Faculty of Science at Qena **South Valley University**

Analytical Chemistry (1)

For 3rd year students (Faculty of Education – Chemistry Group)

English Program

Prepared by:

Dr. Ibrahim A. I. Hassan

Department of Chemistry Faculty of Science, South Valley University

اعداد أستاذ المقرر:

د/ إبراهيم عبدالله إسماعيل حسن

قسم الكيمياء – كلية العلوم بقنا – جامعة جنوب الوادي

Email: I.Hassan@bath.edu

WhatsApp:. +1 (416)-948-9468

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الرموز المستخدمة

🎞 فيديو للمشاهدة.

📖 نص للقراءة والدراسة.

🔗 رابط خارجي.

❓ أسئلة للتفكير والتقييم الذاتي.

📋 أنشطة ومهام.

🖥 تواصل عبر مؤتمر الفيديو.

Introduction to Analytical Chemistry

Analytical Chemistry comprises of:

Qualitative analysis:

Identifies the elements, species and compounds in a sample

Quantitative analysis:

Determines absolute or relative amounts of elements, species and compounds in a sample.

Structural analysis:

Determines the spatial arrangements of atoms or identifies the functional groups.

VOLUMETRIC ANALYSIS

Volumetric (titrimetric) analysis:

Quantitative chemical analysis by measure consists essentially in determining the volume of solution of accurately known concentration which is required to react quantitatively with the solution of the substance being determined. The solution of accurately known strength is called the standard solution. It contains a definite number of gram equivalents per liter. The process of adding the standard solution until the reaction is just complete is termed a titration, and the substance to be determined is titrated. The point at which this occurs is called the equivalence point or the theoretical end point. The completion of the titration should, as a rule, be detectable by some change, unmistakable to the eye, produced by the standard solution itself (e.g. potassium permanganate) or, more usually by the addition of an auxiliary reagent known as an indicator. After the reaction between the substance and the standard solution is practically complete, the indicator should give a clear visual change in the liquid being titrated. The point at which this occurs is called the end point of the titration. The reagent of known concentration is called titrate and the substance being titrated is termed the titrate. For l use in volumetric

(titrimetric) analysis a reaction must fulfill the following conditions:

1- The substance to be determined should react completely with the reagent in stoichiometric or equivalent proportions.

2- The reaction should be practically instantaneous or proceed with very great speed.

3- There must be a marked change in some physical or chemical property of the solution at the equivalence point.

4- An indicator should be available.

Classification of reactions in volumetric analysis:

The reactions employed in volumetric analysis fall into two main classes.

a- Those in which no change in valence occurs, these are dependent upon the combination of ions. This type of reaction are divided into three main classes.

i- Neutralization reactions:

These include the titration of free bases or those formed from salts of weak acids by hydrolysis, with a standard acid (acidimetry and the titration of free acid or those formed by the hydrolysis of salts of weak bases, with s standard base (alkalimetry). These reactions involve the combination of hydrogen and ions to form water.

ii- Complex formation reactions:

These doped upon the combination of ions, other than hydrogen or hydroxide ions, to form a soluble slightly

dissociation ion or compound as in the titration collation of a cyanide with silver nitrate.

$$2\ CN^- + Ag^+ \rightleftharpoons [Ag\ (CN)_2]$$

or of chloride ion with mercuric nitrate solution.

$$2\ Cl^- + Hg^{**} \rightleftharpoons Hg\ Cl_2$$

Ethylene diamine tetra-acetic acid (EDTA) is very important reagent for complex formation titrations.

$$Cu(H_2O)_4^{--} + 2\ EDTA \rightarrow [Cu\text{-}(EDTA)_2]^{--} + 4\ H_2O$$

iii- <u>Precipitations reactions</u>:

These depend upon the combination of ions, other than hydrogen or hydroxide ions, to form a simple precipitate as in the titration of silver ion with a solution of a chloride.

$$Ag^+ + NO_3^- - Na^+ + Cl \rightarrow AgCl \downarrow + Na^+ + NO_3^-$$

b- Oxidation reduction; these involve a change of valence or otherwise expressed, transfer of electrons, for example:

$$MnO_4^- + 5\ Fe^{++} + 8\ H^+ \rightarrow Mn^{++} + 5\ Fe^{+++} + 4\ H_2O$$

Concentration of solution:

The ways in which concentration can be expressed are giving in the following:

1- The strength of a solution is determined by its concentration or the quantity of reagent in a given volume. This method of expressing concentrations in weight per unit volume is a very common one.

2- Sometimes the concentration is expressed in weight of solution par unit weight of solvent. Thus, the nitrate solution just referred to will contain 25 g silver nitrate in 997.2 g of water at 20°C.

3-The physical chemist usually fines it is convenient to express concentration in moles per liter, the designation meaning a molecular weight in grams. A solution containing 36.46 g of HCl per liter is called, therefore molar solution Whereas a solution containing one mole 1000 g of solvent is often called a molar solution.

4-The most convenient method, however of expressing the concentrations of solutions for the purposes of volumetric analysis is with reference to equivalent weight. By a normal solution is understood 1 gram equivalent of the active reagent dissolved in one liter of solution. For convenience in concentrations of solutions used for volumetric purposes are expressed in terms of their normality; that is a solution is 2 normal, 0.5 normal, 0.1 normal etc. The letter N is used as an abbreviation for normal.

General method of computing result:

The most important advantage of the equivalent system is than the calculations of volumetric analysis are rendered very simple, since at the end point the number to the number of equivalents of the standard solution employed. We may write:

Normality = $\frac{\text{Number of gram-equivalents}}{\text{Number of liters}}$

= $\frac{\text{Number of milligram-equivalents}}{\text{Number of milliliters (ml.)}}$

Hence ; number of mg-equivalents

= number of ml. x normality .

If the volumes of solutions of two different substance A add B which exactly react with one another are V_A ml land V_B ml. respectively, then these volumes severally contain the same number of g. equivalents or mg – equivalents of A and B. Thus,

V_A x normal V_A = V_B x normality V_B

In practice V_A , V_B and normality N_A (The standard solution) are known, hence normality N_B (the unknown solution) can be readily calculated .

Example:

How many ml., of 0.2 N-hydrochloric acid are required to neutralize 25.0 ml. 0.1 N-sodium hydroxide?

Solution:

$$V_A \text{ x } N_A = V_B \text{ x } N_B$$

$$V_A = 0.2 = 25.0 \text{ X } 0.1$$

where V_A = 12.5 ml.

Example 2:

25 ml. of a ferrous sulphate solution react completely with 30 ml. of 0.125 N-$KMnO_4$. Calculate the strength of the ferrous sulphate solution in grams of $FeSO_4$ per liter.

Solution:

A normal solution of $FeSO_4$ as a reluctant contain 1 mol. Per liter or 151.90 g. per liter. Let the normality of the ferrous sulphate solution be N_A . Then:

$$25 \times N_A = 30 \times 0.125$$

$$N_A = 30 \times 0.125/25 = 0.150 \text{ N}$$

Hence the solution will contain

$$0.150 \times 151.90 = 22.78 \text{ g. } FeSO_4 \text{ per liter}$$

Example 3:

What volume of 0.127 N reagent is required for the preparation of 1000 ml. of 0.1 N solution.

Solution:

$$V_A \times \text{normality} = V_B \times \text{normality B}$$

$$V_A \times 2.127 = 1000 \quad 0.1$$

$$\text{or} \quad V_A = \frac{1000 \times 0.1}{0.127} = 787.4 \text{ ml.}$$

Preparation of standard solutions:

If a reagent is available in the pure state, a solution of definite normality is prepared simply by weighing out an equivalent weight, or a definite fraction or multiple there of, dissolving it in the solvent, usually water, making up the

solution to a known volume. It is not really essential to weigh out the equivalent weight. In practice it is often more convenient to prepare the solution a little more concentrated than is ultimately required, and then to dilute it with distilled water until the desired normality is obtained. If N_1 is the required normality, V_1 volumes after dilution, N_2 the normality originally obtained and V_2 the original volume taken.

$$N_1 V_1 = N_2 V_2 \text{ or } V_1 = \frac{N_2 V_2}{N_1}$$

The substances which can be obtained in a state of high purity and are therefore suitable for the preparation of standard solutions: sodium carbonate potassium hydrogen phthalate, benzoic acid, borax, sodium oxalate, and potassium dichromate

When the reagent is not available in the pure form as in the cases of most alkali hydroxides, some inorganic acid and various deliquescent substances, solutions of the approximate normality required are first prepared. These are then standardized by titration against a solution of a pure substance of known normality.

Primary standard substances:

A primary standard substance should satisfy the following requirements .

1-It must be easy to obtain, to purify, to dry (preferably at 110-120 °C) and preserve in pure state.

2-The substance should not unaltered in air during weighing, this condition implies that it should not be hygroscopic, nor oxidized by air, nor affected by carbon dioxide.

3-The substance should be capable of being tested for impurities by qualitative and other tests of known sensitivity.

4-It should have a high equivalent weight so that the weighing errors may be negligible.

5-The substance should be readily soluble under the conditions in which it is employed. The substances commonly employed as primary standards are: Sodium carbonate, borax, potassium hydrogen phthalate, and sodium chloride.

THEORY OF ACID-BASE TITRATIONS

INTRODUCTION

Acidimetry is the determination of acid substances by titration, and alklimetry is the corresponding process for alkaline substances. The two processes are also called neutralization although the solution at the stoichiometric point often has a reaction that is slightly different from that of the solvent.

General conception of acids and bases (The Bronsted theory):

It is, desirable to have some knowledge of the general theory of acids and bases proposed by Bronsted since this is applicable to all solvents. According to Bronsted in acid is a species having a tendency to lose a proton and a base is a species having a tendency to add on a proton. This may be represented as:

$$\text{Acid} \rightleftharpoons \text{proton} + \text{conjugate base}$$

$$A \rightleftharpoons H^+ + B$$

(It must be emphasized that the symbol H^+ represents the proton and not the "hydrogen ion". Since the free proton cannot exist in solution in measurable concentration, eaction does not take place unless a base is added to concept the proton from the acid. By combining the equations.

$$A_1 \rightleftharpoons B_1 + H^+ \text{ and } B_2 + H^+ \rightleftharpoons A_2$$

We obtain $A_1 + B_2 \rightleftharpoons A_2 + B_1$

A_1 - B_1 and A_2 - B_2 are two conjugate acid-base pairs. This is the most important expression for reactions involving acids and bases, it represents the transfer of a proton from A_1 to B_2 or from A_2 to B_1. The stronger acid loses its proton more readily than the weaker, similarly, the stronger base accepts a proton more readily than does the weaker base. It is evident that the base or acid conjugate to a strong acid or strong base is always strong.

Acids may thus be arranged in series according to their relative combining tendencies with the base water

$$\underset{Acid_1}{HCl} + \underset{Base_2}{H_2O} \rightarrow \underset{Acid_2}{H_3O^+} + \underset{Base_1}{Cl^-}$$

This process is essentially complete for al typical" strong" (i.e. highly ionized) acids. In marked contrast with "strong " acids, the reaction a typical " weak " or slightly ionized acid, such as acetic, proceeds only slightly to the right in the sense of the following:

$$\underset{Acid_1}{HC_2H_2O_2} + \underset{Base_2}{H_2O} \rightleftharpoons \underset{Acid_2}{H_3O^+} + \underset{Base_1}{C_2H_3O_2}$$

The conjugate base, in this theory, have strengths that vary inversely, as the strengths of the respective acids. The basic ionization constant of the conjugate base is given by the following equation;

$$K_B\ ,\ \text{conj.} = \frac{K_W}{K_A\ ,\ \text{conj.}}$$

where K_W is the ionic product of water. Another definition of acids and bases is due to Lewis. He relates the properties of acids to the acceptance of electron pairs, and bases as donators of electron pairs to form covalent bond regardless of whether protons are involved. Compound of the type of HF_3 are usually described as Lewis acids or electron acceptors. The Lewis bases (e.g. ammonia, pyridine) are virtually.

The Equivalent weight of an acid:

It is that weight of it which contains one g. atom of replaceable hydrogen, i.e. 1 .008g. of hydrogen. The equivalent weight of a monobasic acid such as hydrochloric, hydrobromic, hydroiodic, nitric acid, is identical with its molecular weight. A normal solution of a monobasic acid will therefore contain 1 g. molecular weight (or 1 mol.) in a liter of solution. The equivalent weight of a dibasic acid (e.g. phosphoric acid) is likewise 1/2 and 1/3 respectively of its molecular weight.

The equivalent weight of a base:

It is that weight of it which contains one replaceable hydroxyl group, i.e. 17.008g. of ionisable Hydroxyl. 17.008 g. of hydroxyl are equivalent to 1.008g. of hydrogen. The equivalent weights of sodium hydroxide and potassium hydroxide are 1 mol. Of calcium hydroxide; and barium hydroxide 1/2 mol.

Salts of strong bases and weak acids possess alkaline reactions in aqueous solution because of hydrolysis sodium carbonate, with methyl orange as indicator, reacts with 2 mols. of HCl to form 2 mols. of NaCl, hence it equivalent weight is 1/2 mol.

$$Na_2CO_3 + 2\,HCl \rightarrow 2\,NaCl + CO_2 + H_2O$$

Borax, under similar conditions, also reacts with 2 mols. of HCl acid, and its equivalent weight is, likewise, 1/2 mol.

$$Na_2B_4O_7 + 2\,HCl + 5\,H_2O \rightarrow 2\,NaCl + 4\,H_3BO_3$$

Hydrogen-ion concentration and the pH scale:

The equilibrium in the self-ionization of water may be formulated:

$$\frac{[H_3O^+]\,[OH^-]}{[H_2O]^2} = K\,,$$

at constant temperature. Since in any dilute aqueous solution the concentration of water is essentially constant at approximately 55.5 molar, we may write:

$$[H_3O^+]\,[OH^-] = [H_2O]^2\,,\ K = K_W$$

K_W is the ion product of water. At room temperature the constant may be assumed to 10^{-14} for approximate calculations. At any temperature in pure water:

$$[H_3O^+]\,[OH^-] = K_W$$

For any aqueous solution we need to use only one of the quantities $[H^+]$ or $[OH^-]$ to express the acidity or basicity of the solution, since either may be derived from the other by the relation:

$$[H^+] = \frac{K_W}{[OH^-]} \quad \text{or} \quad [OH^-] = \frac{K_W}{[H^+]}$$

For example, in a solution that is 0.1 M in hydrogen ion. $[OH^-] = \frac{10^{-14}}{10^{-1}} = 10^{-13}$ **at room temperature.**

Sorensen suggested a scale based on the exponent of the hydrogen ion concentration but with sign reversed. For example a solution of hydrogen ion concentration 10^{-13} would have an index number 13 to represent acidity. These "hydrogen exponents", constitute the pH scale of acidity. This is related to hydrogen ion concentrations as follows;

$$[H^+] = 10^{-pH} \ , \ pH = \log \frac{1}{[H^+]} = -\log [H^+]$$

A quantity pOH is defined in similar way be the relation.

$$[H^+] = 10^{-pOH} \ , \text{ or } \ pOH = \log, \ \frac{1}{[H^+]} = -\log [H^+]$$

The following summary indicates the relationships

H	10^0	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10-10	10^{-11}
pH	0	1	2	3	4	5	6	7	8	9	10	11
pOH	14	13	12	11	10	9	8	7	6	5	4	3

Acid Netural Alkaline

The reaction of any aqueous solution at room temperature is defined by

$pH < 7 < pOH$ acidic reaction

$pH = 7 = pOH$ neutral reaction

$pH > 7 > pOH$ basic reaction

Example:

i - Find the pH of a solution of which $[H^+] = 4.0x10^{-5}$

$$pH = -\log[H^+] = -\log[4 \times 10^{-5}]$$

$$= 5.802 + -4.398 = 4.398$$

ii - Fine the hydrogen ion concentration corresponding to

$$pH = 5.643$$

$$pH = -\log[H^+] = 5.643 \qquad \log[H^+] = 5.643$$

$$= 6.365 = 2.28 \times 10^{-6}$$

iii- Calculate the pH of a 0.01 N solution of acetic acid (the degree of dissociation is 12.5 percent).

The hydrogen ion concentration is $0.125 x0.01= 1.25x 10^{-3}$

Now $\log 1/25 = 0.97$.

$$pH = -(-3 + 0.098) = 2.903$$

<u>The calculation of $[H^+]$ of pH from ionization constants</u>

The ionization constant of an acid or base, together with the ionization constant of the solvent may be used to calculate the pH of a solution at any point in the course of a titration. If a solution of an acid in water is being considered. The ionization constant of the acid is used in the following winner

$$K_a = \frac{[H^+]\ [B^-]}{[HB]}$$

Where HB represents the un-ionized ion.

A still more rigorous calculation would involve the use of activity coefficients as exposited is the following:

$$K_a = \frac{f_{H+}\ [H^+]\ f_{B-}\ [B^-]}{f_A\ \ [A]}$$

where f refers to the activity coefficients and the square brackets to the molar concentrations.

The course of $[H^+]$ or pH during a titration may be calculated for various intermediate points by substituting values for A and B into the expression for the ionization constant . To calculate hydrogen ion concentration:

$$[H^+] = K_a \frac{[A]}{[B]} = \frac{[\text{acid not yet titrated}]}{[\text{salt already formed}]} \qquad (3)$$

Concentrations are of course expressed in moles per liter. The molecular concentration of the base B, is equal to the moles of base added, divided by the volume in liters. This is identical with the salt concentration since the base is converted quantitatively into the corresponding salt prior to the end point region. To calculate pH directly, transform equation.

$$\mathbf{pH = pK_a - \log \frac{[A]}{[B]}} \qquad (4)$$

It is thus easy to calculate the $[H^+]$ or the pH at any point where some definite fraction of the acid has been titrated e.g., 1/2 etc.

Buffer solution:

A buffer may be defined as a mixture of an acid and its conjugate base in generally a weak acid and its sodium or potassium salt or a weak base and its corresponding salt, such mixture have the ability to resist changes in pH upon addition of small amounted of strong acids or bases or upon appreciable dilution. Typical mixtures are: acetic acid and mono potassium phosphate, plus ammonium chloride, boric acid and Borate, etc. The pH values of such mixtures will lie at point on the rather flat regions of the titration graphs, pH vs. milliters, for the various weak acids or bases Buffer action is readily understandable in terms of the mass action principle applied to the equilibrium

$A \rightleftharpoons H^+ + B^-$: the acid A and the base B being conjugate , e.g. ; NH_4^+ and $NH_3.HC_2H_3C_2$ and $C_2H_3O_2$, etc.

$$\mathbf{X_e = \frac{[H^+]\ [B^{--}]}{[A]}} \qquad (1)$$

$$\mathbf{[H^+] = K_a \frac{[A]}{[B^-]}} \qquad (2)$$

$$\mathbf{pH = pK_a - \log A + \log B^- = pK_a - \log \frac{[B^-]}{[A]}} \qquad (3)$$

Expression (3) shows the ratio of [A] to $[B^-]$ determines the pH rather than the absolute values of the concentrations. This is true in close approximation, but activity effects vary with concentration. This explains why the pH of a good buffer is only slightly altered by a considerable dilution. The following measurements show the slight effect of dilution on acetate buffers.

