



# Physical, Analytical and Inorganic chemistry

Course code: 105 SCBIO

## Part 2: Analytical Chemistry

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**References:**

- 1- Vogel's Textbook of Quantitative Chemical Analysis, Arthur Vogel and John Mendham, Pearson, 6th Edition, 1 January 2000.
- 2- Principles of Analytical Chemistry - A Textbook, Miguel Valcárcel, Springer-Verlag, Berlin Heidelberg 2000

## **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 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.

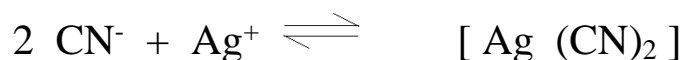
a- Those in which no change in valence occurs, these are dependent upon the combination of ions. This type of reaction are divided into three main classes.

#### 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 a standard base (alkalimetry). These reactions involve the combination of hydrogen and ions to form water.

#### ii- Complex formation reactions:

These depend upon the combination of ions, other than hydrogen or hydroxide ions, to form a soluble slightly dissociation ion or compound as in the titration of a cyanide with silver nitrate.



or of chloride ion with mercuric nitrate solution.

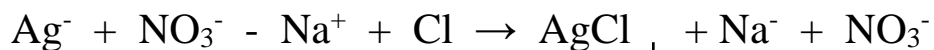


Ethylene diamine tetra-acetic acid (EDTA) is very important reagent for complex formation titrations.

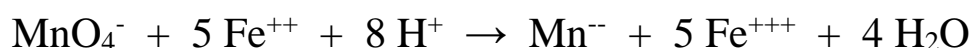


### iii- Precipitations reactions:

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.



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



### Concentration of solution:

The ways in which concentration can be expressed are given 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 per 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 finds 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 that the calculations of volumetric analysis are rendered very simple, since at the end point the number of equivalents of the standard solution employed is equal to the number of equivalents of the standard solution employed. We may write:

$$\begin{aligned} \text{Normality} &= \frac{\text{Number of gram-equivalents}}{\text{Number of liters}} \\ &= \frac{\text{Number of milligram-equivalents}}{\text{Number of milliliters (ml.)}} \end{aligned}$$

Hence ; number of mg-equivalents  
 $= \text{number of ml.} \times \text{normality} .$

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

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

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 1:

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

Solution:

$$V_A \times N_A = V_B \times N_B$$

$$V_A = 0.2 = 25.0 \times 0.1$$

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<sub>4</sub>. Calculate the strength of the ferrous sulphate solution in grams of FeSO<sub>4</sub> per liter.

Solution:

A normal solution of FeSO<sub>4</sub> as a reductant 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:

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

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

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

### 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 thereof, 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.

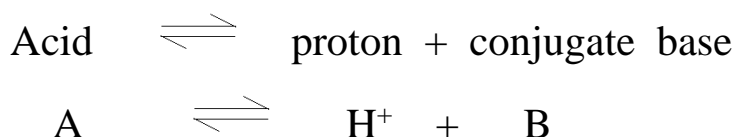
# THEORY OF ACID-BASE TITRATIONS

## INTRODUCTION

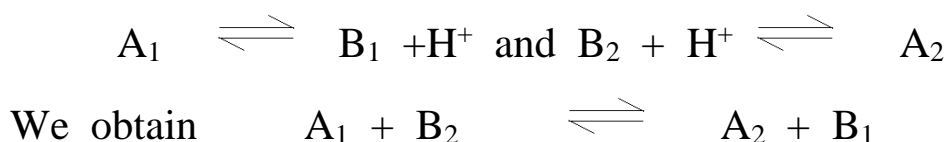
Acidimetry is the determination of acid substances by titration, and alklimetry is the corresponding process for alkaline substances. The two processes are also called neutralization although the solution at the stoichiometric point often has a reaction that is slightly different from that of the solvent.

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:



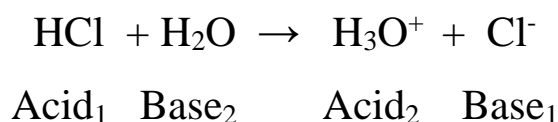
(It must be emphasized that the symbol  $\text{H}^+$  represents the proton and not the "hydrogen ion". Since the free proton cannot exist in solution in measurable concentration, eaction does not take place unless a base is added to concept the proton from the acid. By combining the equations.



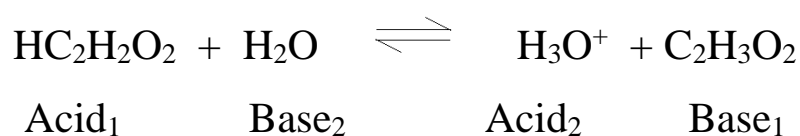
$\text{A}_1 - \text{B}_1$  and  $\text{A}_2 - \text{B}_2$  are two conjugate acid-base pairs. This is the most important expression for reactions involving acids and bases, it represents the transfer of a proton from  $\text{A}_1$  to  $\text{B}_2$  or from  $\text{A}_2$  to  $\text{B}_1$ . The

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



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



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 donors of electron pairs to form covalent bond regardless of whether protons are involved. Compound of the type of  $\text{HF}_3$  are usually described as Lewis acids or electron acceptors. The Lewis bases (e.g. ammonia, pyridine) are virtually.

