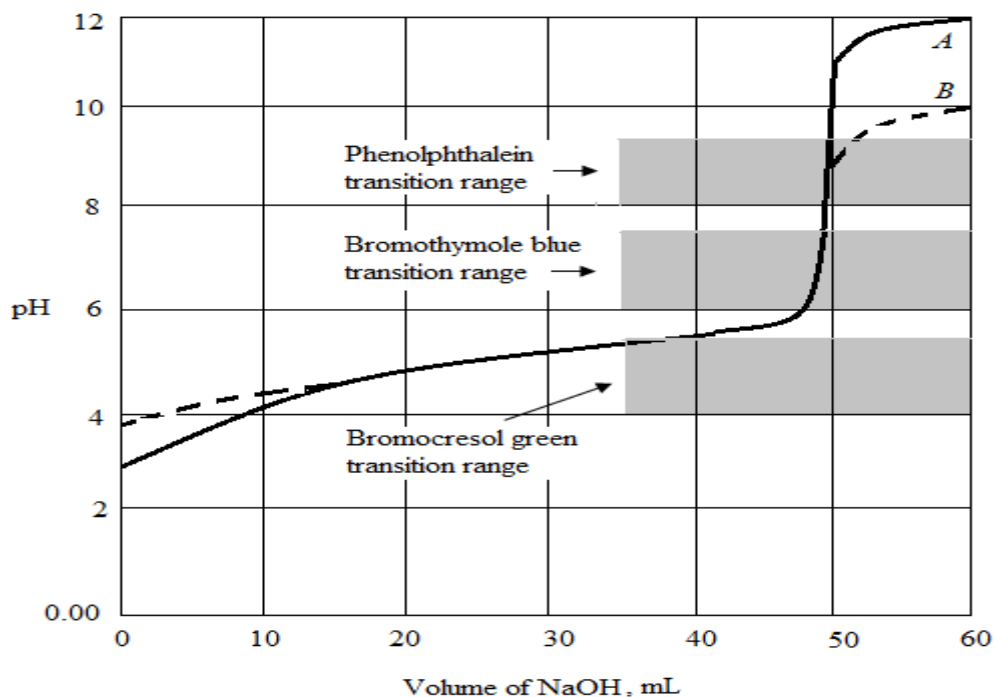


Figure 5-2 Titration Curves for CH₃COOH with NaOH. Curve A: 0.1000 M acid with 0.1000 M base. Curve B: 0.001000 M acid with 0.001000 M base.

*** *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.

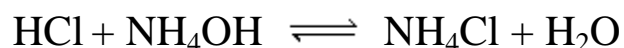
The end-point pH associated with the titration of 0.001000 M acetic acid (curve B) is so small that a significant titration error is

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 a reproducibility of a few percent relative.

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:



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 NH₄OH.