<u>Mixtures 0.1 M in Total Acetates</u> :

Sodium acetate, M	**0.02**	**0.03**	**0.04**	**0.05**	**0.06**	**0.07**	**0.08**
Acetic acid, M	**0.08**	**0.-7**	**0.06**	**0.05**	**0.04**	**0.03**	**0.02**
pH	**4.11**	**4.34**	**4.52**	**4.69**	**5.86**	**4.05**	**5.28**

The addition of a light amount of an acid, such as hydrochloric, to an acetate buffer forms roughly an equivalent amount of no ionized hydrogen acetate and thus diminishes the concentration of acetate ion slightly. Thus results in slightly lower pH because the ration $[HC_2H_3O_2]$, $[C_2H_3O_2]$ is only slightly changed. The addition of a small amount of sodium hydroxide produces the opposite effect.

<u>Example</u>: Calculate the pH of the solution product by adding 10.0 ml of N-hydrochloric acid to 1 liter of a solution which is 0.1 M in acetic acid and N in sodium acetate ($K_a = 1.82 \times 10^{-5}$).

$$pH = pK_a + \log \frac{[Salt]}{[Acid]} = 4.74 = 0.09 = 4.74$$

Neglecting the volume change from 1000 to 1010 ml. the hydrochloric acid reacts with acetate ion forming practically undissocieted acetic acid

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

$$[CH_3COO^-] = 0.1 - 0.01 = 0.09$$

$$[CH_3COOH] = 0.1 = 0.01 = 0.11$$

$$pH = 4.74 + \log 0.09/0.11 = 4.74 - 0.09 = 4.65$$

Hence on adding the strong acid. the pH changes only by 4.74 – 4.65 = 0.09 pH unit, whereas, if 10 ml of N-hydrochloric acid were added to 1 liter of pure water (pH=7), the pH would have changed from 7 to -log (0.01)= 2, i.e. by 5 pH units. This illustrates the action of the acetic acid sodium acetate buffer.

Acid-Base Indicators:

Acid-base indicators are substances whose presence during a titration renders the end-point visible. Thus, at a certain pH very near, or at, the equivalence point of the titration the indicator produces in the system a changes which is easily perceptible to the eye and may consist of:

a- Sharp transformation from one color to another or to colorless.

b- Formation of a turbidity in a clear solution, or clearing up of a turbidity.

c- Development or disappearance of a fluorescence .

Most of the color acid base indictors of practical value are organic in nature. As the color changes these indictors depend on the change of the pH, they must themselves by acids or bases. The equi2librium between the indicator molecules and their ions may be represented, as follows:

Acidic Indicator HIn $\rightleftharpoons$ $H^+ + In^-$ **(1)**

Basic Indicator InOH $\rightleftharpoons$ $OH^- + In^+$ **(2)**

where HIn is the unionized form of the acidic indictor which give the acid color .

In$^-$ is the ionized form, which produces the basic color .

InOH is the unionized form of the basic indicator, which given the basic color. In$^+$ is the ionized form, which produces the acid color .

If the acid indicator is added to an acidic term on the right-hand side of equation (I) is increase and the ionization of the indicator is repressed by the common ion effect. The indictor is then predominate, in the unionised form of HIn. The acid color. If on the other hand, the indicator is added to a basic solution, the [H$^+$] is reduce by reaction of the acid indicator with the base, and reaction (1) proceeds to the right yielding more ionized indicator [In$^-$] and the basic color predominates. The reverse is true for basic indicators, in acid solution the reaction (2) proceeds to the left and the basic color is prominent. In other words, the change in color of indicators is a process of automatism and the degree of

ionization of indicators, as controlled by the pH, is the factor which determined tautomer predominates. The nature of this process may be demonstrated in the case of the nitro phenol. In basic solutions, p-nitro phenol is present chiefly in the yellow ion, while in acid solution it is present as the color less nitro compound:

Colorless Yellow Yellow

It should be noted that not all substances which show tautomeric properties can be used as indicators. the tautomeric change must be rapid, and must occupy a rather small range of pH. Therefore consideration of the tautomeric equilibrium modifies the Ostwald equation. If the formula HIn represents the normal indicator molecule, and the formula HIn represents the molecule formed by the arrangement (the tautomer), then the indicator salts is eventually produced from neutralization of weak equilibrium :

$$\mathbf{HIn} \rightleftharpoons \mathbf{HIn''} \rightleftharpoons \mathbf{H^{+}} \quad \mathbf{In''^{-}}$$

Considering the two equilibria separately

$$\frac{[\mathrm{HIn}"]}{[\mathrm{HIn}]} = \mathrm{Keq} \quad \text{and} \quad \frac{[\mathrm{H}^{+}]\ [\mathrm{In}"^{-}]}{[\mathrm{HIn}"]} = \mathrm{K}_{a}$$

Multiplying these two equations:

$$\frac{[\mathrm{H}^{+}]\ [\mathrm{In}"^{-}]}{[\mathrm{HIn}]} = \mathrm{K}_{\mathrm{Ind}}$$

This is called the indicator constant, and not the ionization constant of the indicator. The equation can also be written in the manner of Henderson equation for buffers:

$$\mathrm{pH} = \mathrm{pK}_{\mathrm{Ind}} \quad \frac{[\mathrm{In}"^{-}]}{[\mathrm{HIn}]} \quad = \qquad \ldots\ldots\ldots\ldots \quad (1)$$

It is thus clear that any change in the pH, causes a change in the ratio of the logarithm term.

$$\frac{[\mathrm{In}"^{-}]}{[\mathrm{HIn}]} \quad \text{i.e.} \quad \frac{[\text{basic color}]}{[\text{acid color}]}$$

so that at any pH value, both colors are present.

In case of indicators in which the colored ion is the action and not the anion it is possible to derive a relation between color and pH , similar to the above relation

$$\mathrm{OHIn} \rightleftharpoons \mathrm{In}" + \mathrm{OH}^{-}$$

$$\frac{[\mathrm{OH}^{-}][\mathrm{In}"]}{[\mathrm{OHIn}]} = \mathrm{K}_{\mathrm{Ind}}$$

$$\text{and} \quad \mathrm{pOH} = \mathrm{pK}_{\mathrm{Ind}} = \log \frac{[\mathrm{OHIn}]}{[\mathrm{In}"^{-}]}$$

$$\mathrm{pH} = \mathrm{pK}_{W} = \mathrm{pK}_{\mathrm{Ind}} - \log \frac{[\mathrm{In}"^{-}]}{[\mathrm{OHIn}]} \quad \ldots\ldots\ldots \quad (2)$$

In other words any change in the pH l causes a change in the ratio.

$$\frac{[In"^{-}]}{[OHIn]} \quad \text{i.e.} \quad \frac{[\text{acid color}]}{[\text{basic color}]}$$

The most efficient transition range of acid-base indicators, corresponding to the effective buffer intervals is about 2 pH units, i.e., pK_{Ind} - 1. The reason for the width of this color range may be explained as follows. The ability of the human eye is not every acute; and in general, the first change in the acid color of an indicator becomes discernible when the ration [basic color] [acid color] becomes 1/10 .

The pH value at which this color change is perceived is given by the equation:

$$pH = pK_{Ind} + \log - \frac{1}{10} = pK_{Ind}^{-1} = 1$$

Conversely, the eye cannot discern a change in the basic color of the indicator until the ratio

[basic color] / [acid color] has become 10/1 or

$$pH = pK_{Ind} + \log - \frac{10}{1} = pK_{Ind}^{+1}$$

Between the two ratios: 1/10 and 10/1 one observes an intermediate color. An indicator therefore, does not change color abruptly at a definite pH. but changes color gradually over a certain pH range called the transition range of the indicator.

Factors Affecting Indicator Transition Range:

1- Effect of Indicator concentration:

Increasing l the concentration of indicators has a serious effect on one-color indicators such as phenolphthalein

Let us writ the equilibrium expression for the dissociation of the color less acid form of phenolphthalein as

$$\frac{[In^-]\,[H^+]}{HIn} = K_a \quad \text{or as}$$

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

Where K_a is the dissociation constant and $[In^-]$ is the minimum detectable concentration of the pink base form, which we may assume to be constant, hence

$$[H^+] = K_a\ [HIn]$$

From the above equation, it is seen that the pH at which the pink end point color appears will depend upon the indicator is present, the pH at the end point will be lower. Conversely, if less indicator is present, the end point pH will shift toward higher values.

In the case of the two color indicators where the acidic and the basic forms are both colored, the transition range is independent of the concentration. Thus, if the total concentration of a two color indicator is increased, the individual concentrations of the acid and the base forms will increase proportionally and the pH transition range should

remain unchanged even though the color intensities are increased.

2- Effect of temperature :

The ionization constants of acidic indicators rise with temperature up to a certain maximum, then fall as temperature is increased further. This fall is associated with the drop in dielectric constant (D) of water rising temperature, which makes it harder to separate the ionic charges.

If the indicator process does not involve a separation of charge for it to change color (as in case azo indicators) then the indicator constant, K_{Ind}, rises with temperature causing a decrease in its transition range. On the other hand if separation of change is involved in the indicator precise, the drop in dielectric constant plays its role; but this is usually composites by the increase in k_{Ind} with rise in temperature.

Effect of Solvents:

The addition of a miscible solvent, e.g. ethanol to water decreases its dielectric constant, and thereby the ionization of the indicator decreases. Because of this, acid indicators change color at higher pH in the presence of ethanol than they do in pure water, whereas basic indicators change color at lower pH.

Effect of Diverse Ions (Salt effect):

The effect of diverse ions on indicators may be due to one or more of the following; (1) changes in the absorption spectrum of one or both forms (i.e.; colors) on the indicator; (2) electrostatic attractions which may shift the equilibrium between the acidic and basic form of the indicator; (3) removal of hydrogen ions from the solution by their interaction with the salt, thus changing the pH of the solution .

Effect of large Molecules and colloids:

Often an active site in a large molecules will " react " with an indicator and thus alter the pH at which it undergoes a color change. Proteins often influence the color change of an indicator and the effect is most pronounced when the net charge on the protein is different from that of the indicator.

Mixed Indicators:

These indictors are used when it is necessary to locate the pH of an end point within close limits. This close adjustment of pH may be obtained by using a suitable mixture of two indicators, chosen to produce a definite and characteristic color change within a very narrow range of pH. An example of such a mixed indicator is bromocresol and methyl red the acidic and basic colors of the mixture are orange and green respectively.

Screened Indicators:

Screened indicators increase the sharpness of the color change at the end point of a titration. A screened indictor is a mixture of an indicator and an inert dye whose color does not change with pH. The effect of the dye is to decrease the range of wavelengths transmitted by the solution, so that the light transmitted by the two colored forms of the indicator is not masked by light of other wave lengths. An example is the so-called modified methyl orange it is a mixture of methyl orange with the inert dye xylene-cyanol F.I. This screened indicator is purple-red in acid medium and green in alkaline medium, and gray at its intermediate point.

Turbidity Indicators:

Turbidity indicators its salts of mixed organic acids or bases of high molecular weight which coagulate and settle out of the solution at a definite pH value. It should be noted not only the pH of the solution influences the coagulation of the indicator but also the temperature, the presence of other salts and protective collides, the speed of the titration and the presence of non electrolytes as glycerin, alcohol, etc. Nevertheless, these turbidity indicators are useful in titrating weak acids or bases.

Fluorescence Indicators :

Fluorescence indicators are organic substances, which fluoresce under the influence of ultraviolet light and from

which the change of intensity disappears completely by change of pH. They are most salts of organic acids which emit visible light, when exposed to ultraviolet radiation and lose this property when their ionic state changes by changing the pH of the solution. They may be used in very cloudy or strongly colored solution, as far as cloudiness or color of the solution does not effect the fluorescence of the indictor, but provided the liquid itself does not fluoresce in ultraviolet light. Indicators which have their fluorescent change between pH 4 - 10 may be used for titration of strong acid with strong bases and vice versa. in case of titrating weak bases with strong acids indicators with a fluorescent change at low pH values must be used and vice versa in titrating weak acids with strong bases. Examples of fluorescent indicators are Eosin phioxin, chromo tropic acid, acridine orange etc.

Neutralization Curves :

An insight into the mechanism of neutralization processes is obtained by studying the changes in the hydrogen ion concentration during the course of the appropriate titration. The curve obtained by plotting pH as ordinates against the percentage of acid neutralized (or the number of ml of alkali added) as abscises is known as the neutralization curve.

Neutralization of a strong acid and a strong base :

We shall assume that both the acid and the base are completely dissociated and that the activity coefficients of the ions are unity in order to calculate the change of pH during the course of the neutralization of the strong acid and strong base or vice versa. For simplicity of calculate, we have 100 ml of 1N HCl acid and the add drop wise of 1N NaOH solution. And calculate the pH values at different points during titration process and from them calculate the pH values fro them to plot a titration curve. Consider, for example, the following points in the titration:

a- At the beginning of titration:

We have an acid concentration of 100 x 1 = 100 mil equivalents per 100 ml , $[H^+] = 1$ N

$$pH = -\log [H^+] = -\log 1 = \text{zero} .$$

b- During the titration:

for 50 ml of base $[H^+] = 50 \times 1/150 = 3.33 \times 10^{-1}$

or $pH = 0.48$

for 25 ml of base $[H^+] = 25 \times 1/175 = 1.43 \times 10^{-1}$

$pH = 0.94$

for 90 ml of base $[H^+] = 10 \times 1/190 = 5.27 \times 10^{-2}$

$pH = 1.3$

for 98 ml of base $[H^+] = 2 \times 1/198 = 1.01 \times 10^{-2}$

$pH = 2.0$

for 99 ml of base $[H^+] = 1 \times 1/199 = 5.03 \times 10^{-3}$

pH = 2.3

For 99.0 ml of base [H^+] = 0.1 x 1.199.9 = 5.01 $x10^{--}$

pH = 3.3

c- At the equivalence point:

(i.e. when acid and alkali have been added in exactly equivalent point). The solution curtains only NaCl and water. Since NaCl is not hydrolyzed the pH value of the solution is 7.00.

pH + pOH = 14   pH = 7

d- Beyond the equivalence point :

The solution contains excess alkali .

With 100.1 ml of base H^+] = 0.1/200

= 5.00 x 10^{-4} , pOH = 3.3 and pH = 10.7

With 101 ml of base [H^+] = 1/201 = 5.0 $x10^{-3}$,

pOH = 2.3 , and pH = 11.7

The results show that as the titration proceeds the pH rises slowly, but between the addition of 99.9 and 100.1 ml of alkali, the pH of the solution rises from 3.3 to 10.7, i.e. in the vicinity of the equivalence point the rate of change of pH of the solution is very rapid. The appropriate indicator is one that changes color between pH 3.5 an pH 10.5 Pheno-lphthalein, methyl red, and methyl orange are most often used. (Fig. 1).

pink

Ph.Ph

colorless

Yellow

M.O

Red

mL of titrant

Fig (1)

<u>Neutralization of a weak acid with a strong base</u>:

Let us now follow the changes in hydrogen ion concentration during the titration of 100 ml. o.1 N acetic acid with 0.1 N NaOH .

a- At the beginning of titration:

In this case the hydrogen ion concentration at the first is less than before, since acetic acid is less ionized than hydrochloric acid. It can be calculated from the ionization constant of acetic acid which at 25°C is 1.86 x 10^{-5} thus:

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

$$\frac{[H^+]\,[CH3COO^-]}{[CH_3COOH]} = Ka = 1.86 \times 10^{-5}$$

$$[CH_3COO^-] = [H^+]$$

$$[H^+]^2 = K_a\,[CH_3COOH]$$

$$[H^-]^2 = K_a\,[CH_3COOH]$$

$$[H^+] = 1.86 \times 10^{-5} \times 0.1 = 1.36 \times 10^{-3}$$

(The dissociation of the acid is relatively small that is may be neglected in expressing the concentration).

Whence $$pH = \log \frac{1}{1.36 \times 10^{-3}} = 2.87$$

b- During the titrations :

The addition of NaOH to the acetic acid solution continually forms sodium acetate in solution and the acetate ions repress the ionization of the un neutralized acetic acid. The approximate hydrogen ion concentration at any point prior to the equivalence point can be found by substituting

the relative concentration of acetate and undissocate acid in the ionization constant expression for acetic acid :

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

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

$$pH = pKa\ -\ \log\ \frac{[\ Salt\ ]}{[\ Acid\ ]}$$

When 50 ml of 0.1 N alkali have been added

$$[\ Salt\ ] = 50\ x\ 0.1/150 = 3.33\ x\ 10^{-2}$$

$$\text{and } [\ acid\ ] = 50\ x\ 0.1/150 = 3.33\ x\ 10^{-2}$$

$$pH = \log\ 1.86\ x\ 10\text{-}5 + \log\ \frac{3.33\ x\ 10^{-2}}{3.33\ x\ 10^{-2}} = 4.74$$

The pH values at other points on the titration curves are similarly calculated.

<u>c At the equivalence point:</u>

At the equivalence point the solution contains sodium acetate salt. Such a solution would not be neutral but would be slightly alkaline due to the hydrolysis of the salt.

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

The equilibrium constant in this case is

$$K = \frac{[\ OH^-\ ]\ [\ CH_3COOH\ ]}{[\ CH_3COO^-\ ]} \qquad (1)$$

But the ionization constant of acetic acid .

$$K_a = \frac{[\,CH_3COO^-][H^+]}{[\,CH_3COOH^-\,]} \qquad (2)$$

The ion product constant of water :

$$[\,H^+\,]\;[\,OH^-\,] = K_W$$

The equation in is also obtained by dividing the ion product constant of water, by the ionization constant of acetic acid.

$$\text{Hence}\quad K = \frac{K_W}{K_a} \quad \frac{[\,OH^-\,]\,[\,CH_3COOH\,]}{[\,CH_3COO^-\,]}$$

But in the preceding hydrolysis equilibrium, $[OH^-]= [CH_3COOH]$ and provided the extent of hydrolysis is not too great, the acetate ion concentration is approximately equal to the concentration of the salt (C) at the equivalence point :

$$\text{Therefore}\qquad \frac{[\,OH^-\,]^2}{[CH_3COO^-]} = \frac{K_W}{K_a}$$

$$[\,OH^-\,[\; = \sqrt{C\,\frac{K_W}{K_a}}$$

$$\text{and since}\qquad [H^+] = \frac{K_W}{[OH^-]}$$

$$[H^+] = \frac{K_W}{\sqrt{C\,\frac{K_W}{K_a}}} = \sqrt{\frac{K_W\,K_a}{C}}$$

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

$pH = 1/2 \log K_W - 1/2 \log K_a + 1/2 \log C$

$= 1/2\ pK_W + 1/2\ pK_a + 1/2 \log C$

(Where $pK_W = \log \frac{1}{K_W}$ (log K_W) ; and $pK_a = \log \frac{1}{K_a}$

$= -\log K_a$

In the sample under consideration,

$K_W = 1 \times 10^{-14}$, $pK_W = 14$, $K_a = 1.86 \times 10^{-5}$, $pK_a = 4.74$

And C = o.o5

$pH = 1/2 \times 14 + 1/2 \times 4.74 + 1/2 \log 0.05$

$= 7 + 2.37 - 0.54 = 8.83$

d- <u>Beyond the equivalence point</u>:

NaOH is added, and the ions in the solution have no appreciable effect on the hydrogen ion concentration

With 100.1 ml of base:

$$pOH = -\log \frac{0.1 \times 0.1}{200.1} = 4.3$$

$$pH = 14 - 4.3 = 9.7$$

The preceding pH values and other values in the titration are depicted graphically in Fig. 2. The common indicator suitable for this titration is phenolphalein, and the use of an indictor like methyl red or methyl orange would lead to erroneous results

Indicator ranges

Ph.Ph.

M.O.

Fig (2) Alkali added ml .