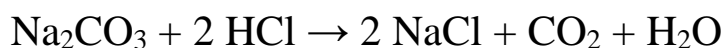
### The Equivalent weight of an acid:

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 its equivalent weight is 1/2 mol.



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



### Hydrogen-ion concentration and the pH scale:

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

$$\frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2} = K,$$

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

$$[\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}_2\text{O}]^2, K = K_w$$

$K_w$  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:

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

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

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

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

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

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

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

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	<u>14</u>	<u>13</u>	<u>12</u>	<u>11</u>	<u>10</u>	<u>9</u>	<u>8</u>	<u>7</u>	<u>6</u>	<u>5</u>	<u>4</u>	<u>3</u>
	Acid				Neutral				Alkaline			

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

$$\text{pH} < 7 < \text{pOH} \quad \text{acidic reaction}$$

$$\text{pH} = 7 = \text{pOH} \quad \text{neutral reaction}$$

$$\text{pH} > 7 > \text{pOH} \quad \text{basic reaction}$$

**Example:**

i - Find the pH of a solution of which  $[\text{H}^+] = 4.0 \times 10^{-5}$

$$\begin{aligned} \text{pH} &= -\log[\text{H}^+] = -\log [4 \times 10^{-5}] \\ &= 5.802 + -4.398 = 4.398 \end{aligned}$$

ii - Find the hydrogen ion concentration corresponding to

$$\begin{aligned} \text{pH} &= 5.643 \\ \text{pH} &= -\log [\text{H}^+] = 5.643 \quad \log [\text{H}^+] = -5.643 \\ &= -6.365 = 2.28 \times 10^{-6} \end{aligned}$$

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  $0.125 \times 0.01 = 1.25 \times 10^{-3}$

$$\text{Now } \log 1/25 = 0.97 .$$

$$\text{pH} = -(-3 + 0.098) = 2.903$$

## The calculation of [H<sup>+</sup>] of pH from ionization constants

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 manner

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

Where HB represents the un-ionized ion.

A still more rigorous calculation would involve the use of activity coefficients as expounded 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<sup>+</sup>] 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:

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

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.

$$\text{pH} = \text{pK}_a - \log \frac{[\text{A}]}{[\text{B}]} \quad (4)$$

It is thus easy to calculate the  $[\text{H}^+]$  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 amount 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. milliliters, for the various weak acids or bases Buffer action is readily understandable in terms of the mass action principle applied to the equilibrium

$\text{A} \rightleftharpoons \text{H}^+ + \text{B}^-$  : the acid A and the base B being conjugate , e.g. ;  $\text{NH}_4^+$  and  $\text{NH}_3$ ,  $\text{HC}_2\text{H}_3\text{O}_2$  and  $\text{C}_2\text{H}_3\text{O}_2^-$ , etc.

$$K_e = \frac{[\text{H}^+][\text{B}^-]}{[\text{A}]} \quad (1)$$

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

$$\text{pH} = \text{pK}_a - \log \frac{[\text{A}]}{[\text{B}^-]} = \text{pK}_a - \log \frac{[\text{A}]}{[\text{B}^-]} \quad (3)$$



Expression (3) shows the ratio of [A] to [B<sup>-</sup>] 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.

Mixtures 0.1 M in Total Acetates :

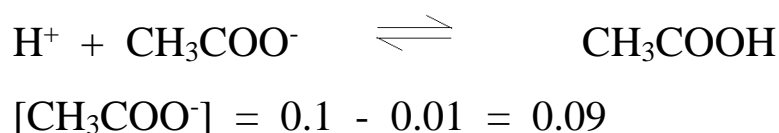
Sodium acetate, M	0.02	0.03	0.04	0.05	0.06	0.07	0.08	Acetic
acid, M	0.08	0.07	0.06	0.05	0.04	0.03	0.02	
pH		4.11	4.34	4.52	4.69	5.86	4.05	5.28

The addition of a light amount of an acid, such as hydrochloric, to an acetate buffer forms roughly an equivalent amount of non ionized hydrogen acetate and thus diminishes the concentration of acetate ion slightly. Thus results in slightly lower pH because the ratio  $\frac{[\text{HC}_2\text{H}_3\text{O}_2]}{[\text{C}_2\text{H}_3\text{O}_2]}$  is only slightly changed. The addition of a small amount of sodium hydroxide produces the opposite effect.