Neutralization of weak base with a strong acid:

The titration of a weak base with a strong acid is illustrated by the titration of 100 ml of 0.1 N NH_4OH with of 0.1 N HCl .

a- At the beginning or titration :

The pH value at the beginning of the titration can be calculated in a way similar to that of the acetic acid titration, namely from the ionization constant NH_4OH :

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$\underline{[NH_4^+]\ [OH^-]} = K_b = 1.75 \text{ x } 10\text{-}5$$

$$[\ NH_4OH\ ]$$

$$[\ NH_4^+\ ] = [\ OH^-]$$

$$[\ OH^-]^2 = K_b\ [\ NH_4OH\ ]$$

$$[\ OH^-] = \sqrt{\ }\ K_b\ [\ NH_4OH]$$

$$[\ OH^-] = \sqrt{\ }\ K_b\ .\ NH_4OH$$

$$[\ OH^-] = \sqrt{\ }1.75 \times 10^{-5} \times 0.1 = 1.36 \times 10^{-3}$$

$$pOH = -\log 1.36 \times 10-3 = 2.67$$

$$pH = 14 - 2.287 = 11.13$$

b- <u>pH During titration</u> :

Additions of acid to the solution result in the formation of NH_4Cl, thus giving a buffer mixture consisting of NH_4Cl and NH_4OH. During the titration, the NH_4^+ formed suppresses the ionization of NH_4OH and

$$K_b = \frac{[\ NH_4^+\ ]\ [\ OH^-\ ]}{[\ NH_4OH\ ]}$$

$$[\ OH^-]\ K_b \quad \frac{[\ NH_4^+\ ]\ [\ OH^-\ ]}{[\ NH_4\ ]}$$

$$pH = PK_w - pK_b + \log \frac{[\ Salt\ ]}{[\ Base\ ]}$$

c- <u>pH at the equivalence point</u>:

At the equivalence point the solution contains ammonium chloride salt. Such a solution would not be neutral but would be slightly acidic due to the hydrolysis of the salt:

$$NH_4Cl + H_2O \rightleftharpoons H^+ + Cl^- + NH_4OH$$

For which

$$K_b = \frac{[\,NH_4OH\,]\,[H^+\,]}{[\,NH_4^+\,]}$$

(K_b is the hydrolysis constant) and since

$$\frac{K_w}{K_b} = [\,H^+\,]\,[\,OH^-\,] \times \frac{[\,NH_4\,OH\,]}{[\,NH_4^+\,]\;[\,OH^-\,]}$$

Then ,

$$\frac{K_w}{K_b} = \frac{[\,NH_4\,OH\,]\,[\,H^+\,]}{[\,NH_4^+\,]} = K_h$$

Let [H^+] = [NH_4OH], because for each mole of NH_4OH produced, one mole of H^+ is formed. Let the concentration of the ammonium ion concentration approximately equal to the concentration C , of the salt at the equivalence point.

Therefore $\frac{[\,H^+\,]^2}{C} = \frac{K_w}{K_b}$

$$[\,H^+\,] = \sqrt{\frac{K_w\;C}{K_b}}$$

$$pH = 1/2\;pK_w - 1/2\;pK_b - 1/2\;\log\;C$$

The pH value at the equivalence point in the titration can be found from the latter equation.

d- <u>pH Beyond Equivalence point</u>:

After the equivalence point has been reached, the solution contains excess of H^+ ions, hydrolysis changes may be assumed, with sufficient accuracy for our purpose, to be those due to the excess of acid present pH = - log [H^+]. The

values completed in the above manner are represented graphically in Fig 3 . The common indicator suitable for this titration is methyl red, or methyl orange .

Fig (3) ml added

<u>Titration of a weak acid with a weak base or the reverse :</u>

The titration of a weak acid, like acetic acid, with a weak base like ammonium hydroxide gives a curve like that of (E)(C): the diagram of Fig. 4 . The (F) (F) . Such titrations are of little practical value for as seen from the curves, there is no sharp inflection at the equivalence point and to simple

indicator will give a sudden change of color at this point. A mixed indicator, which exhibits a sharp color change over a very limited pH range may sometimes be suitable. Titrations of this type are seldom made in volumetric analysis .

Fig. 4 ml. of titration solution

But, if necessary, the approximate hydrogen ion concentrations and the approximate pH value at the equivalence point can be calculated from the following formulas :

$$[H^+] \quad \sqrt{\frac{K_w \; K_a}{K_b}}$$

$$pH = - 1/2 \log K_w - 1/2 \log K_a + 1/2 \log K_b$$

$$pH = 1/2\, pK_w + 1/2\, pK_a = 1/2\, pK_b$$

Titration of polybasic acids wit strong base :

a- Ionization polybasic acids :

When a polybasic acid is dissolved in water , the various hydrogen atoms undergo ionization to different extents . For a dibasic H_2o, the primary and secondary ionizations can be represented by the equations :

$H_2A \rightleftharpoons H^+ + HA^-$ . . . . (1)

$H\ A \rightleftharpoons H^+ + A$ . . . . (2)

If the dibasic acid is a weak electrolyte, the law of mass action may be applied, and the following expressions are obtained .

$[H^+] \times [HA^-] / [H_2A] = K_1$ . . . . (1)

$[H^+] \times [A^-] / [HA^-] = K_2$ . . . . (2)

K_1 land K_2 are known as the primary and secondary dissociation constants respectively. Each stage of the dissociation process has its own ionization constant, and the magnitude of these constants give a measure of the extent to which each ionization has proceeded at any given concentration. The greater the value of K_1 relative to K_2, the smaller will be the secondary dissociation and the greater must be the dilutor before the latter becomes appreciable. It is therefore possible that a dibasic (or polybasic) acid may behave, so far as dissociation is concerned as a monobasic acid.

A tribasic acid H_3A will similarly yield three dissociation constants, K_1 , K_2 and K_3 which may be computed in analogous manner:

$$H_3A \rightleftharpoons H^+ + H_2A^-$$

$$H_2A^- \rightleftharpoons H^+ + HA^{--}$$

$$HA^{--} \rightleftharpoons H^+ + A^{---}$$

b- <u>Example</u> :

An example of a relatively weak polybasic acid we can consider the case of orthophosphoric acid. The graph for the titration is shown if Fig. 5. The first inflection is that corresponding to the formation of $H_2PO_4^-$:

$$H_3PO_4 + OH^- \rightleftharpoons H_2PO_4^- + H_2O \ (K_1 = 1.1 \times 10^{-2})$$

The second inflection corresponds to the formation of HPO_4^{--} ions :

$$H_3PO_4 + OH^- \rightleftharpoons H_2PO_4^- = + H_2O \quad (K_2 = 2.0 \times 10^{-7})$$

There is no third inflection, for the ionization constant $HPO_4^=$ is extremely small (3.6×10^{-13}). The graph shows that H_3PO_4 can be accurately titrated to $H_2PO_4^-$. If methyl orange is used as the indicator that $H_2PO_4^-$ can be titrated to $HPO_4^=$ with fair precision if phenolphthalein is used as the indicator and that H_3PO_4 cannot be titrated according to the equation:

$$H_3PO_4 + 3\ OH^- \rightleftharpoons PO_4^{---} + 3\ H_2O$$

Fig. 5 ml of titrating solution

c- <u>Calculation of the pH of each inflection</u> :

The [H^+] of the first stoichiometric point depends upon both the acid functions that are expressed by K_1 and K_2 . Multiply these two expression together to give :

$$\frac{[\,H^+\,]^2\,[HPO_4^{=}]}{[\,H_3PO_4\,]} = K_1\,K_2$$

If, as is generally the case the ratio $\frac{[HPO_4^{=}]}{[\,H_3PO_4\,]}$

The ratio of the concentration of the strongest acid function to that of the weakest, is close to 1 at this point; then as a good first approximation :

$$[\,H^+\,] = \quad K_1 \quad K_2$$

or $pH = 1/2\ (\,pK_1 + pK_2\,)$

Showing that $[\,H^+\,]$ or pH is independent of the dilution. In the case or phosphoric acid at the first stoichiometric point :

$$[\,H^+\,] = \ \surd\ 2.0 \times 10^{-3} \times\ 7.0 \times 10^{-8} = 2.2 \times 10^{-5}$$

Or $pH = 1/2\ (\,2.16 + 7.17\,) = 4.66$

In similar fashion the pH of the second stoichiometric point is, in good approximation:

$$pH = 1/2\ (pK_2 + pK_3\,) = 1/2\ (\,7.16 + 12.3\,) = 9.73$$

Titration of anions of weak acids (Bronsted bases) with strong acids . " Displacement titrations " :

In titration of potassium cyanide with hydrochloric acid the following equilibria were considered :

$KCN \rightleftharpoons K^+ + CN^-$ (salt highly ionized)

$CN^- + H_2O = HCN^- + OH^-$ (hydrolysis)

$H^+ + OH^- \rightleftharpoons H_2O$ (strong acid reacts with OH^- from hydrolysis) :

$$KCN + HCl \longrightarrow HCN + KCl \qquad \text{or}$$

$$CN^- + H^+ \longrightarrow HCN$$

The net result appeared to be the displacement of the weak hydrocyanic acid by the strong hydrochloric acid, and the process was referred to as a displacement titration. On the Bronsted theory the so-called titration of solution of hydrolyzed salts is merely the titration of weak Bronsted base with a strong (highly ionized) acid. When the anion of a weak acid is titrated with a strong acid the titration curve is identical with that observed in the reverse titration of a weak acid itself with a strong base .

A few examples encountered in practice will not be considered:

1- Titration of cyanide with strong acid :

Let us consider the titration of 100 ml. of 0.1 N-KCN with 0.1 N HCl acid at the laboratory temperature. The pH at the true and point can be calculated from the dissociation constant and the concentration of the weak at the equivalence pint. Thus in our example the volume is doubled at the equivalence point, hence the concentration of hydrocyanic acid is 0.1 N. K_a for HCN acid is 7.2 x 10-^{10} , i.e. :

$$[H^+] \times [CN^-] / [HCN] = 7.2 \times 10^{-10}$$

Hence $[H^+] = 7.2 \times 10^{-10} \times 0.1$

Since $[H^+] = [CN^-]$ **or pH = 5.1**

If 100.1 ml. of HCl acid are added, the pH will be 4, with 100.2 ml., the pH will be 3.7 with 101 ml. the pH will be 3,

etc. There will be a fairly abrupt decrease of pH in the neighborhood of the equivalence point. If the titration error is not to exceed 0.2 percent, any indicator covering the pH range 3.7 - 5.1, may be used. Suitable indicators are promo cresol green methyl orange, bromo-phenol blue and methyl red.

2- <u>Titration of borate ion with a strong acid</u>:

The titration of the pyro borate ion (using borax) with hydrochloric acid is similar. The net result of the displacement titration is given by:

$$Na_2B_4O_7 + 2\,HCl + H_2O \rightleftharpoons 2\,NaCl + 4\,H_3BO_3$$

Or $$B_4O_7^{-} + 2\,H^{+} + 5\,H_2O \rightleftharpoons 4\,H_3BO_3$$

Boric acid behaves as a weak monobasic acid with a dissociation constant of 6.4 x 10^{-10} . The pH at the equivalence point in the titration of 0.2 N borax with 0.2 N hydrochloric acid is that due to 0.1 N boric acid, i.e. 5.1 further addition of hydrochloric acid will cause a sharp decrease of pH as in the case of potassium cyanide. Similar indicators may therefore be used.

3- <u>Titration of carbonate ion with a strong acid</u>:

A solution of sodium carbonate may be titrated to the bicarbonate stage (i.e. with one equivalent of acid), when the net reaction is:

$$Na_2CO_3 + HCl \rightleftharpoons NaHCO_3 + NaCl$$

or $$CO_3^{--} + H^{+} \rightleftharpoons HCO_3^{-}$$

The equivalence point for the primary stage of ionization of carbonic acid is at pH (1/2 pK_1 + 1/2 pK_2 = 8.3,)

and we have seen that thymol blue and, less satisfactorily phenolphthalein may be employed to

Detect the end point . sodium carbonate solution may also be titrated until all the carbonic acid is displaced (two equivalents of acid) . The net reaction is then

Acid added ml.

Fig. 6 Titration of 100 ml. of 0.1 N-Na_2CO_3 with 0.1 N HCl .

$$Na_2CO_3 + HCl \rightleftharpoons 2NaCl + H_2CO_3 .$$

Or

$$CO_3^{--} + 2H^+ = H_2CO_3$$

The same end point is reached by titrating sodium bicarbonate solution with HCl acid :

$$NaHCO_3 + HCl \rightleftharpoons NaCl + H_2CO_3$$

or $$HCO_3^- + H^+ \rightleftharpoons H_2CO_3$$

The pH at the equivalence point is very approximately 3.9, and suitable indictors are therefore methyl yellow, methyl orange and cong red.

VOLUMETRIC PRECIPITATION TITRATIONS

("PRECIPITIMETRY')

Precipitation titrations are volumetric methods based on the formation of a slightly soluble precipitate. They are in many ways simpler than gravimetric methods. The precipitate needs not be separated, and needs not be pure, as long as the impurity does not consume titrant The sought for substance us determined simply be converting it into an insoluble form of known composition by adding a standard solution of the titrant The equivalence point is reached when an equivalent amount of the titrant has been added. From the volume of the sought for substance is calculated. The precipitate must be sufficiently insoluble to ensure completion of the reaction and to ensure a marked change in the concentration of the ions of precipitate at the equivalence point of the titration.

Limitations of volumetric precipitation Titrations :

Volumetric precipitation reactions have several limitations combining those of the titrimetric methods in general, and some of those of the gravimetric methods. In particular, few points need here be stressed in comparing volumetric

precipitation reactions with the other volumetric reactions, where no precipitates form.

1- <u>The stoichiometry</u> :

Purity and definitions of composition of the precipitate may be affected by the adsorption of entrain mint of impurities whose nature and extent depend on the conditions under reaction takes place, e.g. concentration speed of precipitation, temperature , etc. so that it becomes difficult to force or allow for, this type of interference. In such cases, it is recommended to apply an empirical method, namely: to standardize the solution of the reagent against known volume of the substance to be analyzed under exactly the same conditions as are used in the actual analysis of the unknown substance.

2- <u>The rate of reaction</u>:

Particularly in dilute solutions, is often slow so that a long wait is necessary for each addition of titrant to react completely. As the equivalence point is approached, a high degree of super saturation will not exist, and the rates of precipitation and attainment of solubility equilibrium become too slow for convenience of titration. The most suitable alternative, and often the only one is to take advantage or a more rapid precipitation in the reverse

direction, i.e. to add a measured excess of titrant and pack-titrate.

3- <u>Although the solubility</u>: of the precipitate may be depressed in gravimetric analysis, by adding an excess of the precipitant (the common ion effect); yet in precipitation titrations, the solubility of the precipitate must be low enough that precipitation is quantitative within experimental error when only a drop of excess titrant is added.

4- <u>The lack of suitable indicators</u>: for many precipitation titration imposes another limitations in such titrations.

Not with standing these limitations, the value of precipitation titrations has long been recognized. Generally the silver halides, silver thiocyanate and few mercury, lead and zinc salts are the most important compounds involved in precipitation titrations. The argent metric titrations, in particular are precise, simple and illustrative of almost all the important principles, and methods.

<u>Limitations of Argent metric Titrations</u> :

1- Reducing agents, such as, sulphur dioxide interfere by reducing the silver ions, and must be removed by previous oxidation

2- Colored compounds of any sort obscure the end point which is taken as the faintest ting of color detectable n the precipitated silver halide or in solution, as the case may be.

3- Silver halides are sensitive to photodecomposition, and the titration should be carried out in diffuse daylight or artificial light.

4- Most actions except the alkalis and alkaline earths interfere in several ways. (a). Some, such as Fe^{+3} form insoluble colored hydroxide in neutral or slightly acid medium (t). Some; such as Al^{+3}, hydrolyze to insoluble basic salts in neutral or slightly acid solution, showing a tendency to co precipitate chloride (c) Hg^{2+} form soluble complexes with halides of the type $[HgI_4]^{2--}$.

Solubility Product:

Ionic reactions are usually complete when any change occurs that lowers the concentrations of ions to very small values. The factor governing the completeness of a precipitation reaction is the solubility of the precipitate formed. The more insoluble l the precipitate, the more complete is the reaction at the equivalence point of the titration, and the larger is the change in concentration of the reacting ions. The equilibrium concentration of the reacting ions. The equilibrium constant expressing the solubility of a precipitate is the familiar solubility product constant.

Let us consider what happens when the sparingly soluble salt AB comes in contact with water. Some of the salt dissolves in water and assuming this compound to be an ionic solid, dissociated into its ions A^+ and B^- This reaction

can be represented in its simplest form (i.e., without considering hydration of the ions) by the equation.

$$AB \longrightarrow A^+ + B^- \qquad (1)$$

However, as the salt AB dissolves, more and more A^+ and B^- are in solution, with the net result that the change of their recombining to form AB increases; that is, the equilibrium represented simply by equation 2.

$$A\,B\ (\text{sold}) \rightleftharpoons A^+\ B^-\ (\text{solution}) \qquad (2)$$

for a saturated solution is established. The equilibrium constant for this reactions is :

$$K = \frac{[\,A^+\,]\ [\,B^-\,]}{[\,AB\,]}$$

Since the concentration of AB is constant as long as the temperature remains constant and there is some solid AB in contact with the solution (in other words the solubility of AB is independent of the amount of AB present as long as some solid exists, which implies that the speed of the reaction represented by equation (1) is constant), this equilibrium expression becomes.

$K \times \text{const} = [\,A^+\,]\,[\,B^-\,] = S_{AB}$ = Solubility product constant.

Let consider in the same way the saturated solution of the sparingly soluble salt $X_m\,Y_n$ which dissociates into m action, X^{n+} and n anions, Y^{m-}. The equilibrium for this saturated solution can be represented by the equation.

$$[\,X^{n+}\,]m\ \ [\,Y^{m-}\,]n = SX_m\,Y_n$$

A more deduction of the solubility product principle can be obtained along the following lines. For simplicity, we shall consider a binary electrolytes

$$AB \rightleftharpoons A^{+} + B^{-}$$

The velocity of the forward reaction depends, only upon the temperature and at any given temperature:

$$V_1 = K_1$$

Where K_1 is a constant. The velocity of the reverse reaction is proportional to the concentration of each of the reacting substances, hence at any given temperature

$$V_2 = K_2 \text{ x } = [Ag^{+}] \ [Cl^{-}]$$

where K_2 is another constant. At equilibrium the two velocities are equal i.e

$$K_1 = K_2 \text{ x } [Ag^{+}] \ [Cl^{-}]$$

or $[Ag^{+}] / [Cl^{-}] = K_1 / K_2 = S_{AgCl}$

Course of Ion concentration during a precipitation:

The nature of precipitation equilibrium may be studied by use of calculations involving solubility product constant, and plotting the values of the negative logarithm of ionic concentrations of the substance being determined against the volume of titrant added. The resulting titration curve illustrates the change occurring in reactant concentration during the course of a titration especially near and at the equivalence point.

Consider, for example, the course of the chloride ion concentration during the titration of 100 ml. of 0.1 N sodium chloride with 0.1 N $AgNO_3$.

1- <u>At the start the Titration :</u>

The concentration of chloride ion is the same at the initial concentration of the sodium chloride.