Example: 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 ( $K_a = 1.82 \times 10^{-5}$ ).

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} = 4.74 + 0.09 = 4.74$$

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



$$[\text{CH}_3\text{COOH}] = 0.1 = 0.01 = 0.11$$

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

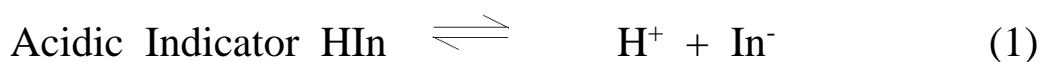
Hence on adding the strong acid, the pH changes only by  $4.74 - 4.65 = 0.09$  pH unit, whereas, if 10 ml of N-hydrochloric acid were added to 1 liter of pure water (pH=7), the pH would have changed from 7 to  $-\log(0.01) = 2$ , i.e. by 5 pH units. This illustrates the action of the acetic acid sodium 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 change 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 indicators of practical value are organic in nature. As the color changes these indicators depend on the change of the pH, they must themselves be acids or bases. The equilibrium between the indicator molecules and their ions may be represented, as follows:



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

$\text{In}^-$  is the ionized form, which produces the basic color .

$\text{InOH}$  is the unionized form of the basic indicator, which given the basic color.  $\text{In}^+$  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 indicator is then predominate, in the unionised form of  $\text{HIn}$ . The acid color. If on the other hand, the indicator is added to a basic solution, the  $[\text{H}^+]$  is reduce by reaction of the acid indicator with the base, and reaction (1) proceeds to the right yielding more ionized indicator  $[\text{In}^-]$  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:

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  $\text{HIn}$  represents the normal indicator molecule, and the formula  $\text{HIn}$  represents the molecule formed by the arrangement (the tautomer), then the indicator salts is eventually produced from neutralization of weak equilibrium :



Considering the two equilibria separately

$$\frac{[\text{HIn}'']}{[\text{HIn}]} = K_{\text{eq}} \quad \text{and} \quad \frac{[\text{H}^+][\text{In}''^-]}{[\text{HIn}'']} = K_{\text{a}}$$

Multiplying these two equations:

$$\frac{[\text{H}^+][\text{In}''^-]}{[\text{HIn}]} = K_{\text{Ind}}$$

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:

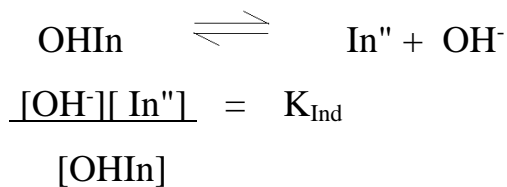
$$\text{pH} = \text{p}K_{\text{Ind}} + \log \frac{[\text{In}''^-]}{[\text{HIn}]} \quad \dots \dots \dots (1)$$

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

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

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



and  $\text{pOH} = \text{p}K_{\text{Ind}} + \log \frac{[\text{OHIn}]}{[\text{In}'']}$

$$\text{pH} = \text{p}K_{\text{w}} = \text{p}K_{\text{Ind}} - \log \frac{[\text{In}''^-]}{[\text{OHIn}]} \quad \dots \dots \dots (2)$$

In other words any change in the pH 1 causes a change in the ratio.

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

The most efficient transition range of acid-base indicators, corresponding to the effective buffer intervals is about 2 pH units, i.e.,  $\text{pK}_{\text{Ind}} - 1$ . 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  $[\text{basic color}] / [\text{acid color}]$  becomes 1/10 .

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

$$\text{pH} = \text{pK}_{\text{Ind}} + \log - \frac{1}{10} = \text{pK}_{\text{Ind}}^{-1}$$

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

$[\text{basic color}] / [\text{acid color}]$  has become 10/1 or

$$\text{pH} = \text{pK}_{\text{Ind}} + \log - \frac{10}{1} = \text{pK}_{\text{Ind}}^{+1}$$

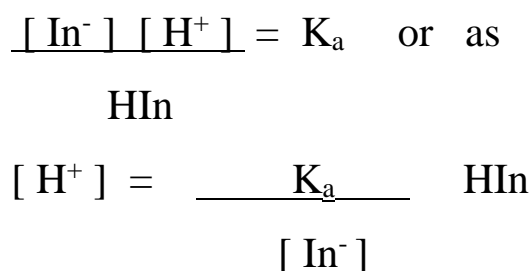
Between the two ratios: 1/10 and 10/1 one observes an intermediate color. An indicator therefore, does not change color abruptly at a definite pH. but changes color gradually over a certain pH range called the transition range of the indicator.

## Factors Affecting Indicator Transition Range:

### 1- Effect of Indicator concentration:

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

Let us write the equilibrium expression for the dissociation of the colorless acid form of phenolphthalein as



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

$$[ \text{H}^+ ] = K_a [ \text{HIn} ]$$

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,  $K_{\text{Ind}}$ , rises with temperature causing a decrease in its transition range. On the other hand if separation of charge is involved in the indicator process, the drop in dielectric constant plays its role; but this is usually compensated by the increase in  $k_{\text{Ind}}$  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 indicators 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 indicator 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:

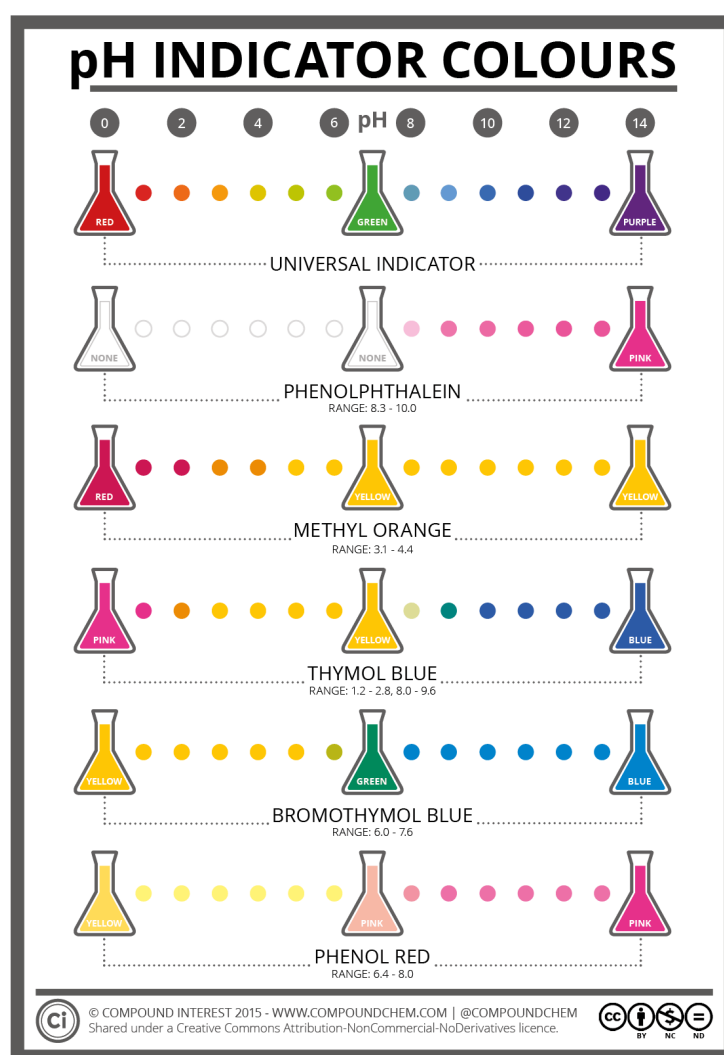
Turbidity indicators are salts of mixed organic acids or bases of high molecular weight which coagulate and settle out of the solution at a definite pH value. It should be noted not only the pH of the solution influences the coagulation of the indicator but also the temperature, the presence of other salts and protective colloids, 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 indicator, 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 phloxin, chromotropic 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  $100 \times 1 = 100$  mil equivalents per 100 ml ,  $[H^+] = 1 \text{ N}$

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

b- During the titration:

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

$$\text{or pH} = 0.48$$

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

$$\text{pH} = 0.94$$

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

$$\text{pH} = 1.3$$

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

$$\text{pH} = 2.0$$

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

$$\text{pH} = 2.3$$

For 99.0 ml of base  $[H^+] = 0.1 \times 1.199.9 = 5.01 \times 10^{-4}$

$$pH = 3.3$$

c- At the equivalence point:

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

$$pH + pOH = 14 \quad pH = 7$$

d- Beyond the equivalence point :

The solution contains excess alkali .

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

$$= 5.00 \times 10^{-4}, \quad pOH = 3.3 \text{ and } pH = 10.7$$

With 101 ml of base  $[H^+] = 1/201 = 5.0 \times 10^{-3},$

$$pOH = 2.3, \text{ and } pH = 11.7$$

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 and pH 10.5. Phenolphthalein, methyl red, and methyl orange are most often used. (Fig. 1).



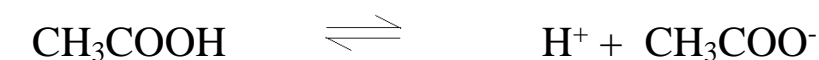
Fig (1)

### Neutralization of a weak acid with a strong base:

Let us now follow the changes in hydrogen ion concentration during the titration of 100 ml. 0.1 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  $1.86 \times 10^{-5}$  thus:



$$\frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = K_a = 1.86 \times 10^{-5}$$

$$[\text{CH}_3\text{COOH}]$$

$$[\text{CH}_3\text{COO}^-] = [\text{H}^+]$$

$$[\text{H}^+]^2 = K_a [\text{CH}_3\text{COOH}]$$

$$[\text{H}^+]^2 = K_a [\text{CH}_3\text{COOH}]$$

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

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

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

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 undissociated acid in the ionization constant expression for acetic acid :

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

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

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

When 50 ml of 0.1 N alkali have been added

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

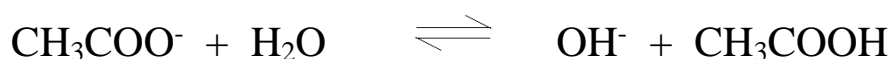
$$\text{and } [acid] = 50 \times 0.1/150 = 3.33 \times 10^{-2}$$

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

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

c At the equivalence point:

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.