$[Cl^-] = 0.1$, $p\ Cl^- = \log [Cl^-] = \log 0.1 = 1$

2- <u>During the titration</u> :

On adding 50.0 ml. of silver nitrate solution, the chloride ion concentration will be decreased, not only because of precipitate formation, but also l because of increase in volume of solution. Since the total volume of solution is now 150 ml. the

$[Cl^-] = \frac{50 \times 0.1}{150} = 0.033$ and $pCl = 1.48$

Now $[Ag^+] \times [Cl^-] = 1.2 \times 10^{-10} = S_{AgCl}$

or $pAg^+ + pCl^- = 9.92 = pAgCl$

in the last calculation $pCl^- = 1.48$, hence $pAg^+ = 9.92 - 1.48 = 8.44$. In this manner the various concentrations of chloride and silver ion can be computed up to the equivalence point.

3- <u>At the equivalence point</u>:

This point reached when 100.0 ml. of silver nitrate have been added. There is neither chloride nor silver ion, and the concentration of each is given by the square root of K_5 .

$[Ag^+] = [Cl^-] = \sqrt{\ } S_{AgCl}$

$pAg+ = pCl^- = 1/2\ pAgCl = 9.92/2 = 4.96.$

4- Beyond the end point:

With 100.1 ml of silver nitrate solution $[Ag^+] = 0.1 \times 0.1/ 200.1= 5x10^{-5}$ or $pAg^+ = 4.30$, hence $pCl^- = pAgCl^- - pAg^+ = 9.92 - 4.30 = 5.62$. The results calculated as illustrations as well as some additional points are shown graphically in Fig.9. This illustrates clearly the change in pCl^- or pAg^+ at vicinity of the equivalence point.

Fig . 7. 0.1 N $AgNO_3$

Equivalent weights:

Here the equivalent weight is the weight of the substance which contains or reacts with 1 g. atom of a univalent action M^+ (which is equivalent to 1.009 g. of hydrogen) 1/2 g. atom of a bivalent action M^{2+} , 1/3 g atom of a trivalent action M^{3+}, etc. For the action, the equivalent weight is the atomic weight divided by the valence. For a reagent which reacts with this action, the equivalent weight is the weight of it which reacts with one equivalent of the action. The equivalent weight of a salt in precipitation reactions is the gram molecular weight of the salt divided by the total valence of the reacting ion) Thus the equivalent weight of silver nitrate in the titration of chloride ion is its molecular weight. In a complex formation reaction the equivalent weight is most simply deduced by writing down the ionic equation of the reaction. For example, the equivalent of KCN in the titration with silver ions is 2 mols , since the reaction is :

$$2\,CN^- + Ag^+ \rightleftharpoons [\,Ag(CN)_2\,]^-$$

In the titration of zinc ion with potassium ferrocyanide solution:

$$3\,Zn^{++} + 2\,K_4Fe(CN)_6 \rightleftharpoons 6\,K^+ + K_2Zn[Fe(CN)_6]_2$$

the equivalent weight of the ferrosyanide is one third of the formula weight.

Determination of end points in precipitation reaction:

Many methods are utilized in determining end points in these reaction, but only the most important will be mentioned here.

A- Formation of a colored precipitate (Mohr method):

The method may be summarized as follows: In the titration of a neutral solution of, say, chloride ions with silver nitrate solution, a small quantity of potassium chromate is added to serve as indicator. At the end point the chromate ions combine with silver ion to form the sparingly soluble red silver chromate. The theory of the process is as being silver chloride) S.P. 1.7 x 10^{-12}). Let us consider an actual example encountered in practice, viz., the titration of say 0.1 N sodium chloride with 0.1 N silver nitrate in the presence of a few ml. of dilute potassium chromate solution. Silver chloride is the less soluble salt and furthermore the initial concentration is high lance silver chloride will be precipitated.

At the first point where red silver chromate in just precipitated we shall have both salts in equilibrium with The solution hence:

$$[Ag^+] \times [Cl^-] = S_{AgCl} = 1.2 \times 10^{-10}$$

$$[Ag^+]^2 \times [CrO_4^{--}]\ S_{Ag_2CrO_4} = 1.7 \times 10^{-12}$$

$$[\,Ag^{+}\,] = \frac{S_{AgCl}}{[\,Cl^{-}\,]} = \frac{S_{AgCrO4}}{\sqrt{[\,CrO_4^{--}\,]}}$$

$$= \frac{[\,Cl^{-}\,]}{\sqrt{[\,CrO_4^{--}\,]}} = \frac{S_{AgCl}}{\sqrt{[Ag_2CrO_4^{--}\,]}} = \frac{1.2 \times 10^{-10}}{1.7 \times 10^{-12}} = 9.2 x 10^{-5}$$

At the equivalence point $[\,Cl^{-}\,] = \sqrt{S_{AgCl}} = 1.1 \times 10^{-5}$.

If silver chromate is to precipitate at this chloride ion concentrations:

$$[CrO_4^{--}] = \left[\frac{Cl^{-}}{9.2 \times 10^{-5}}\right]^2 = \left[\frac{1.1 \times 10^{-5}}{9.2 \times 10^{-5}}\right]^2 = 1.4 \times 10^{-2}$$

or the potassium chromate solution should be 0.014 M. it should be noted that a slight excess of silver nitrate solution must be added before the red color of silver chromate is visible. In practice, a more dilute solution (0.003– 0.005 M) of potassium chromate is generally used since a chromate solution of concentration 0.01 - 0.02 M imparts a distinct deep orange color to the solution, which renders the detection of the first appearance of silver chromate somewhat difficult. We can readily calculate the error thereby introduced, for it $[\,CrO_4^{=}\,] = 0.003$ silver chromate will be precipitated when :

$$[Ag^+] = \sqrt{\frac{S_{Ag_2\,CrO_4}}{CrO_4^{=}}} = \sqrt{\frac{1.7 \times 10^{-12}}{3 \times 10^{-3}}} = 2.4 \times 10^{-5}$$

if the theoretical concentration of indicator is used :

$$[Ag^+] = \; = \sqrt{\frac{1.7 \times 10^{-12}}{1.4 \times 10^{-2}}} = 1.1 \times 10^{-5}$$

The difference is 1.3 $\times 10^{-5}$ g. equivalent per liter. If the volume of the solution at the equivalence point is 150 ml. then this corresponds to 1.3 x 10^{-5} x 150/0.1 = 0.02 ml of 0.1 $AgNO_3$. This error however is negligible, but with very dilute solutions, a correction should be made by determining an indicator blank, i.e, by determining the silver ion consumption of chloride free calcium carbonate in about the same volume and with the same quantity of indicator as the sample

Interferences and Limitations of Mohr Methods:

1- The Mohr titration is applicable only neutral or faintly alkaline solution with pH values from about 6 to 10. In acid solution, the CrO_4^{--} concentration is greatly decreased: being converted to the slightly ionized $HCrO_4^-$. The decrease in $CrO_4^{=}$ .The decrease in $CrO_4^{=}$ makes it necessary to add a large excess of silver ions to bring about the precipitation silver chromate, and thus leads to large errors. If the acid pH is too high, the equilibrium.

$$2\,H^+ + 2\,CrO_4^{2-} \rightleftharpoons 2\,HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} - H_2O$$

is displaced to the right, and dichromate is formed whose silver salt is soluble. Therefore no indicator precipitate forms. If, on the other hand, the medium is alkaline, silver will precipitate as its oxide:

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

This interferes with the titration, the silver oxide may even precipitate before silver chromate especially where the solubility product of Ag_2O is exceeded. If ammonium salts are present, the P^H of the solution must not exceed pH 8 otherwise free ammonia will be produced and dissolve the silver chloride precipitate. Therefore, the salide solution should be neutralized before titration if necessary, by adding $NaHCO_3$ or dilute HNO_3, as the case may be.

2- cations which give insoluble chromate e.g. barium ions. They must be absent or removed before the titration.

3- The reverse titration of silver ion with chloride ion using chromate as indicator is not feasible, the flocculated Ag_2CrO_4 formed initially, reacts slowly with chloride especially near the end point of the titration. However to determine silver by Mohr method, it is possible to add excess standard chloride solution and then back-titrate using the chromate indicator .

4- Titration of iodide; and of thiocyanate is not successful because silver iodide and silver thio-cyanate adsorb

chromate ions so strongly that a false and somewhat indistinct end point is obtained.

B- Formation of a soluble colored compound:

This procedure is exemplified by the method of Volhard for the titration silver in the presence of free nitric acid with standard potassium or ammonium thiocyanate solution. The indicator is a solution of ferric nitrate or of ferric ammonium alum. The addition of the thiocyanate solution produces first a precipitate of silver thiocyanate (S.O. 7.1 x 10-^{13})

$$Ag^{+} + SCN^{-} \rightleftharpoons Ag\ SCN$$

When this reaction is complete, the slightest excess of thiocyanate produces a reddish-brown coloration, due to the formation of the complex ferri-thiocyanate ion :

$$Fe^{+++} + SCN^{-} \rightleftharpoons [\,Fe\ SCN\,]^{++}$$

This method may be applied to the determination of chlorides, bromides and iodides in acid solution. Excess of standard silver nitrate solution is added, and the excess is back-titrated with standard thiocyanate solution. For the chloride estimation, we have the following two equilibria during the titration of excess of silver ions:

$$Ag^{+} + Cl^{-} \rightleftharpoons AgCl\ ;\quad Ag + SCN \rightleftharpoons AgSCN$$

The two sparingly soluble salts will be in equilibrium with the solution hence:

$$\underline{[\ Cl^{-}\ ]} = \underline{S_{AgCl}} = \underline{1.2 \times 10^{-10}} = 170$$

$$[\ SCN^-\ ] \quad S_{AgSCN} \qquad 7.1\ x\ 10^{-13}$$

When the excess of silver has reacted, the thiocyanate may react with the silver chloride, since silver thiocyanate is the less soluble salt until the ratio [Cl⁻] / [SCN⁻] in the solution is 170 .

$$AgCl + SCN^- \rightleftharpoons AgSCN + Cl^-$$

This will take place before reaction occurs with the ferric ions in the solution and there will consequently be a considerable titration error It is therefore absolutely necessary to prevent the reaction between the thiocyanate, and the silver chloride. This may be effected in several ways, of which the first is probably the most reliable:

i - The silver chloride is filtered off before back titration.

ii - After the addition of the silver nitrate, potassium nitrate is added as coagulant, the suspension is boiled for about 3 minutes, cooled and then titrated immediately.

iii- An immiscible liquid is added to "coat" the silver chloride particles and thereby protect then from interaction with the thiocyanate. The most successful liquid is nitro-benzene, the suspension is well shaken to coagulate the precipitate before back-titration. With bromides, we have the equilibrium:

$$\frac{[\ Br^-\ ]}{[SCN^-]} = \frac{S_{AgBr}}{S_{AgSCN}} = \frac{35\ x\ 10^{-13}}{7.1\ x\ 10^{-13}} = 0.5$$

The titration error is small, and no difficulties arisen the determination of the end point. Silver iodide (S.P. 1.7x 10^{-16}) is less soluble than the bromide, the titration is negligible but the ferric ion indicator should not be added until excess of silver is present, since the dissolved iodide reacts with the ferric iron.

$$2\ Fe^{+++} + 2\ I^{-} \rightleftharpoons 2\ Fe^{++} + I_2$$

C - <u>Use of adsorption indications</u>:

Fagan has introduced a useful type of indicator for precipitation reactions as a result of his studies on the nature of adsorption. The action of these indicators is due to the indicator is adsorbed by the precipitate, and during the process of adsorption a change occurs in the indicator which leads to a substance of different color, they have therefore been termed adsorption indicators. The substances employed are either acid dyes, such as those of the fluorescein series. (e.g. fluorescein, eosin, rose Bengal, di chloro fluorescein, and di iodo di methyl fluorescein); or basic dyes, such as those of the rhodamine series (e.g. rhodamine 6 G, which are applies as the halogen salts .

<u>The theory of the action</u> of these indictors is based open the properties of colloids. When a chloride solution is titrated with a solution of silver nitrate, the precipitated silver chloride adsorbs chloride ions (a precipitate has a tendency to adsorb its own ions); this may be termed the primarily

adsorbed layer, and it will bold by secondary adsorption oppositely charged ions present in solution (shown diagrammatic ally in Fig. 6a). As soon as the stoichiometric point is reached silver ions are preset in excess; these will now be primarily adsorbed, and nitrate ions will be held by secondary adsorption (Fig. 8b). If fluorescein is also present in the solution, the negative fluorescein ion ,

(a) (b) (c)

Fig. (8)

Which is much more strongly adsorbed than the nitrate ion, is immediately adsorbed and will reveal, its presence on the precipitate, not by its color, which is that of the solution, but by the formation of a pink complex of silver and a modified fluoresceinate ion in the surface with the first trace of excess of silver ions.

(Fig. 8c) .

An alternative view is that during the adsorption of the fluorescein ion a re-arrangement of the structure of the ion occurs with the formation of a colored substance. It is

important to notice that the color change taxes place at the surface of the precipitate. If chloride is now added, the suspension will remain pink until chloride ions are present in excess, the adsorbed silver will than be converted into silver chloride, which will then primarily adsorbed chloride ions. The fluorescent ions secondarily adsorbed will pass back into solution, to which they impart a greenish-yellow color.

The following conditions will govern the choice of a suitable indicator:

i- The precipitate should separate as far as possible in colloidal condition. The solution should not be too dilute as the amount of precipitate formed will small and the color change far from sharp with certain indictors.

ii- The indicator ion must be of opposite change to the ion of the precipitating agent.

iii- The indicator ion should not be adsorbed be the particular compound has been completely precipitated but it should be strongly adsorbed immediately after the equivalence point.

Some Adsorption Indicators and Their Applications:

1- Fluorescein: For the titration of chlorides fluorescein may be used. This is a very weak acid (K_a= Ca.1 x 10^{-8}) hence even a small amount of other acids reduces the already minute ionization, thus rendering the detection of the end

point (which depends essentially upon the adsor-ption of the free anion) either impossible or difficult to observe. The optimum pH range is between 7 and 10.

2- Dichloro fluorescein: is a stronger acid and my be utilized in slightly acid solution of pH greater than 4.4 this indicator has the further advantage that is applicable in very dilute solutions.

3- Eosin (tetrabromo fluorescein): is a stronger acid and can be used down to a pH of 1.2. The color change is sharpest in an acetic acid solution. Eosin is so strongly adsorbed on silver halides that it can be used for chloride ion before the equivalence point and thereby gives a premature indication of the end point. With the more strongly adsorbing ions, Br^-, I^- and SCN^-, the competition is not serious and a very sharp end point is obtained in the titration of bromide, iodide and thiocyanat eves even in dilute solutions. Rose Bengal (dichloro tetra iodofluorescein) and dimethyl di-iodo-fluorescein have been recommend for the titration of iodides. Shod amine 6 G: The hydrochloride of a basic dye (0.05 per cent aqueous solution), is a good indicator for the titration of silver ions with a standard bromide solution in dilute nitric acid solution (the acidity should not exceed 0.5 N). As long as silver ions are present is express the indicator action is not noticeably adsorbed by silver bromine. At the equivalence point or after a very

slight excess of bromine has been added, the precipitate adsorbs the dye strongly and acquires a blue violet color.

D- <u>Turbidity method</u>:

The appearance of a turbidity sometimes utilized to mark the end point of a reaction, as Liebig's method for cyanides. When a solution of silver nitrate is added to a solution containing cyanide ions (e.g. an alkali cyanide) a white precipitate is formed when the liquids first come into contact with one another, but on stirring it re-dissolves owing to the formation of a stable complex cyanide the alkali salt of which is soluble

$$AgNO_3 + 2\,KCN \rightleftharpoons K\,Ag\,(CN)_2 + KNO_3$$

or $$Ag^+ + 2\;CN^- \rightleftharpoons [\,Ag(CN)_2\,]^-$$

When the above reaction is complete, further addition silver nitrate solution wields the insoluble silver argent cyanide.

$$Ag^+ + [\,Ag(CN)_2\,]^- \rightleftharpoons [\,Ag(CN)_2\,]$$

The end point of the reaction is therefore indicated by the formation of permanent turbidity. The only difficulty in obtaining a sharp end point lies in the fact that silver cyanide, precipitated by local excess concentration of silver ion somewhat prior to the equivalence point, is very slow to redissolve and the titration is time–consuming.

<u>In Denige modification of Liebig method</u> . iodide ion is used as indicator and aqueous ammonia is introduced to solubilitse the silver cyanide:

$$Ag^{+} \; [Ag(CN)_2]^{-} + 4\,NH_3 \rightleftharpoons 3\;[Ag(NH)_3]^{+} + 2CN^{-}$$

The iodide ion and ammonia solution are added before the titration is commenced, the formation of silver iodide (as turbidity) will indicate the end point.

$$[Ag(NH)_3]^{+} + I^{-} \rightleftharpoons AgI + 2\,NH_3$$

During the titration any silver iodide which would be formed will be kept in solution by the excess of cyanide ion always present until the equivalence point is reached:

$$AgI + +CN^{-} \rightleftharpoons [Ag(CN)_2]^{-} + I^{-}$$

The method may also be applied to the analysis of silver halides by dissolution in excess of cyanide solution and back-titration with standard silver nitrate. It can also be utilized indirectly for the determination of several metals, notably nickel, cobalt, and zinc, which form stable stoichiometric some complexes with cyanide ion. Thus if a Ni (II) salt in ammoniacal solution is heated with excess of cyanide ion, the Ni ion is formed quantitatively, since it is more stable than Ag [(CN_2) $]^{-}$ ion, the excess of cyanide may be determined by the Liebig-Deniges method.

COMPLEX FORMATIONS TITRATIONS ("COMPLEXIMETRY")

Introduction:

Titrations that cause the formation of a stable complex ion or a slightly dissociated molecule will be considered complex forming titrations. Although there are numerous reactions that fall into there two categories, actually only a few are suitable for analytical determinations. This is due to the fact that the equilibrium constant for many complex forming reactions is to small to permit the accurate detection of the equivalence point. Furthermore, a number of complex ions of different composition may be formed during the same titration. Finally, indicators for the detection of the equivalence point of complex forming reactions are not as easily found as for precipitation reaction, even though the requirements for an indicator in both types of reactions are similar. Only three complex – forming action that have been developed into titrimetric

method will be discussed in this chapter. These examples illustrate the various types of reactions that are suitable for analytical methods and probably represent some of the most practiced of these methods.

A- Argentimetric Ti-ration of Cyanide:

When a solution of silver nitrate is added to that of a cyanide, the slightly dissociated complex $Ag(CN)_2$, formed. When enough silver has been added to unit with all the cyanide in this way, any more silver will react with this complex ion and precipitate silver cyanide. The reactions can be illustrated by the equations:

$$Ag^+ + 2\,CN^- \rightleftharpoons [\,Ag(CN)_2\,]^-$$

$$Ag^+ + [\,Ag(CN)_2\,]^- \rightleftharpoons Ag\,[\,Ag(CN)_2\,]\downarrow$$

The chloride, bromide, iodide ions, etc., do not interfere. The only difficulty in obtaining a sharp end-point lies in that silver cyanide, precipitated by local concentration of silver ion somewhat prior to the equivalence pint, precipitating in a cruddy form which is slow to redissolve in the excess cyanide. The formation of silver cyanide can be prevented by addition of ammonia which complexes the silver ion and dissolve the precipitate.

$$Ag\,[\,Ag(CN)_2\,] + 4\,NH_3 \rightleftharpoons 2\,[\,Ag(NH_3)_2\,]^+ + 2\,CN^-$$

If now iodide ion, usually as a solution of potassium iodide is added to the solution before the titration is started, formation of silver iodide will indicate the end-point.