The equilibrium constant in this case is

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

But the ionization constant of acetic acid .

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

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.

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

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 :

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

$$[OH^-] = \sqrt{\frac{C K_w}{K_a}}$$

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

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



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

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

$$= 1/2 \text{p}K_W + 1/2 \text{p}K_a + 1/2 \log C$$

(Where  $\text{p}K_W = \log \frac{1}{K_W}$  ( $\log K_W$ ); and  $\text{p}K_a = \log \frac{1}{K_a}$ )

$$= -\log K_a$$

In the sample under consideration,

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

$$\text{And } C = 0.05$$

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

$$= 7 + 2.37 - 0.54 = 8.83$$

d- Beyond the equivalence point:

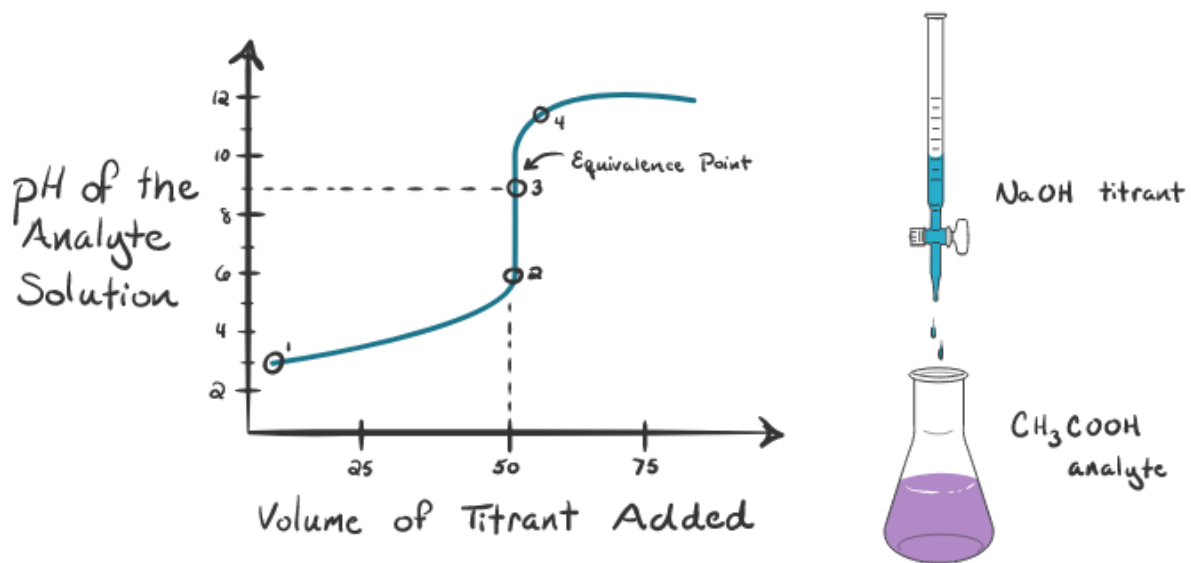
NaOH is added, and the ions in the solution have no appreciable effect on the hydrogen ion concentration

With 100.1 ml of base:

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

$$\text{pH} = 14 - 4.3 = 9.7$$

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 indicator like methyl red or methyl orange would lead to erroneous results



Titration curve of 25ml of weak acid (0.1M CH<sub>3</sub>COOH(aq)) with strong alkali (0.1M NaOH(aq))