$[Ag(NH_3)_2]^+ + I^- \rightleftharpoons AgI\downarrow + 2NH_3$

During the titration any silver iodide would have a tendency to form will be kept in solution by excess cyanide always present until the end-point is reached.

$AgI + 2CN^- \rightleftharpoons Ag(CN)_2^- + I^-$

When the last of the cyanide has been removed from the solution at the equivalence point, an opalescence caused by the iodide will appear. This is due to the fact that the first addition of the silver nitrate in excess will react with the iodide to form AgI. The cyanide in which this precipitate was soluble through out the titration is no longer present to keep it in solution, and it does not dissolve in. When viewed against a black, this end-point is easily seen and the method gives excellent results.

Determination of cyanide and halide in admixture:

By a combination of Liebig and Volhard methods. it is possible to determine cyanide and halide in admixture. The solution containing cyanide and halide is titrated with standard silver nitrate solution until the first turbidity which marks the completion of the precipitation of cyanide (Liebig method). An additional amount to the standard silver nitrate is then added, in excess of the amount required for the complete precipitation of both cyanide and halide .

$Ag(CN)_2^- + Ag^+ \rightleftharpoons 2AgCN$

$Cl^- + Ag^+ \rightleftharpoons AgCl$

The precipitates are filtered off, washed, and the excess silver ion in the filtrate and washings is back titrated with standard thiocyanate solution, using ferric alum indicator (Volh-ard method). If the halide is bromide, no filtration required .

Determination of Nickel or Copper:

In additional to the reaction between silver, and cyanide ions, a standard cyanide solution can be used to determine nickel or copper. If the cyanide solution is added to an ammonical solution of nickel ion containing a small of silver iodide, the nickel cyanide complex, $NiCN)_4^{=}$, formed followed by the disappearance of the insoluble silver iodide. The disappearance of the precipitate indicates the end point, the following reaction takes place.

$$Ni(NH_3)_4^{++} + 4\,CN^- \longrightarrow Ni(CN)_4^{=} + 4\,NH_3$$

Since iron does not interfere and is kept in solution by the addition of citrate, this method is widely used for the rapid determination of nickel in steel .

Cyanide ions react with ammoniacal cupric solutions in a rather unexpected way to produce cuprous cyanide $Cu(CN)_3^{=}$ and a cyanate according to the equation:

$$2\,Cu(NH_3)_4^{++} + 7\,CN^- + H_2O \longrightarrow$$

$$2\,Cu(CN)_3^{=} + CNO^- + 4\,NH_4^+ + 6\,NH_3$$

The disappearance of the blue copper ammonia complex marks end point of the titration, Because this titration does not always proceed stoichiomettically according to the equation and due to the difficulty of detecting the last trace of blue color the method is not very accurate for this determination.

B- Mecurimetric Titrations:

Mecurimetric titration consist in using highly ionized mercuric salt as titrants to determine halides, thiocyanate and other anions to form very slightly ionized mercuric salts. The best known example is the determination of chloride with mercuric nitrate standard solution. The mercuric ion-chloride system is unusual in that the last two of the successive complexes in the formation of $HgCl_4^{2-}$ are much less stability than the first two, as shown by the successive formation (stability constants given below);

$$Hg^{2+} + Cl^{-} \rightleftharpoons HgCl^{-} ,$$

$$K_1 = \frac{[HgCl^{+}]}{[Hg^{2+}][Cl^{-}]} = 10^{6.7}$$

$$HgCl^{+} + Cl^{-} \rightleftharpoons HgCl_2 ,$$

$$K_2 = \frac{[HgCl]}{[HgCl^{+}][Cl^{-}]} = 10^{6.5}$$

$$HgCl_2 + Cl^{-} \rightleftharpoons HgCl_3 ,$$

$$K_3 = \underline{[HgCl_3^{-}]} = 10^{0.9}$$

$$[HgCl_2][Cl^-]$$

$$HgCl_3^- + Cl^- \rightleftharpoons HgCl_4 ,$$

$$K_4 = \frac{[\,HgCl_4^{2-}\,]}{[HgCl_3^-][Cl^-]} = 10^{1.0}$$

Thus, in the titration of a chloride solution with an ionized mercuric salt such as mercuric nitrate, on perchlorate there is a sudden drop in pHg when the formation of $HgCl_2$ is essentially complete.

One of the common indicators for this titration is sodium nitroprusdide. After the equivalence point of the chloride reaction is reached, the first excess of mercuric ion titration produces a white turbidity of mercuric nitroprusside:

$$Fe(CN)_5NO^{2-} + Hg^{2+} \rightleftharpoons HgFe(CN)_5NO$$

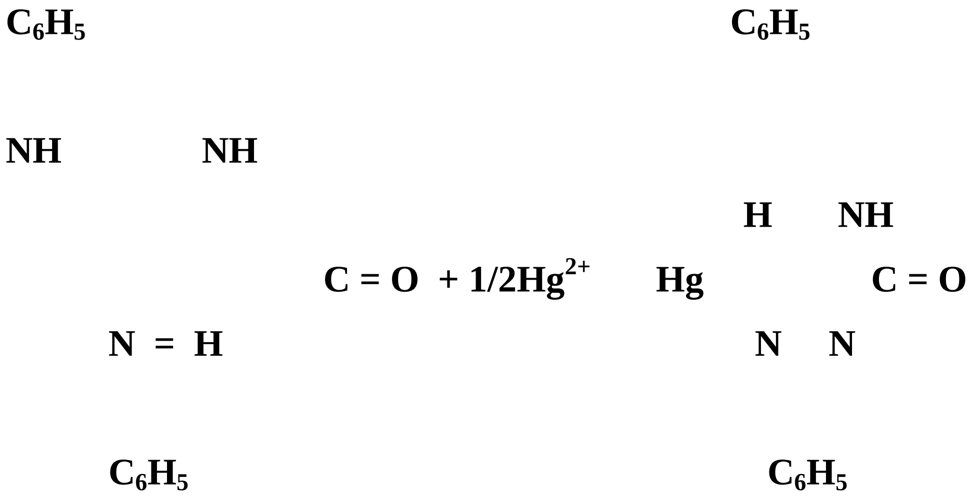
The pH at the equivalence point of the titration is not as low as might be expected from the consumption of mercuric is in the following reaction:

$$Hg^{2+} + HgCl_2 \rightleftharpoons 2\ HgCl^+ \qquad (1)$$

$$K = \frac{K_1}{K_2} = 1.8$$

Actually, the mercuric nitroprusside precipitate is first so somewhat after the equivalence point, and a correction must be applied. The correction is not really the same an indicator blank run with distilled water, because the above reaction (1) does not then take place appreciably. The correction

depends upon the final concentration of mercuric chloride and hence varies with the quantity of the sample and the final volume. An advantage of this mercurimetric method over Mohr method, is that the titration may be performed in solutions which are quite acidic and fairly, dilute, e.g. at levels of chloride which frequently occur in natural water. But some actions e.g. Cd^{2+}, Cu^{2+}, etc. interfere by forming slightly soluble nitroprussides. Certain organic compounds which form colored complexes with mercuric ions have also been used as indicators for the mercu-imetric titration of chloride. The best known is diphenyl-carbazone (orange) which gives intense violet mercuric complex:

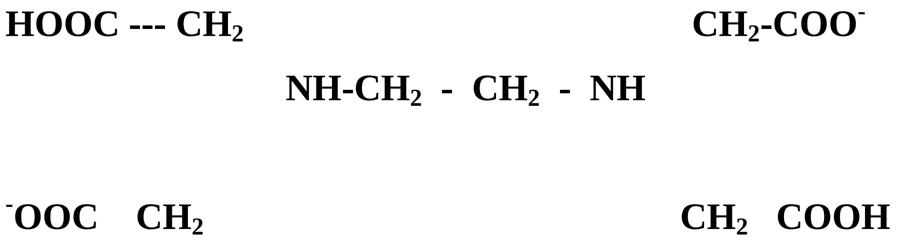


from the above equation, it is clear that the pH of the solution being titrated must be controlled. Good results are obtained at a pH of about 3.3, as adjusted by the acid-base indicator bromophenol blue whose greenish yellow color change at the end-point of the titration.

C- <u>Titrations with Multidentate Complexes</u>:

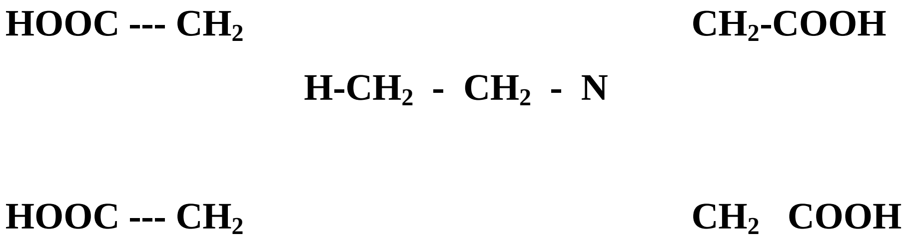
Multidentate complexes also called chelating agents are suitable metal-ion titrations, because the chelating involves very few steps that differ widely in stability constants. Certain chelating agents such as ethylene-diamine tetra acetic acid , possess enough legends.

To fill the whole coordination sphere of metal ions in one-step chelating reactions. The formula (I) is preferred to (II) . Since it has been



$$\begin{array}{lcr} HOOC{-}{-}{-}CH_2 & & CH_2\text{-}COO^- \\ & NH\text{-}CH_2\ -\ CH_2\ -\ NH & \\ {}^-OOC\ \ \ CH_2 & & CH_2\ \ \ COOH \end{array}$$

(I)

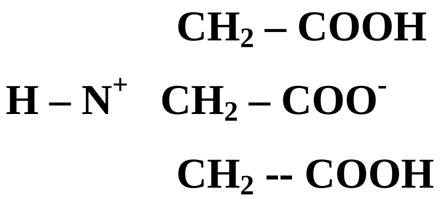


$$\begin{array}{lcr} HOOC{-}{-}{-}CH_2 & & CH_2\text{-}COOH \\ & H\text{-}CH_2\ -\ CH_2\ -\ N & \\ HOOC{-}{-}{-}CH_2 & & CH_2\ \ \ COOH \end{array}$$

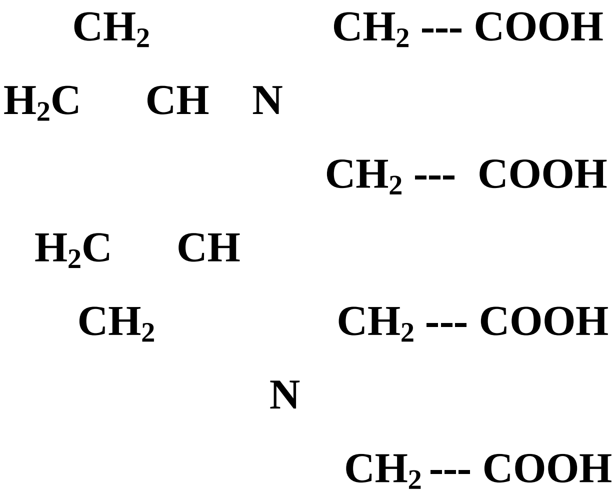
(II)

shown from measurements of the dissociation constants that two hydrogen atoms are probably held in the form of Zwitter ion. The value of pK are respectively pK_1= 2.0, pK_2 = 2.7 . pK_3 = 2.6 and pK_4 = 10.3 at 20 ^oC, these values suggest that it behaves as a bicaroxylic acid with two strongly acidic groups end that there are two protons of

which the first ionizes in the pH region of about 6.3 and the second at a pH of about 11.5. Various trivial names are used for ethylenediamine tetracetic acid and its sodium salts, and these include. Trilon B, complexone III, Sequestrane, Verseme, and Chelaton, 3. The di sodium salt is most widely employed in titrimetric analysis. To avoid the constant use of the long name, the abbreviation EDTA will be utilized for the di sodium salt when describing its use in titrations. Other complexing agents (complexiones) which are sometimes used include nitrilotriacetic acid (III) or NTA or complexone I, this has $pK_1 = 1.9$, $pK_2 = 2.5$, and $pK_3 = 9.7$) and 1.2-diamino cyclohexane- N,N,N',N' tetra acetic acid (IV), this should presumably be formulated as a Zwitter ion structure like (I), it is probably the trans- form; the abbreviated here is DCYTA or DCTA or complexon (IV).



$$\begin{array}{ll} & CH_2-COOH \\ H-N^{+} & CH_2-COO^{-} \\ & CH_2--COOH \end{array}$$



$$\begin{array}{llll} & CH_2 & & CH_2---COOH \\ H_2C & CH & N & \\ & & & CH_2---COOH \\ H_2C & CH & & \\ & CH_2 & & CH_2---COOH \\ & & N & \\ & & & CH_2---COOH \end{array}$$

(III) (IV)

The last-name forms metal complexes rather more slowly than EDTA, so that the end point in titration tends to be drawn out, with the former reagent. However, EDTA is likely to have widest general application in analysis because of (i) its relatively low price and (ii) the spatial structure of its anion which has six ligand atoms, thus corresponding with the co-ordination number most frequently encountered among the metals and in addition, it forms stainless five-membered rings on chelating.

To simplify the following discussion ethylene diamine tetracetic acid will be assigned the formula H_4Y: the disodium salt is therefore Na_2H_2Y and affords the complex forming ion H_2Y^{--} in aqueous solution. The usefulness of EDTA as a titrant is due to the presence of four or six atoms which are available for coordination to a metal action in such a way that five member rings are produced, 1:1 – complexes are usually formed and these are the most important. The reactions with actions, e.g. M^{++}, may be written as: $M^{--} + H_2Y^{--} \quad\quad MY^{--} + 2\ H^+$ (1)

For other actions, the reaction may be expressed as:

$$M^{3+} + H_2Y^{--} \rightleftharpoons MY^{--} + 2\ H^+ \quad (2)$$

$$M^{4-} + H_2Y^{--} \rightleftharpoons MY^{--} + 2\ H^+ \quad (3)$$

or $$M^{n-} + H_2Y^{--} \rightleftharpoons (MY)^{(n-4)} + 2\ H^+ \quad (4)$$

One gram ion of the complex forming H_2Y^{--} reacts in all cases with one gram ion of the metal and in each case, also

two gram ions of hydrogen ion are formed. The resulting complexes have similar structures but differ from one another in the charge that they carry. One such structure, suggested for the complex one with a divalent metal is shown in Fig 9.

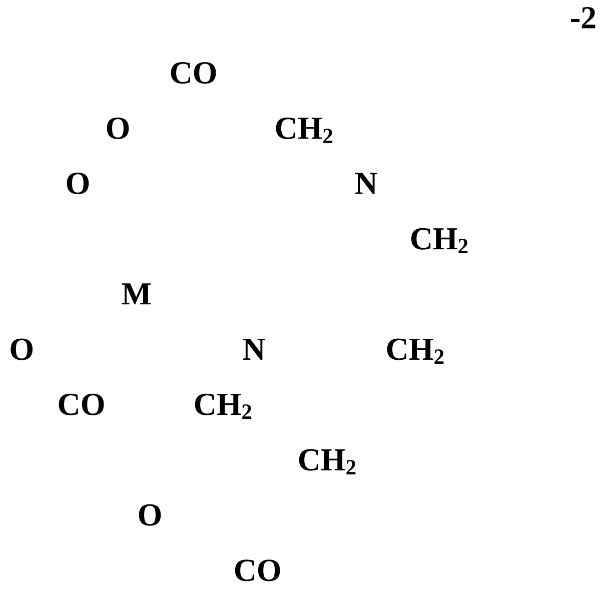


Fig. 9

<u>Stability constants</u>:

The stability of a complex is characterized by the stability constant (or formation constant K .

$$M^{n-} + Y^{4-} \rightleftharpoons (MY)^{(N-4)+}$$

$$K = [\,(MY)^{(n-4)+}\,] \;/\; [\,M^{n+}\,]\;[\,Y^{4-}\,]$$

The apparent, or conditional stability constant (or complex formation constant) at a particular pH may be calculated from the relationship K/ α, where α is the fraction of EDTA present as Y^4 only and not as the other ions formed by the

ionization H_4Y. The efficiency of complex formation with EDTA, which is affected by the variation of the pH of the solution. A decrease in pH will reduce the concentration of the complexing species, hence EDTA forms complexes with metal ions best in basic solutions with the exception of calcium and other alkaline earth metal ion, the compelling efficiency does not decrease appreciably unit the pH of the solution is relatively low-thus copper is almost complexed at pH 3.5. For magnesium and calcium a slight reduction in complexing efficiency occurs when the pH falls below 7.5. With increase in pH of the solution, the tendency to form slightly soluble metallic hydroxides in enhanced. This is be expressed:

$$(MY)^{(n-4)+} + nOH^{-} \rightleftharpoons M(OH)_n + Y^{4-}$$

The extent of hydrolysis of $(MY)^{(n-4)+}$ depends upon the characteristics of the metallic ion and is largely controlled by the solubility product of the hydroxide and, of course by its stability constant, thus iron (III) (S.P. 1×10^{-36}) is precipitated as the hydroxide in basic solution but nickel (S.P. 5.6×10^{-18}) remains complexed. The use of excess of EDTA reduces the influence of hydrolysis in basic solution.

Titration Curves:

If, in the titration of a strong acid, pH is plotted against the volume of solution of the strong base added .A point of inflexion occurs at the equivalence similarly in the EDTA

citation, if pH (negative logarithm the free metal ion concentrations: pH = -Log [M^{n+}]) is plot against the volume of EDTA solution added, a point of inflexion occurs at the equivalence point; in some instances this sudden increase may exceed 10 pH units. The general shape of titration curves obtained by titrating 10.0 ml of a 0.01 M solution of a metal ion M

With a 0.01 MEDTA solution is shown in Fig. 10

The stability constants of various metal EDTA complexes are indicated at the extreme right of the curves. It is evident that the greater the stability constant, the sharper is the end point provided the pH maintained constant.

ml. of 0.01 M EDTA

Fig. 10

Calculation the change of pH during the titration:

The calculations involved in obtaining chemometric curve may be illustrated by the reaction between magnesium

ion and EDTA. Consider the titration of 50.0 ml of a 0.1 M solution of Mg^{2+}(buffered at pH 10) with 0.10 M EDTA solution. In calculating the Mg^{2+} concentrations during the titration the effect of hydrolysis will be neglected.

1- pMg before the addition of titrant:

Since the Mg^{2+} ion concentration is given as 0.01 M, the

$$pMg = -\log [Mg^{2+}] = 1.0$$

2- pMg during titration:

Suppose that 10.0 ml of EDTA have been added. The stability constant of Mg-EDTA chelate is sufficiently high to indicate that the reaction between Mg^{2+} and EDTA is substantially complete. The EDTA chelates its equivalent of Mg^{2+}; so that the Mg^{2+} will be :

$$Mg^{2+} = \frac{(50.0 \times 0.1) - (10 \times 0.1) \text{ m.moles}}{(50 - 10) \text{ ml}} = 0.067$$

pMg values for other points before the equivalence point would be determined in a similar manner.

3- pMg at the Equivalence point:

At this point, 50.0 ml. of 0.01 M EDTA have been added. The reaction :

$$Mg^{2+} + Y^{4-} \rightleftharpoons MgY^{2-} \qquad (1)$$

Now proceeds to a degree of completion defined by the stability constant:

$$K_{stab.} = \underline{\quad [MgY^{2-}] \quad} = 5.0 \times 10^{8} \qquad (2)$$

$$[\,Mg^{2+}\,]\,[\,Y^{4-}\,]$$

At the equivalence point

$$[\,Mg^{2+}\,] \;=\; [\,Y^{4-}\,] \;=\; a$$

$$[\,MgY^{2-}\,] = \frac{5.0 \text{ m moles}}{100 \text{ ml}} - a = 0.05 - a$$

Substituting in equation (2) ; $0.05 - a = 5.0 \times 10^{8}$. The " a " in the term: (o.05 - a), is negligibly small a may be dropped and the above equation becomes:

$$\frac{0.05}{a^{2}} = 5.0 \times 10^{8}$$

$$a^{2} = [Mg^{2+}\,] = 1.0 \times 10^{-5} \text{ , and } pMg = 5.0$$

4- <u>pMg after the equivalence point</u> :

Consider that 60.0 ml. of the 0.10 M EDTA solution have been added. Then, in reaction, (1)

$$[Mg^{2+}\,] = a$$

$$[\,Y^{4-}\,] = \frac{(60 \times 0.1) - (50 \times 0.1) \text{ m.moles}}{(50 - 60) \text{ ml.}} - a$$

$$[\,MgY^{2-}\,] = \frac{(50 \times 0.1) \text{ m.mole}}{(50 + 60) \text{ ml.}} - a$$

Since the term " a " is negligible with respect to the term to which it is added, or from which it is subtracted, and substituting in equation (2):

$$\frac{0.05 \times 110}{110 \times a \times 10} = 5.0 \times 10^{8}$$

$$A = [\,Mg^{2+}\,] = 1.0 \times 10\text{-}8 \text{ , and } pMg = 8.0$$

The titration curve obtained by plotting data obtained in the above manner is given in Fig 11. The titration curve is of Familiar shape, with sharp break in the value of the equivalence.

Mililiter of EDTA

Fig. 11

Types of EDTA titrations:

The most important procedures for the titration of metal ions with EDTA are:

1- Direct titration:

The solution containing the metal ion to be determined is buffered to the desired pH (e.g. to pH with NH_4^+ - aq. NH_3) and titrated directly with the standard EDTA solution. It may be necessary to prevent precipitation of the hydroxide of the metal (or a basic salt) by the addition f some auxiliary complexing agent, such as tartrate or citrate

or triethanolamine. At the equivalence point the magnitude of the concentration of the metal ion being determined decreases abruptly. This is generally determined by the change in color of a metal indicator which responds to changes in pM: the end point may also be determined by amperometric, conductimetric (high frequency), spectrophotometric, or in some cases by potentiometric methods.

2- <u>Back titration</u>:

Many metals cannot, for various reasons, be titrated directly: thus they may precipitate from the sol. ion in the pH range necessary for the titration, or they may form complexes too slowly, or a suitable metal indicator is not available. In such cases an excess of standard EDTA solution is added, the resulting solution is buffered to the desired pH, and the excess of the tragent is back-titrated a standard metal ion solution. A solution of zinc chloride or sulphate or of magnesium chloride or sulphate is often use for this purpose. The end point is detected with the aid of the metal indicator which responds to the metal ion introduced in the back-titration.

3- <u>Replacement or substitution titration</u>s:

Substitution titrations may be used for metal ions that do not react (or react unsatisfactorily) with a metal indicator or for metal ions which form EDTA complexes that are more stable than those of other metal such as magnesium

and calcium. The metal action M^{n+} to be treated with to magnesium complex of EDTA, when the following reaction occurs:

$$Mn^{n+} + MgY^{--} \rightleftharpoons (MY)^{(n-4)+} + Mg^{++}$$

The amount of magnesium ion set free is equivalent to the action present and can be titrated with a standard solution of EDTA and a suitable metal indicator.

4- <u>Alkalimetric titration :</u>

When a solution of disodium ethylenediamine triacetate, Na_2H_2Y, is added to a solution containing metallic ions, complexes are formed with the liberation of two equivalents of hydrogen ion .

$$Mn^{n+} + H_2Y^{--} \rightleftharpoons (MY)^{(n-4)+} + 2\ H^{+}$$

The hydrogen ions thus set free can be titrated with a standard solution of sodium hydroxide using an acid-base indicator or a potentiomtric end point; alternatively, an iodate iodide mixture is added as well as the EDTA solution and liberated iodine is titrated with a standard thiosulphate solution.

The solution of the metal to be determined must be accurate neutralized before titration, this is often a difficult matter on account of the hydrolysis of many salts and constitutes a weak feature of alkali metric titration.

5- <u>Miscellaneous Methods</u>:

Change reactions between the nickel cyanide ion $[Ni(CN)_4]^{--}$ the potassium salt is readily prepared and the element to be determined. whereby nickel ions are set free have a limited application. Thus silver, palladium, and gold which themselves cannot be titrated complex metrically can be determined in this way.

$$[\ Ni(CN)_4\ ]^{--} + 2Ag^{+} \rightleftharpoons 2[\ Ag(CN)_2\ ]^{-} + Ni^{++}$$

$$[\ Ni(CN)_4\ ]^{--} + 2Pd^{++} \rightleftharpoons 2[\ Pb(CN)_2\ ]^{--} + Ni^{++}$$

These reactions cake place with sparingly soluble silver salt, and hence provide a method for the determination of the halide ions Cl^{-}, Br^{-}, I^{-} and the thiocyanate ion SCN. The anion is first precipitated as the silver salt, the latte dissolved in a solution of $[\ Ni(CN)_4\ ]^{--}$, and the equivalence amount of nickel thereby set free is determined by rapid titration with EDTA using an appropriate indicator (Murexide, Bromopyrogalol Red, or Eriochrome Red B).

Sulphate may be determined by precipitation as barium sulphate or as lead sulphate, the precipitate is dissolved in an excess of standard EDTA solution, and the excess of EDTA is back-titrated with a standard magnesium or zinc solution Eriochrome Black T as indicator. Phosphate may be determined by precipitating as: $Mg(CN)_4\ PO_4.6\ H_2O$ dissolving the precipitate in dilute hydrochloric acid, adding an excess of standard EDTA solution, buffering at pH = 10,

and back–titrating with standard magnesium ion solution in the presence of Eriochrome Black T.

Titration of mixtures (Masking and demasking agents):

EDTA is a very unselective reagent because it complexes with numerous di-, tri-, and tetra-valent actions. The following procedures help to increase the selectivity.

(a) By suitable control of the pH or the solution; this, of course, utilize the different stabilities of EDTA complexes. Thus bismuth and thorium can be titrated in a acidic solution (pH = 2-3) with pyrocatechol Violet or Xylenol orange as indicator, and iron (III) in acid solution (pH Ca. 3) with Variamine Blue as indictor; divalent metal actions do not interfere. A further example is the determination of calcium in the presence of magnesium in strongly alkaline solution using Murexide or Calcon as indicator: these indicators respond only to calcium.

(b) By the use of masking agents: Masking may be defined as the process in which a substance, without physical separation of it or its reaction products, is so transformed that is does not enter into a particular reaction. Damasking is the process in which the masked substance regains it ability to enter into a particular reaction.

Some of the actions in a mixture can often be "masked" so that they can be longer react with EDTA or with the indicator. An effective masking agent is the cyanide ion; this forms stable cyanide complexes with the actions of Cd, Zn, Hg(II), Cu, Co, Ni, Ag, and the platinum metal but not with the alkaline earths, manganese, and leas:

$$M^{++} + CN^{-} \rightleftharpoons [M(CN)_4]^{--}$$

It is therefore possible to determine such actions as those of Ca, Mg, Pb, and Mn in the presence of the above-mentioned metals by masking with an excess of potassium or sodium cyanide. A small amount of iron may be marked by cyanide if it is first reduces to be ferrous state by the addition of ascorbic acid. Titration (IV), iron (III), and aluminum can be masked with triethanolamine, mercury with iodide ions, and aluminum, ion (III), titanium (IV), and beryllium with ammonium fluoride actions of the alkaline-earth metals yield slightly soluble fluorides.

(c) The cyanide complexes of zinc and cadmium may be damasked with formaldehyde-acetic acid solution or, letter, with chloride hydrate:

$$[Zn(CN)_4]^{--} + 4H^{+} + 4HCHO \rightleftharpoons 4HOCH_2.CN$$

The use of masking and selective damasking agents permits the successive titration of many metals. Thus a solution containing Mg, Zn and Cu can be titrated as follows :

i- Add excess of standard EDTA and back-titrate with standard Mg solution using Eriochrome Black T as indicator. This gives the sum of all metals present.

ii- Treat an aliquor portion with excess of KCN and titrate as before. This gives Mg only.

iii- Add excess of chloral hydrate (or of formal-dehyde acetic acid solution, 3 :1) to the titrated solution in to liberate the Zn from the cyanide complex, and titrate until the indicator turns blue. This gives the Zn only. The Cu content may then be found by difference.

(d) Classical separations my be applied if these are not tedious, thus the following precipitated may be used for separations in which, after being rediscover, the actions can be determined complex metrically: CaC_2O_4, nickel dimethylglyoximate. Mg $(NH_4^-)PO_4$, 6 H_2O and CuSCN.

(e) Solvent extraction is occasionally of value. The zinc can be separated from copper and lead by adding excess of ammonium thiocyanate solution and extracting the resulting zinc thiocyanate with isobutyl methyl ketone the extract is dilute with water and the zinc content determined with EDTA solution.

(f) The formation of the metal indicator complex and its reaction with EDTA must be sufficiently rapid to permit establishment of the end point without under waiting, and should preferably be reversible

(g) Anions, such as orthophosphate, which can interfere in complex metric titrations may be removed using ion exchange resins.

Metal ion indicators:

Principally, metal ion indicator are organic dyes with acid-base indicator properties, that under go color change when a proton is transferred to, or from dye molecule. In addition, the dye molecule also contains chelating group which includes the transferable proton, and which is joined to the conjugated system responsible for the color. The electrochemical series of the metals is obtained. The greater the negative value of the potential, the greater is tendency of the metal to pass into the ionic state. A metal will formally displace any other metal below it in the series from solutions of its salts. Thus magnesium aluminum zinc, or iron will displace copper from solutions of its salts, lead will displace copper, mercury or silver, copper will displace silver. The standard electrode potential is a quantitative measure of the readiness of the element to lose electrons. It is therefore a measure of the strength of the element as a reducing agent in aqueous solution the more negative the potential of the element, the more powerful is its action as a reducdane.

Concentration cells:

An electrode potential varies with the concentration of the ions in the solution. Hence by bringing two electrodes of the same metal, but immersed in solution, may form a cell. Such a cell is termed a concentration cell. The e.m.f. of the cell will be the algebraic difference of the two potentials, if a salt bridge be inserted to eliminate the liquid junction potential. It may be calculated as follows: At 25°C.

$$E = \frac{0.59}{n} \log C_1 + E_o + \left(\frac{0.059}{n} \log C_2 + E_o \right)$$

$$= \frac{0.059}{n} \log \frac{C_1}{C_2}, \text{ where } C_1 > C_2$$

$AgNO_3$ aq. $AgNO_3$ aq.

Ag $Ag^+ = 0.00475$ M $Ag+ = 0.043$ M Ag

$\longleftarrow$ $\longrightarrow$

E_2 E_1

Assuming, there is no potential difference at the liquid junction.

$$E = E_1 - E_2 = \frac{0.059}{1} \log \frac{0.043}{0.00475} = 0.056 \text{ volt}$$

Oxidation – reduction cells:

In a system containing both an oxidizing agent and its reduction product, there will bean equilibrium between them and electrodes. If an inert electrode, such as platinum

is placed in a redox system, for example, one containing ferric and ferrous ions, it will assume a definite potential indicative of the position of equilibrium. If the system tends to act as an oxidizing agent, then Fe^{3+} Fe^{2+} and it will take electrons from the platinum, leaving the latter positively charged, if however, the system has reducing properties. ($Fe^{2+} \longrightarrow Fe^{3+}$), electrons will be given up to the metal, which will then acquire a negative charge. The magnitude of the potential will thus be a measure of the oxidizing or reducing properties of the system. To obtain comparative value of the " strengths " of oxidizing agent it is necessary as in the case of the electrode potentials of the metals to measure under standard experimental conditions the potential difference between the platinum and the solution relative to as standard of reference. Thus for a ferric-ferrous ,

$Fe^{3-} \longrightarrow Fe^{2+}$ electrode, the redox cell would be :

Fe^{3+} (a = 1)
Pt , H_2 H^+ (a = 1) Pt
Fe^{2+} (a = 1)

The potential measured in this way is called the standard (reduction) potential. The standard potentials enable us to predict which ions will oxidize or reduce other ions an unit activity (or molar concentration). Thus permanganate ion can oxidize Cl^- , Br^-, I^-, $Fe^{2+}$and ($Fe(CN)_6)^{4-}$; ferric ion must

be emphasized that for many oxidant's the pH of the medium is of great importance, since they are generally used in acidic media. Thus in measuring the standard potential of the MnO_4^{--} - Mn^{2+} system it is necessary to state that the hydrogen-ion activity is unity, this leads to E^o =+1.52 volts. Similarly the value of E^o for $Cr_2O_7^{2-}$ -- Cr^{3+} electrode is 1.33 volts. This means that the MnO^{4-} - Mn^{2+} system is a better oxidizing agent that the $Cr_2O_7^{2-}$ - Cr^{3+} system. Since the standard potentials for Cl_2 - $2Cl^-$ and Fe^{3+} - Fe^{2+} electrodes - 1.14 and 0.77 volt respectively permanganate and dichromate will oxidize ferrous ion but only permanganate will oxidize chloride ion; this explain, why dichromate but not permanganate can be used for the titration of ferrous ion hydrochloric acid solution.

<u>Calculation of the standard (reduction) potential</u> :

A reversible oxidation– reduction system may be written in the form (oxidant= substance in oxidized state, reductant = substance in reduced state) :

$$\text{Oxidant} + ne \rightleftharpoons \text{Reductant}$$

or

$$\text{Ox} + ne \rightleftharpoons \text{Red}$$

The electrode potential which is established when an inert or unattackable electrode is immersed in a solution containing both oxidant and reductant is given by the expression:

$$E_T = E^o + \frac{RT}{nF} \text{ In } \frac{a_{Ox}}{a_{Red}}$$

Where E_T is the observed potential or the redox electrode at temperature T relative to the standard or normal hydrogen electrode taken as zero, E^o is the standard potential, n the number of electrons gained by the oxidant in being converted into the reductant, and a_{Ox} and a_{Red} are the activities of the oxidant and reductant respectively.

Since activities are often difficult to determine directly they may be replaced by concentrations: the error thereby introduced is usually of no great importance. The equation becomes:

$$E = E^o + \frac{RT}{nF} \; In \; \frac{C_{Ox}}{C_{Red}}$$

substituting the known values of R and F, and changing from natural to common logarithms, we have for a temperature of 25°C (T = 298°) :

$$E_{25o} = E^o - \frac{0.059}{n} \; \log \; \frac{[\ Ox.\ ]}{[\ Red.\ ]}$$

If the concentrations of the oxidant and reductant are equal $E_{25}\ C^o = E^o$, i.e. the standard (reduction) potential. It follows from this expression that, for example, a ten-fold change in the ration of the concentrations of the oxidant to the reductant will produce a change in the potential of the system of 0.059/n volts.

Equilibrium constants of oxidation-reduction reactions:

It is of interest to consider the calculation of the equilibrium constant of the general redo reaction viz :

$$a\ OX_1\ -\ B\ Red_{11} \rightleftharpoons b\ Ox_{11}\ +\ A\ Red$$

The complete reaction may be regarded as combine of two oxidation-reduction electrodes. a Ox_1, a Red_1 and B Ox_{11}, b Red_{11}, combined together into a cell; at equilibrium, the potentials of both electrodes are the same

$$E_1 = E_1^o + \frac{0.059}{n} \log \frac{[\ Ox_1\ ]^a}{[\ Red_1]^a}$$

$$E_2 = E_2^o + \frac{0.059}{n} \log \frac{[\ Ox_1\ ]^b}{[\ Red_1]^b}$$

At equilibrium, $E_1 = E_2$ hence

$$E_1^o + \frac{0.059}{n} \log \frac{[\ Ox_1\ ]^a}{[\ Red1]^a} = E_2^o + \frac{0.059}{n} \log \frac{[\ Ox_1\ ]^b}{[\ Red1]^a}$$

$$\text{or} \quad \log \frac{[OX_{11}]^b}{[Red_{11}]^b} \times \frac{[\ Red_1]^a}{[\ Ox_1]^a} = \log k = n \quad (E_1^o - E_2^o)$$

This equation may be employed to compute the equilibrium constant of any redox reaction provided the two standard potentials E_1^o are known; from the value of K thus obtained the feasibility of the reaction in analysis may be ascertained. Let us consider the simple reaction:

$$Cl_2 + 2\,Fe^{++} \rightleftharpoons 2Cl^- + 2\,Fe^{+++}$$

The equilibrium constant is given by:

$$\frac{[\mathbf{Cl}^-]^2 \ \mathbf{x} \ [\mathbf{Fe}^{+++}]^2}{[\mathbf{Cl}_2] \ \mathbf{x} \ [\mathbf{Fe}^{++}]^2} = \mathbf{K}$$

The reaction may be regarded as taking place in a voltaic cell, the two half cells being a Cl_2,.$2Cl^{1-}$ electrode and a Fe^{+++}, Fe^{++} electrode. The reaction is allowed to proceed to equilibrium the total voltage or e.m.f. of the cell will then be zero, i.e., the potentials of the two electrodes will be equal.

$$E^o \ Cl_2 \ , \ 2\,Cl^- + \frac{0.059}{2} \log \frac{[Cl_2]}{[Cl^-]^2} = E_{lCl2} \, , Cl^-$$

$$E^o \ Fe^{3+} \ , \ Fe^{2+} + \frac{0.059}{1} \ \log \frac{[Fe^{3+}]}{[Cl^-]^2} = E_2Fe^{3+}/Fe^{+2}$$

Now E^oCl_2, $2Cl^-$ = 1.36 volts and E^o Fe^{3+}, Fe^{2+} = o.75 volts hence,

$$\text{Log} \ \frac{[Fe^{+++}]^2 [Cl^-]^2}{[Fe^{++}]^2[Cl_2]} = \frac{o.61}{0.02965} = 20.95 = \log \ K$$

The large value of the equilibrium constant signifies that the reaction will proceed from left to right almost to completion, i.e a ferrous salt is almost completely oxidized by chlorine.

Change of the electrode potential during the titration of an oxidant and reductant (oxidation-reduction curve):

A suitable example for purposes of illustration is the titration of 100 ml. of o.1 N-ferrous iron with o.1 ceric cerium in the presence of dilute sulphuric acid:

$$\mathbf{Ce^{++++} + Fe^{++} \rightleftharpoons Ce^{+++} + Fe^{+++}}$$

For (1) at 25^{o}C

$$E_1 = E^o{}_1 + \frac{0.059}{1} \log \frac{[Fe^{+++}]}{[Fe^{++}]} = +0.75 - 0.059 \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

For (2) at 25^{o}C

$$E_2 = E^o{}_2 + \frac{0.059}{1} \log \frac{[Ce^{-4}]}{[Ce^{+3}]} = 1.45 + 0.059 \log \frac{[Ce^{4+}]}{[Ce^{3+}]}$$

The equilibrium constant of the reaction is given by:

$$\text{Log } K = \log \frac{[\,Ce^{3+}\,] \times [\,Fe^{3+}\,]}{[\,Ce^{4+}\,] \times [\,Fe^{2+}\,]}$$

$$= \frac{1}{0.059}\,(1.45 - 0.75) = 11.84$$

Or $K = 7 \times 10^{11}$

The reaction it therefore virtually complete. during the addition of ceric solution at: the equivalence point, its only effect will be the exist the ferrous iron (Since K is large) and consequently change the ration $[Fe^{3+}] / [Fe^{2+}]$ when 10 ml. of the oxidizing agent have been added, $[Fe^{3+}] / [Fe^{2+}] = 10/90$ (approx.), and $E_1 = 0.75 - 0.059 \times \log 110/90 = 0.75 - 1.59 = 0.69$

volt. with 50 ml. of the oxidizing agent, $E_1 = E_1^o = 0.75$ volt with 90 ml. $E_1 = 0.75 – 0.0591 \log 90/10 = 0.81$ volt .

with 99 ml. $E_1 = 0.75 - 0.0591 \log 99/1 = 0.57$ volt.

with 99.0 ml. $E_1 = 0.75 - 0.591 \log 99.9/0.1 = 0.93$ volt.