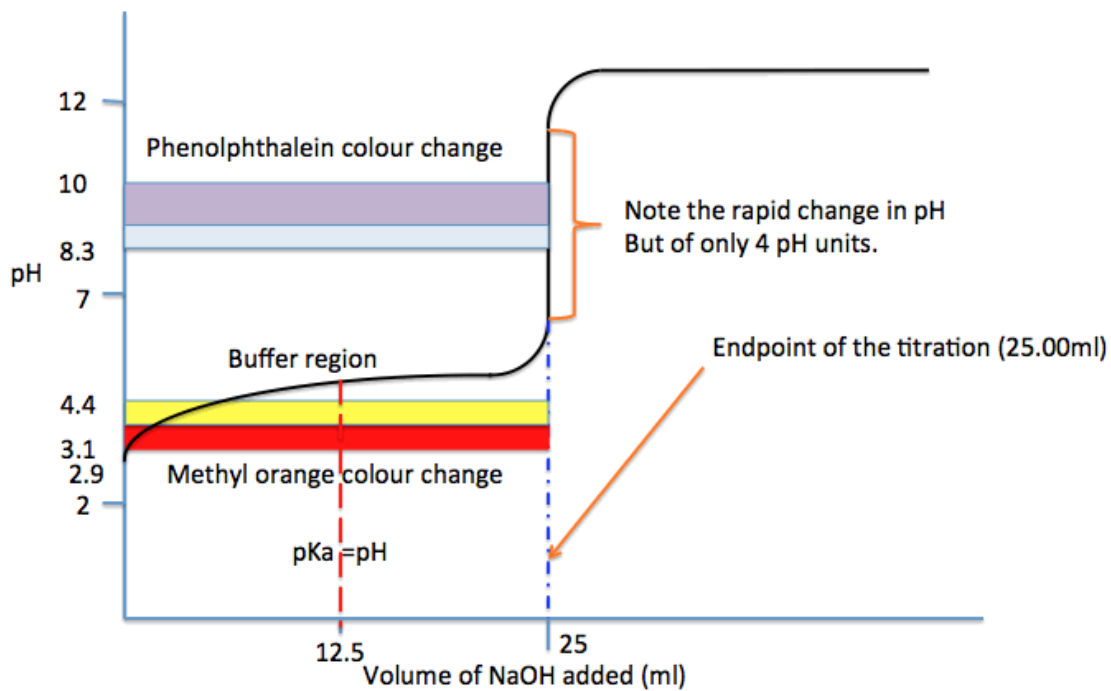


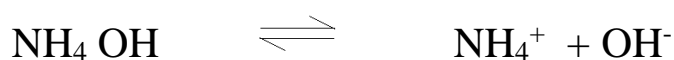
Fig (2) Alkali added ml .

### 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  $\text{NH}_4\text{OH}$  with of 0.1 N  $\text{HCl}$ .

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  $\text{NH}_4\text{OH}$  :



$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} = K_b = 1.75 \times 10^{-5}$$

$$[\text{NH}_4\text{OH}]$$

$$[\text{NH}_4^+] = [\text{OH}^-]$$

$$[\text{OH}^-]^2 = K_b [\text{NH}_4\text{OH}]$$

$$[\text{OH}^-] = \sqrt{K_b [\text{NH}_4\text{OH}]}$$

$$[\text{OH}^-] = \sqrt{K_b \cdot \text{NH}_4\text{OH}}$$

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

$$\text{pOH} = -\log 1.36 \times 10^{-3} = 2.67$$

$$\text{pH} = 14 - 2.287 = 11.13$$

b- pH During titration :

Additions of acid to the solution result in the formation of  $\text{NH}_4\text{Cl}$ , thus giving a buffer mixture consisting of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$ . During the titration, the  $\text{NH}_4^+$  formed suppresses the ionization of  $\text{NH}_4\text{OH}$  and

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

$$[\text{NH}_4\text{OH}]$$

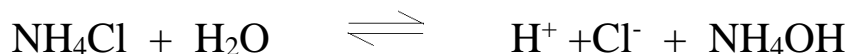
$$[\text{OH}^-] K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4]}$$

$$[\text{NH}_4]$$

$$\text{pH} = \text{pK}_w - \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

c- pH at the equivalence point:

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:



For which

$$K_b = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]}$$

( $K_b$  is the hydrolysis constant) and since

$$\frac{K_w}{K_b} = \frac{[\text{H}^+][\text{OH}^-] \times [\text{NH}_4\text{OH}]}{[\text{NH}_4^+][\text{OH}^-]}$$

Then ,

$$\frac{K_w}{K_b} = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} = K_h$$

Let  $[\text{H}^+] = [\text{NH}_4\text{OH}]$ , because for each mole of  $\text{NH}_4\text{OH}$  produced, one mole of  $\text{H}^+$  is formed. Let the concentration of the ammonium ion concentration approximately equal to the concentration  $C$ , of the salt at the equivalence point.

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

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

$$\text{pH} = 1/2 \text{pK}_w - 1/2 \text{pK}_b - 1/2 \log C$$

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

d- pH Beyond Equivalence point:

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 .