At the equivalence point (100.0 ml.) $[Fe^{3+}] =[Ce^{3+}]$ and $[Ce^{4+}] = [Fe^{2+}]$, and the electrode potential is given by:

$$\frac{E_1^o + E_2^o}{2} = \frac{0.75 + 1.45}{2} = 1.10 \text{ volts}$$

The subsequent addition of the ceric solution will merely increase the ration $[Ce^{4+}] = [Ce^{3+}]$. Thus: with 100.1 ml , $E_1 = 1.45 + 0.0591 \log 0.1/100 = 1.27$ volts

with 101 ml. , $E_1 = 1.45 + 0. 591 \log 1/100 = 1.33$ volts

with 110 ml. , $E_1 = 1.45 + 0.0591 \log 10/100 = 1.39$ volts

with 190 ml. , $E_1 = 1.45 + 0.0591 \log 90/100 = 1.45$ volts

These results are plotted graphically in Fig. 13. It is of interest to calculate the ferrous-ion concentration in the neighborhood of the equivalence point. When 99.9 ml. of the Ceric solution have been added $[Fe^{2+}]$

$=0.1 \times 199.9=5 \times 10^{-5}$

or p Fe2+ = 4.3. The concentration at the at the equivalence point is given by :

0.1 N ceric sulphate added ml.

Fig. 14

$$[Fe^{3+}] / [Fe^{2+}] = K$$

$$= 7 \times 10^{11} = 8.5 \times 10^{5}$$

Now $[Fe^{3+}] = 0.05$ N , hence

$[Fe^{2+}] = 5 \times 10^{-2} / 8.5 \times 10^{5} = 6 \times 10^{-8}$ N ,

or $pFe^{2+} = 7.2$

Upon the addition of 100.1 ml. of cerric solution, the reduction potential is 1.27 volts. The $[Fe^{3+}]$ is practically unchanged at 5×10^{-2} N, may calculate $[Fe^{2+}]$ with sufficient accuracy for out purpose.

From the equations :

$$E = E_1^o - 0.059 \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$1.27 = 0.75 + 0.059 \log \frac{5 \times 10^{-2}}{[Fe^{2-}]}$$

$$[Fe^{2+}] = 1 \times 10^{-10} \text{ or } pFe^{2+} = 10$$

Thus pFe^{2+} changes from 4.3 to 1.0 between 0.1 percent before and 0.1 per cent after the stoichiometric end point.

Detection of the end point on oxidation reduction titrations

1- The reagent may serves as its own indicator :

This is well illustrated by potassium permanganate. One drop (0.05 ml.) of excess of say, 0.1 N-potassium

permanganate will impart a visible pink coloration to several hundred ml. of solution, even in the presence of slightly colored ions, such as ferric ions. This method has the drawback that an excess of oxidizing agent is always present at the end point; for wok of the highest accuracy, the indicator blank may be determined and allowed for, or the error may be considerable reduced by performing the standardization and determination under similar experimental conditions.

b- External indicators:

The best –known example of an external indicator in a redox process is the spot- test method for the titration of ferrous ion with standard potassium dichromate solution. Near the equivalence point drops of the solution are removed and brought into ferricyanide solution on spot plate. The end point is reached when the drop first fails to give a blue coloration .

c- Internal oxidation-reduction indicators:

The oxidation reduction indicator should mark the sudden change in the oxidation potential in the neighborhood of the equivalence point in an oxidation reduction titration. The ideal oxidation-reduction indicator will be one with an oxidation potential intermediate between that of the solution titrated and that of the titrant, and which exhibits a sharp readily detectable color change. An oxidation-

reduction indictor (redox indicator) is a compound which exhibits different colors in the oxidized and reduced forms:

$$In_{Ox} + ne \rightleftharpoons In_{Red.}$$

At a potential E the ratio of the concentrations of the two forms is given by the Nernst equation:

$$E = E^o_{In} - Ri/nF = In \frac{[In_{Ox}]}{[In_{Red}]}$$

Where E^o_{In} is the standard potential of the indicator. If the color intensities of the two forms are comparable a practical estimate of the color change interval corresponds to the charge in the ratio $[In_{Ox}]$ /$[In_{Red}]$ from 10 to 1/10, this leads to an interval of potential.

$$E = E^o_{In} + \frac{0.059}{n} = \text{volts at } 25^oC$$

One of the best oxidation reduction indicators is the diphenyl-amine, and was introduced by Knop for the titration of ferrous ion which $K_2Cr_2O_7$ solution. An intense blue violet coloration is produced at the end point. The addition of phosphoric acid is desirable for it lowers the formal potential, of the ferric-ferrous system so that the equivalence point potential coincides more nearly with that of the indicator. The action of diphenylamine (I) as an indictor depends upon its oxidation first into colorless diphenyl bezidine (II), which is the real indicator and is reversibly further oxidized to diphenyl benzidine violet (III).

(III)

d- Potentiometric methods :

In potentiometric titrations absolute potentials or potentials with respect to a standard half-cell are not usually required, and measurements are made while the titration is in progress. The equivalence point of the reaction will be revealed by a sudden change in potential in the plot of e.m.f. readings against the volume of the titrating solution, any method which will detect this abrupt change of potential may be used. One electrode must maintain at a constant, but not necessarily known, potential the other electrode must serve as an indicator of the changes as in ion concentration, and must respond rapidly.

Gravimetric Analysis

Gravimetric analysis is the process of isolating and weighing of a final product with known, pure stable and definite chemical structure. A gravimeter method is one in which the analysis is completed by a weighing operution .

Gravimetric analysis has the advantage that is the most precise chemical method of analysis and it has a very wide range of applications. The disadvantage of gravimetric methods is that they are generally more time consuming .

The separation of the element or the compound it may be done in a number of ways, the most important of which are:

a) Precipitation methods

b) Volatilization or evolution methods.

c) Electron analytical methods and

d) Extraction and chromatographic method

<u>Precipitation Methods:</u>

These are the most important methods in gravimetric analysis precipitation methods are based on precipitating the substance to be determined from solution as an insoluble compound of known chemical composition .

e.g. Ag^+ NaCl AgCl <u>filtered</u> <u>washed to</u>

soluble salts remove

<u>dried at</u> **<u>weighed as</u>**

150-150^{o}C **silver chloride**

Frequently the constituent being estimated is weighed in a form other the, that in which was precipitated. Thus magnesium is precipitated, as ammonium magnesium phosphate $Mg(NH_4) PO_4 6H_2O$, but is weighed, after ignition as the pyrophosphate $Mg_2P_2O_7$

<u>Choice of precipitant:</u>

One of the important consideration ion gravimetric analysis is the choice of the right precipitating agent specific reagents would react with one single species of compounds thus preventing the precipitation of any other contaminant neither by true nor by co-precipitation. However the ideal of specific reagents for one substance has not bee realised. Reagents are mostly selective, i.e. react with a group of compounds. However selectivity can be improved by adjusting the condition of the experiment e.g. Reduction of Fe^{3+} to Fe^{2+} prevents it precipitation as hydroxide with ammonia.

*** The following requirements should be met in order that a gravimetric method be successful :-**

1) The substance to be determined must be precipitated quantitatively on practice, this usually means that the

quantity reinsuring in solution does not exceed the minimum detectable by ordinary and analytical balance, viz 0.1 mg.

2) The precipitate must be pure not contaminated .

3) The precipitate must be in a physical form suitable for subsequent handling (e.g, acid filtration and washing) .

*** Precipitates of relatively large crystals are very tenement because:**

a- they are retained readily be the filter paper .

b- their surface is not extensive, accordingly, they do not readily impurities from the solution, and

c- they have easily washed .

*** Requirements for the weighed form :**

1) Its composition should correspond exactly to its chemical formula .

2) The weighed form must have adequate chemical stability. Analysis becomes more difficult or even impossible the weighed form readily changes its composition e.g. absorption of water or CO_2 form air.

3) Finally, the content of the element being determined in the precipitate should be as low as possible.

<u>* Gravimetric factor (chemical factor):</u>

In the usual gravimetric procedure a precipitate a precipitate is weighed, and from this value, the weight of analyte in the sample is calculated. The percentage of analyte, A , is then :

$$\% \ A = \frac{\text{weight of A}}{\text{weight of sample}} \times 100$$

e.g. Assume that a 0.4852 gm. sample of iron are is dissolved in acid and iron is oxidized to the +3 state and then precipitated as the hydrous oxide, $Fe_2O_3x.H_2O$. The precipitate is littered washed, and ignited to Fe_2O_3, which is found to weigh 0.2481 gm. Calculate the percentage of iron (Fe) in the sample .

The reaction are $2Fe^{3+} \longrightarrow Fe_2O_3 \text{ x } H_2O \longrightarrow Fe_2O_3(S)$

Since 2 mol of Fe^{3+} produce 1 mol of Fe_2O_3, mol Fe = 2 mol Fe_2O_3 .

$$\frac{\text{gm}}{55.85 \text{ gm/mol}} = 2 \text{ x } \frac{0.2481 \text{ gm.}}{159.69 \text{ gm/mol}}$$

$$\text{gm} - 0.2481 \text{ gm. X } \frac{2 \text{ x } 5589 \text{ gm/mol}}{159.63 \text{ gm/mol}} = 0.1755 \text{ gm}$$

$$\% \text{ Fe} = \frac{0.1735 \text{ gm.}}{0.4582 \text{ gm.}} \text{ X } 100$$

*** Note that in calculating the weight of Fe in the precipitate, the weight of precipitate, O.2481 gm., is multiplied by the factor (2 x 55.85 / 159.69) to give 0.1735 gm. This factor is called a GRAVIMETRIC FACTOR. It is simply the number of grams of Fe in 1 gm. of Fe_2O_3. thus the gravimetric factor for Fe in Fe_2O_3 is commonly written 2 Fe/Fe_2O_3, where Fe in Fe_3O_4 is 3 Fe/Fe_3O_4, and MgO in $Mg_2P_2O_7$ is 2 MgO/ $Mg_2P_2O_7$.**

Example: Calculate the number of milliliters of ammonia, density 0.99 g/ml., 23 % by weight NH_3, which will be required to precipitate as $Fe(OH)_3$, the ion in a 0.70 gm sample that contains 25 % Fe_2O_3

The precipitation reaction is :

$$Fe_3^+ \ 3NH_3 + 3H_2O \longrightarrow Fe(OH)_3\,(S) + 3NH_4^+$$

and 3 X mol Fe^+_3 = mol NH_3

$$\text{mol } Fe_2O_3 \text{ in sample} = \frac{0.0 \text{ x } 0.25}{15969} = 0.011$$

$$\text{mol } Fe^+_3 = 2 \text{ x mol } Fe_2O_3 = 2 \text{ x } 0.011 = 0.0022$$

$$M_{NH3} = \frac{0.99 \text{ gm/mol x } 1000 \text{ ml/liter x } 0.025}{1903 \text{ gm/mol}}$$

$$M_{NH3} = 134 \text{ mol/liter}$$

mol NH_3 - V x M where V = liters of NH_3

Hence

$$3 \text{ x } 0.0022 = V \text{ x } M = -V \text{ x } 1.34$$

$$V = 0.00 - 9 \text{ liters or } -3 \text{ ml}$$

<u>* The purity of the precipitate:</u>

It was assumed that the compound which separated out from the solution was chemically pure, but this is not always the case. The purity of the precipitate depends l upon the substances present in solution both before and at the addition of the reagent, and also upon the exact experimental conditions of precipitation .

* The colloidal state:

The colloidal state of matter is distinguished by a certain range of particle size (0.001 to 0.U) as a consequence of which certain characteristic properties
Become apparent . Ordinary of filter popers will retain particles up to a diameter of 1o U , so the colloidal solutions in this respect behave like true solutions.

* Properties of colloids:

1) The solid is dispersed in the form of aggregates of the ions or molecules while in true solution the dissolved solid is homogeneously dispersed in the form of individual ions on molecules .

2) In contrast to the true solution, the solid present in a colloidal suspension has a negligible effect on such properties as freezing point, boiling point, osmotic pressure .

3) The colloidal suspension have the tendency to scatter visible radiation. This when alight beam, passes through a colloidal solution, its path can be readily seen (Tyndall effect).

4) Owing to the smallness of the size of the particles, the ratio of surface to weight is extremely large. Phenomena which depend upon the size of the surface, such as adsorption, will play therefore an important part with substances in the colloidal state .

5) Typical colloidal solutions may remain without forming a precipitate for a very long time. This clearly proves the existence of certain factors preventing cohesion of the colloidal particles. One of these factors, is the presence of like electric charges on the colloidal particles, these cause mutual repulse on the particles, which are prevented from joining burger aggregates .

*** Surface charge of colloids:**

Colloidal particles are electrically charged because of the adsorption of ions to their surfaces when the AgCl particles are of colloidal size, there are a large number of Ag^+ and Cl^- ions on the surface. Small particles have a large surface to mass ratio, and the surface ions attract ions of opposite charge from the solution. Here the solution contains Na^+ , Cl^- and NO_3^- ions (as well as H^+ and OH^-). The surface Ag^+ ions attract Cl^- and NO^{-3} ions, and the surface Cl^- ions attract Na^+ ions. In general, that ion in solution which is most strongly adsorbed is the one common to the lattice (i.e. every precipitate has a tendency to adsorb own ionic), in this case the chloride ion. It no common ion is present this rule says that the ion in solution that forms the least solute compound with one of the lattice ions is the most strongly adsorbed. This the surface of the particle acquires a layer of chloride ions and the particles become negatively charged.

The process is represented schematically in Figure. Cl^- ions are said to form a primary layer, they in turn attract Na^+ ions Na^+ ions, forming a secondary layer. The secondary-layer is held more loosely than the primary layer

The primary and secondary layers are considered to constitute on electrical double layer which imports a degree of stability to the colloidal dispersion.

These layers cause colloidal particles to repel one another, and the particles therefore resist combination to iron larger particles which will settle iron the solution. The particles can be made to COAGULATE (or FLOCCULATE), that is, to cohere and form larger clumps of material that will settle from the solution, by removal of the charge contributed by the primary layer. In the example of AgCl, coagulation can be achieved by further addition of $AgNO_3$ until equivalent amounts of silver and Cl^- ions are present. Since Ag^+ ions are more strongly attracted to the primary layer of chloride ions than are sodium ions, they replace sodium ions in the secondary layer and then neutralize the negative charge contributed by the primary layer. Stripped of their charge, the particles immediately cohere and form clumps of maternal which are sufficiently large to settle

from the solution i.e. If a small amount of electrolytes is added to a colloidal solution, particles coagulate into larger aggregates. The coagulation effect is explained simple with the assumption that the colloidal particles adsorb oppositely charged ions from electrolyte to these primarily adsorbed. Accordingly, the charge on the colloidal particles are decreased so, much that they can join together. Thus, the coagulating effects of electrolytes increase rapidly with increasing the valence of that ions of the opposite charge to that on the colloidal particles .

Peptization:

Upon washing the precipitate with water, part of the adsorbed electrolyte is removed. The electrolyte concentration in the supernatant liquid may fall below the coagulation value (minimum amount of electrolyte necessary to cause flocculation), the precipitate may pass into colloidal solution again .

* The formation of amorphous precipitates :

In this case addition of each portion of precipitant causes rapid formation of an enormous number of very minute crystalline nuclear in the liquid, these grow not by deposition of the substance on their surfaces but by joining to form larger aggregates which sink by gravity to the bottom of the vessel.

<u>*Amorphous precipitates have:</u>

1) Enormous surface area and therefore adsorb readily various extraneous substances from solutions.

2) Since the bonds between the individual crystal nuclei in the aggregates are relatively weak, the aggregates may break up again to give a colloidal solution .

***Substances of very low solubility form amorphous precipitate for example metal sulphides and hydroxides. Because of the very low solubility, the solubility product is greatly exceeded by addition of even small amounts of precipitant and this favors the rapid formation of numerous crystalline .**

The typed precipitate formed depends not only on the individual properties of substance but also on the precipitation conditions. For example $BaSO_4$ is precipitated in crystalline form out of dilute aqueous solution. However it is precipitated out of mixture of water with 30 -60 % alcohol, which greatly reduces the solubility of $BaSO_4$ of $BaSO_4$, a colloidal solution or an amorphous precipitate is formed.

The supersaturating of the solution must be kept as low as possible so that the S.p. of the substance is not exceeded too much considerable super saturation of the solution of avers rapid formation of numerous new crystal nuclei, naturally, these can not grow sufficiently before the end of the precipitation. On the other hand, in precipitation from

slightly super saturated solution few new crystal nuclei are formed by addition of each portion of precipitant .

To keep the super saturation of the solution during precipitation as low as possible it is necessary.

1-To perform the precipitation from fairly dilute solution with dilute solution of precipitant.

2-To add the precipitant very slowly drop lay drop (especially at the start of precipitation).

3-To stir the solution continuously with glass rod in order to avoid high local super saturations as the precipitant is added

4-To precipitate, from hot solution by a hot solution of precipitant as the solubility of precipitates rises with temperature.

When precipitation occurs, the size of the particles of the precipitant is though to be determined by the relative rates of two processes, (1) the formation of nuclei call a nucleation, and (2) the growth of these nuclei to form particles sufficiently large to precipitate. If the rate of nucleation is small compared to the rate of growth of nuclei , fewer particles are finally produced and these particles are relatively large in size. Such a precipitate is more easily filtered and is frequently purer than a precipitate whose particles are relatively small. Hence the analyst tries to adjust condition during precipitation so that the rate of

nucleation is small compared to the rate at which the particles grow in size.

Van Weimar was the first to make a systematic study of the relationship between the size of the particles of a precipitate and the rate of precipitation. He proposed that the initial rate of precipitation is proportional to the relative super saturation, where

$$\text{Relative super saturation} = \frac{Q - S}{S}$$

Q, is the total concentration of the substance momentarily Produced in the solution by mixing the reagents, and S is the equilibrium solubility. The term Q – S represents the degree of super saturation at the moment precipitation begins. The larger this form, the greater the number of unclear and the smaller the particles of precipitate. The term S in the denominator represents the force resisting precipitation or causing the precipitate to redissolve. The greater the value of S, the smaller the ratio and hence the smaller the number of nuclei formed. Since the analyst is interested in obtaining large particles conditions should be adjusted to make the ratio (Q – S/S) as small as possible.