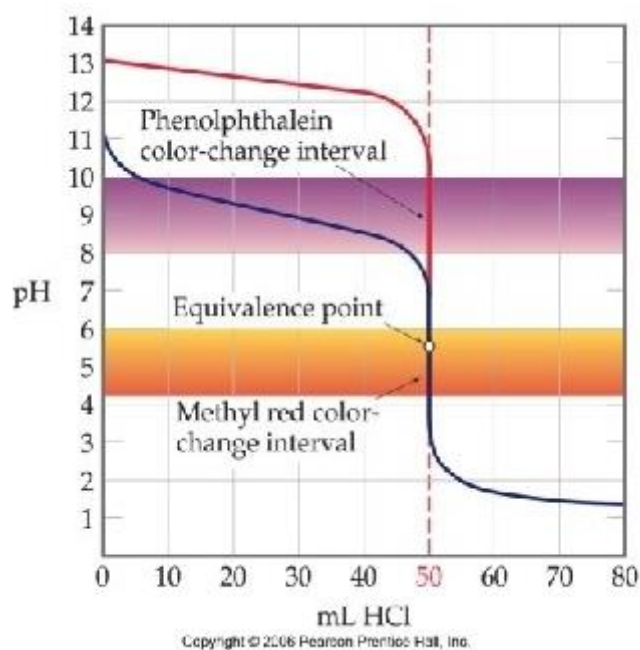


Fig (3) ml added

### Titration of a weak acid with a weak base or the reverse :

The titration of a weak acid, like acetic acid, with a weak base like ammonium hydroxide gives a curve like that of the diagram of Fig. 4 . 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 .

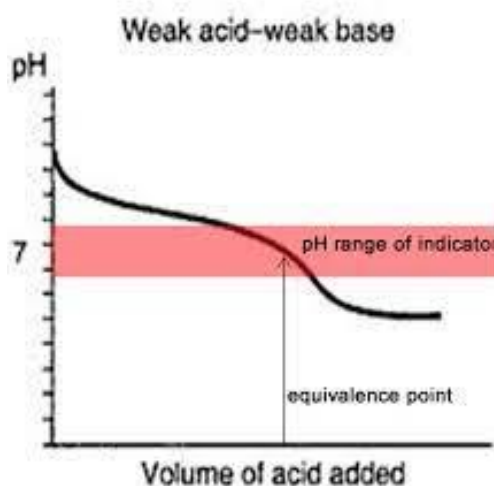


Fig. 4 ml. of titration solution

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

$$[ H^+ ] = \sqrt{\frac{K_w \cdot K_a}{K_b}}$$

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

$$pH = 1/2 pK_w + 1/2 pK_a - 1/2 pK_b$$

## Titration of polybasic acids with 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 :



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

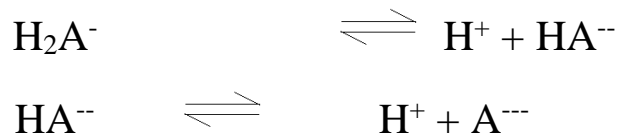
$$[ H^+ ] \times [ HA^- ] / [ H_2A ] = K_1 \dots\dots\dots (1)$$

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

$K_1$  and  $K_2$  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 dilution 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:



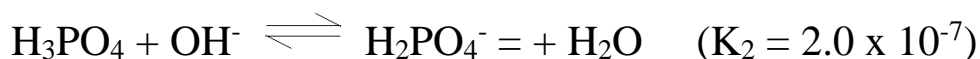


b- Example :

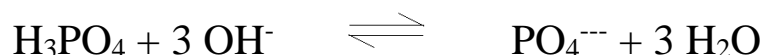
An example of a relatively weak polybasic acid we can consider the case of orthophosphoric acid. The graph for the titration is shown in Fig. 5. The first inflection is that corresponding to the formation of  $\text{H}_2\text{PO}_4^-$ :



The second inflection corresponds to the formation of  $\text{HPO}_4^{2-}$  ions :



There is no third inflection, for the ionization constant  $\text{HPO}_4^{2-}$  is extremely small ( $3.6 \times 10^{-13}$ ). The graph shows that  $\text{H}_3\text{PO}_4$  can be accurately titrated to  $\text{H}_2\text{PO}_4^-$ . If methyl orange is used as the indicator that  $\text{H}_2\text{PO}_4^-$  can be titrated to  $\text{HPO}_4^{2-}$  with fair precision if phenolphthalein is used as the indicator and that  $\text{H}_3\text{PO}_4$  cannot be titrated according to the equation:



c- Calculation of the pH of each inflection :

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

$$\frac{[\text{H}^+]^2 [\text{HPO}_4^{2-}]}{[\text{H}_3\text{PO}_4]} = K_1 K_2$$

If, as is generally the case the ratio  $\frac{[\text{HPO}_4^{2-}]}{[\text{H}_3\text{PO}_4]}$

$$\frac{[\text{HPO}_4^{2-}]}{[\text{H}_3\text{PO}_4]}$$



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 :