Selecting or predicting optimal experimental conditions:-

One does find experimentally that relatively large particles of precipitate are obtained if the degree of super saturation is kept low. The value of (Q – S/S) can be

decreased by decreasing Q or unceasing S. In practice one routinely brings about 0 moderate decrease in Q by (1) using reasonably dilute solutions and (2) adding the precipitating agent slowly. Frequently It is possible to increase the value of S markedly and this effect a large decrease in the ratio. This can be done by taking advantage of the factors that may increase solubility. Temperature, pH or the use of complexing agents precipitations are quite commonly carried out at elevated temperatures for this reason. Salts of weak acids such as CaC_2C_4 and ZnS, are better precipitated in weakly acidic rather than alkaline solution. Barium sulfate is better in 0.01 to 0,05 M HCl acid solution since the solubility is increased by the formation of bisulfate ion. A compound such as $Fe(OH)_3$ is so insoluble that even in acidic solution, the value of (Q – S/S) is still so large that gelatinous precipitate results .

Digestion Ageing of Precipitates:

This is usually carried out by allowing the precipitate, to stand for 12 - 24 hours at room temperature, or sometimes by warming the precipitate for sometime, in contact with the liquid from which it was formed. This process is called also ageing, and it is accompanied by particle growth. This crystal growth is due to the higher solubility of very fine crystals of a substance in comparison with larger crystals under the same condition and redeposit

upon the large particles. Ripening (gaining) is achieved by dissolution of the fine crystals of the precipitate and growth of larger crystals at their expense. Rise of temperature increases the rate of dissolution of fine crystals and ripening is accelerated. Upon digestion, the rapidly formed crystals, which are of irregular shape and possess a comparatively large surface area. The net result of digestion is usually to reduce the extent of co-precipitation and to increase the size of the particles, rendering filtration.

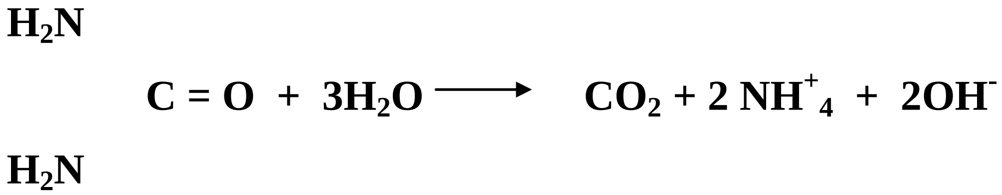
Precipitation from Homogeneous solution:

It's very important to lower the degree of super station order to prouder more easily filtered and lest consummated precipitate. The degree of super saturation can be reduced drop wise addition and by the use of dilute hot dilute with continuous stirring. However, with all the conventional precautions the local super saturation at the point of contact of the precipitant with solution could not be avoided.

In the present technique, the precipitating ion is not added but is generated gradually through out the entire solution by more of suitable chemical reaction.

An important example of homogeneous precipitation involves the use of urea to generate hydroxyl ions for the precipitation of Al^{3+}, Fe^{3-} and other heavy metal ion. The precipitating reagent is formed by the following reaction

that takes place slowly at temperatures just below the boiling point of water .



$$\mathbf{(H_2N)_2C = O + 3H_2O \longrightarrow CO_2 + 2\,NH^{+}_{4} + 2OH^{-}}$$

The urea method can be also applied to precipitation of calcium oxalate. Here the Ca^{2+} and oxalate ions are brought together in a solution that is sufficiently acidic to prevent formation of the precipitate. By heating with urea, large course crystals are produced.

Barium ions have also been precipitated homogeneously as crystalline $BaSO_4$ by slow hydrolysis of dimethyl sulphate according to the following equation

$$\mathbf{(CH_3)_2SO_4 + 2\,H_2O \longrightarrow 2CH_3OH + SO_4^{2-} + 2H^{+}}$$

<u>Washing of precipitates:</u>

Washing serves to remove surface adsorbed impurities and impurities in the mother liquor adhering to the precipitate. The imposition of the wash solution will depend upon various factors such as the solubility of the precipitate, its tendency to undergo peptisation the impurities to be removed ect. Pure water cannot, in general, be employed owing to the possibility of producing partial peptisation of the precipitate. A solution of some electrolyte is employed. This should be easily volatilized during the heating of precipitate ion precipitate in preparation of the weighing

form e.g., ammonium salts, ammonium solution and dilute acids. In order to reduce solubility errors, this electrolyte should posses common ion with the precipitate.

Drying and Ignition of Precipitates:

After a precipitate has been filtered and washed, it must be sought to a constant composition before it can be weighed The other treatment will be either drying or drying and ignition of the precipitate. Drying and ignition are nearly the same except for the temperature, drying is usually done at a temperature below 250°C.

A temperature of 110 – 1345°C is commonly used for drying. An initial drying period of 1-2 hours is used, then the precipitate is cooled in desiccators and weighed. Heating for another half hour, cooling, and weighing are repeated till constant weight is obtained.

Ignition above 2250°C up to say, 1200°C is done in order to transfer substance to a definite chemical composition, e.g., precipitated $Fe(OH)_3$ is first dried at 100°C – 105°C, then ignited to the pure dry Fe_2O_5.

According to the nature of the precipitate, it may be incinerated together or apart from the filter paper.

a)Incinerotion of the precipitate apart from filter paper is done for precipitates which are easily reducible by the action of carbon produced on burning the filter paper such as copper oxide which is reduced to metallic copper and

$BaSO_4$which is reduced to BaS or Fe_2O_3 to Fe_3O_4,etc. For this, the precipitate after drying is separated from filter paper by friction, the filter paper is first inciremted in a crucible until its carbon is completed, burnt off and the precipitate then added to crucible and incineration until the crucible acquires a constant weight.

b)Incinerator of the precipitate and filter paper together. This is used for some precipitate which are very stable and unreducible by the carbon of the burnt filter paper e.g,Al_2O_3

Contamination of Precipitate:

The precipitate formed during gravimetric analysis is not always perfectly pure it may contain varying amounts of impurities depending upon the nature of the precipitate and the condition of precipitation. This contamination can take place by one or other of the following mechanisms which can be grouped under two main groups either:

a) True precipitation or

b) Co-precipitation

a) Contamination by True Precipitation:

Most of the common precipitating agents are not specific, they are only selective in the sense that they form precipitates with a small group of elements.

1) Simultaneous precipitation:

In this case the solubility product constants of both substance to be analyzed and the impurity are exceeded

under the condition of the experiment and accordingly the main precipitate and the impurity are simultaneously thrown dowry together. For example, on precipitation of Ba^{2+} ions as $BaSO_4$ from a solution containing Pb^{2+} ions, the precipitate will be contaminated by $PbSO_4$. Similarly, aluminum and/or chromium ions if present during the precipitation of Fe^{3+} ions as $Fe(OH)_3$, it is quite obvious that all three ions will be precipitated together. This can be prevented by :

a)The use of selective precipitant which gives a precipitate with the desired component only .

b)Modifying the procedure of analysis so as to remove the interfering element before adding the group reagent e.g. lead is removed as sulphide before precipitating the potassium as sulphate.

2) Post precipitation:

It is the gradual precipitation of an impurity on the surface the desired precipitate, when the solution and precipitate are left in contact. For example, in the precipitation of calcium as oxalate in presence magnesium, excess oxalate ions will be adsorbed on the surface of precipitate. The solubility product of magnesium oxalate will be exceeded around the precipitate and accordingly magnesium will be gradually precipitated on the surface of calcium oxalate.

A similar post precipitation takes place during the precipitation of some sulphides; for example S is usually post precipitated on bismuth and copper sulphides in 0.3 N acid solution. In this case, the first formed precipitate tends to adsorb is similar ions form solution, and thus a high concentration of sulphide ions created around the particles of the precipitate. The solubility product of the second sulphide will be exceeded and Zn^{2+} ions will be gradually precipitated as ZnS .

Here, the impurity is not generally precipitated under the given conditions of the experiment by the precipitant used. It is only precipitated in presence of the substance to be determined.

Contamination by post precipitation can be minimized by rapidly filtering of the desired precipitate after short digestion:

*** B) Contamination by Co-precipitation:**

In this case the foreign material is carried down by the precipitate even though. it does not itself form an insoluble compound with the employed reagents.

For example, if sulphuric acid is added to a solution containing a mixture of $BaCl_2$ and $KMnO_4$, and after precipitation, the $KMnO_4$ in solution is then reduced by Na_2SO_3. The solution will be colorless but the formed

precipitate will have a violet color indicating the co-precipitation of $KMnO_4$ together with the $BaSO_4$.

1) Adsorption Co-precipitation :

In this case, in purities are retained on the surface of the precipitated particles by the adsorption power.

Adsorption is a reversible process, it accompanied by opposite process which is known as adsorption, i.e. passage of adsorbed ions or molecules from the adsorbent surface into solution. A state of dynamic equilibrium is achieved, known as adsorption equilibrium. The position of the equal barium depends on several factors.

1) Effect of the adsorbent area. The amount of a substance adsorbed is directly proportional to the total surface area of the adsorbent. Adsorption is mostly encountered with amorphous precipitates formed by aggregation of colloidal particles, owing to enormous surface areas. Adsorption is usually less significant when dealing with crystalline precipitates which have much smaller surface areas.

2) Effect of concentration; adsorption of various substances or ions increases with increase of their concentration in solution; the relationship, however, is not linear.

3) Effect of temperature: rise of temperature favors desorption, i.e, the amount of substance adsorbed decreases as the solution temperature rises.

4) Effect of nature of the adsorbed ions: Adsorption is characterized by a high degree of selectivity. It is known that a precipitate has a tendency to adsorb it is own ions e.g., $BaSO_4$ precipitate preferentially adsorb its own ions, Ba^{2+} and SO_4^{2-}, dependent on which is present in the solution in excess. Among extraneous ions, NO_3^- ions are adsorbed more than Cl^- ions becomes $Ba(NO_3)_2$ is less soluble than $BaCl_2$.

Adsorbed impurity will contribute to errors in gravimetric analysis only if it remains with the precipitate in the final weighing. But it can be removed by washing or if it is volatile it may removed during drying and ignition of the precipitate before weighing. It is also possible, during washing of the precipitate to replace adsorbed nonvolatile ions by volatile ones.

Digestion and re crystallization are useful in further purifying the precipitate. Any adsorbed impurities will become diluted and adsorption is greatly retarded, if the precipitate is subjected to digestion and re crystallization.

2) Occlusion Co-precipitation:

Here, impurities are co- precipitated not on the surface but within the precipitated particles. Therefore occluded impurities can not be removed from a precipitate by washing. It can be divided into:

A) Mechanical occlusion:

It is the simple mechanical enclosure of a portion if mother liquor with small ballots or pockets which are formed during aggregation of amorphous particles or rapid growth crystals. The faster crystallization occurs the more the entrained impurities by mechanical occlusion

B) Adsorptive occlusion:

The trapping of initially adsorbed substances within growing crystals is known as adsorptive occlusion or internal adsorption. This occurs during the building up of the precipitate from the primary particles. The primary formed crystal nuclei will be subjected to a certain amount of surface adsorption. As the crystal grows, these impurities are gradually displaced by the ions constituting the crystal lattice of the precipitate.

However, usually this displacement is incomplete. Accordingly, some impurity initially present on the particle surface, become separated from the solution by the newly deposited layer of substance.

Internal adsorption is influenced by the sequence of addition of the solutions. For example, suppose the precipitation of $BaSO_4$ by drop wise addition of sulphuric acid solution to $BaCl_2$ solution. The $BaSO_4$ crystals grow in a medium containing Ba^{2+} ions in excess, Barium ions become adsorbed as primary layer and Cl^- ions are hold as counter

ions (secondary layer). As more precipitant (H_2SO_4) is added, Cl^- counter ions are displaced by $SO^{2-}{}_4$ ions whit are common to the precipitate. Since this displacement ion incomplete, the precipitate occludes some Cl^- ions. In other word, we obtain a $BaSO_4$ precipitate contaminate with a small amount of $BaCl_2$. The situation is different if the order of precipitation is reversed i.e, if $BaCl_2$ solution is added drop wise to H_2SO_4 acid solution. $BaSO_4$ crystals grow in a medium containing SO_4^{2-} ions in excess. Sulphate ions form the primary layer while H^+ (or Na^+ or K^+ present in solution) are the counter ions. This means that as a result of occlusion, the precipitate contains an admixture of H_2SO_4 or of various sulphate such as K_2SO_4 or Na_2SO_4

Occluded impurities can not be removed by simple washing. Ageing and re crystallization are often used in quantitative determination for removal of such impurities.

3) Isomorphous replacement or formation of mixed crystals:

Ions having the same size as any of the ions constituting the precipitate will have priority in taking positions in the primary or secondary adsorption layers.

For examples :

1) The ionic radii of sodium, K^+ and Ba^{+2} ions are 0.95, 1.33 A^o unite respectively. It is evident that while K^+ ions can replace Ba^{2+} ions in $BaSO_4$ crystals, Na^+ ions can not, a fact

which is supported by experimental findings. The result of such replacement is a mixed crystal .

2) Pb^{2+} ions are isomorphous with Ba^{2+} ions.

3) Chromate ions can replace SO^{2-}_4 ions in $BaSO_4$

4) The co precipitation of $KMnO_4$ and $BaSO_4$, in this case a pair of ions (Ba^{2+} and SO^{2-}_4) is replaced by another pair (K^+ and MnO^-_4), comparable in size to first pair

Organic Precipitants

A number of organic compounds are available which combine with inorganic ions to form sparingly soluble and often colored compounds. They have a number of advantages over inorganic reagents:

1) The compounds formed by the action of organic reagents are usually sparingly soluble in water, so that solubility losses can be avoided in precipitation and washing.

2) Co-precipitation is much less pronounced with organic than with inorganic precipitants.

3) Organic precipitants usually have high molecular weights so that a small amount of the ions will yield a relatively large amount of the precipitate. Consequently sensitivity and precision will be increased .

4) The products formed with organic reagents are often intensely colored. This makes it possible to detect, and to

determine colorimetrically, ions at extremely low concentrations.

5) The ideal organic precipitant should be specific in character, i.e., it should give a precipitate with only one particular ion. In few cases, however, has this ideal been attained; it is more usual to find that the organic reagent will react with a group of ions, but frequently by a rigorous control of the experimental conditions it is possible to precipitate only one of the ions of the group.

6) The presence of some functional group in the precipitated compound allows its volumetric determination Phenolic compounds can be estimated bromometrically.

<u>Organic precipitant can be classified into:</u>

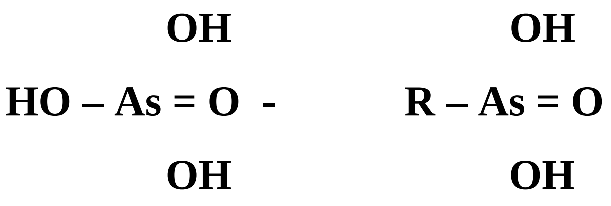
A)Salt forming compounds.

B)Chelate forming reagents.

A) A number of important organic precipitating agents presence tightly soluble compounds in which the been with the species precipitated is ionic in character.

a) Cationic precipitants :

i) Substituted arsonic acid



$$HO-\overset{OH}{\underset{OH}{As}}=O \quad - \qquad R-\overset{OH}{\underset{OH}{As}}=O$$

yield salt like precipitates with such quadric valent metal ions in, zirconium, titanium are thorium. Because they are difficult to dry without decomposition, metallic arsonates are ignited to their respective oxides. The selectivity of arsenic acids can be modified by changing the subsisitent (R) and by adjusting the pH .

NO_2 NO_2

ii) Dipicrylamine: O_2N- NH--- NO_2

NO_2 NO_2

It gives sparingly soluble salt with K^+. It is used for its separation. Interfering actions should be removed first e.g., NH_4^+

iii) Oxalic acid:

Nearly all oxalates are insoluble in water except alkali metals and ammonium oxalate. It is extensively used for precipitating Ca^{2+} from alkaline solutions as Ca oxalate H_2O

b) Anionic precipitants:

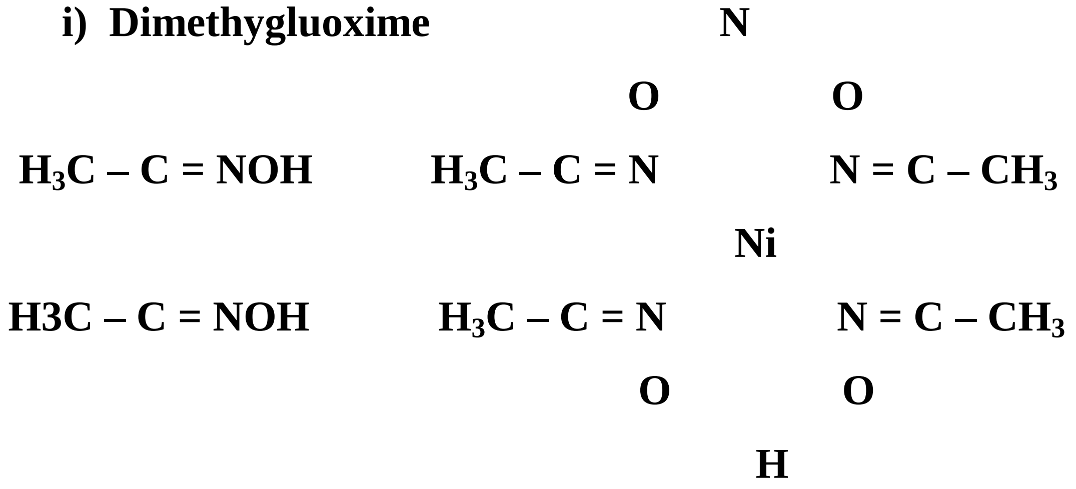
These are organic basic compounds which form insoluble salts with certain anions.

i) Benzidine H_2N NH_2

forms insoluble salts with SO^{2-}_4 and PO^{3-}_4. It precipitate with sulphate is more insoluble in water than $BaSO_4$.

*** Chelate forming reagents:**

i) Dimethygluoxime



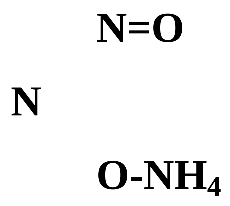
$$\begin{array}{llcr} & & N & \\ & O & & O \\ H_3C-C=NOH & H_3C-C=N & & N=C-CH_3 \\ & & Ni & \\ H3C-C=NOH & H_3C-C=N & & N=C-CH_3 \\ & O & & O \\ & & H & \end{array}$$

It gives a bright red precipitate with nickel salt. solutions, a slight excess of the reagent exerts no action on the precipitate, but a large excess should be avoided because of:

a)The possible precipitation of the dimethylgluoxime itself that its low solubility in water (it is used in ethanolic solution), and

b) the increased solubility of the precipitate in water – ethanol mixtures. iron, aluminum and bismuth give red colors but the reaction is prevented by the presence of tartarates.

ii) Cupferron: It is the ammonium salt of N-nitroso-N-phenylhydroxylamine .



$$\begin{array}{ll} & N=O \\ N & \\ & O-NH_4 \end{array}$$

This reagent was originally proposed from precipitation of cupper and iron, that is who it was given the short name cupferron. It is row also used for precipitation of vanadium, zirconium, titarium, tin, tantahum etc.

Precipitation is always can used out on cold, since it is decomposed into nitrobenzene on heating. It is most useful when employed in strongly acid soln. (5 – 10) of HCl or H_2SO_4, but not HNO_3 acid since oxiding agents destroy the reagent.

iii) -hydroxy quinoline, oxin :

Although hydrxyquinolin forms insoluble complexes with a large number of different actions, yet proper control of pH and by using soluble washing agent the reagent becomes highly solubility.