$$[H^+] = \sqrt{K_1 K_2}$$

$$\text{or } \text{pH} = 1/2 (\text{p}K_1 + \text{p}K_2)$$

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

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

$$\text{Or } \text{pH} = 1/2 (2.16 + 7.17) = 4.66$$

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

$$\text{pH} = 1/2 (\text{p}K_2 + \text{p}K_3) = 1/2 (7.16 + 12.3) = 9.73$$

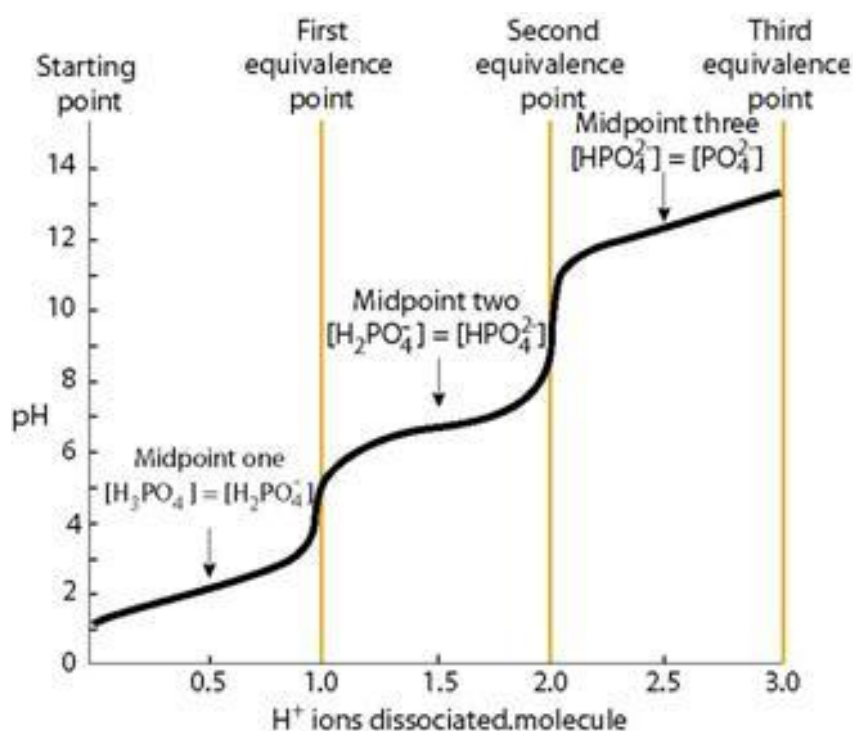
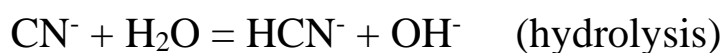


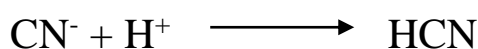
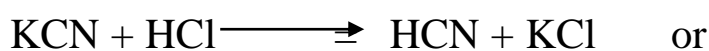
Fig. 5 ml of titrating solution

**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 :



$\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$  (strong acid reacts with  $\text{OH}^-$  from hydrolysis) :



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  $7.2 \times 10^{-10}$ , i.e. :

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

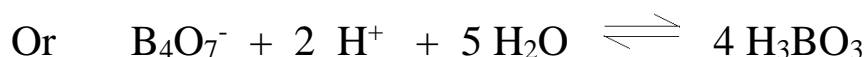
Hence  $[H^+] = 7.2 \times 10^{-10} \times 0.1$

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 promocresol green, methyl orange, bromo-phenol blue and methyl red.

### 2- Titration of borate ion with a strong acid:

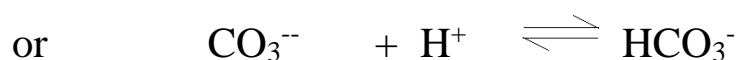
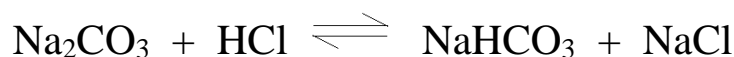
The titration of the pyroborate ion ( using borax ) with hydrochloric acid is similar. The net result of the displacement titration is given by:



Boric acid behaves as a weak monobasic acid with a dissociation constant of  $6.4 \times 10^{-10}$ . 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- Titration of carbonate ion with a strong acid:

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

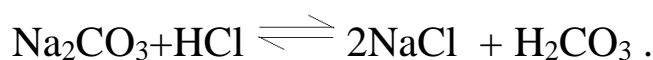


The equivalence point for the primary stage of ionization of carbonic acid is at pH (  $1/2 pK_1 + 1/2 pK_2 = 8.3$ , )

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

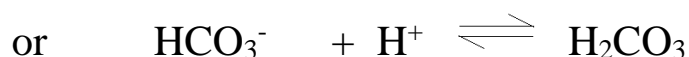
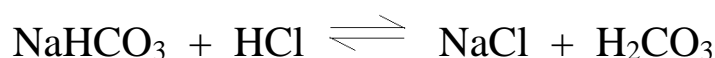
equivalents of acid ). The net reaction is then Acid added ml. of 0.1 N- $\text{Na}_2\text{CO}_3$  with 0.1 N HCl .



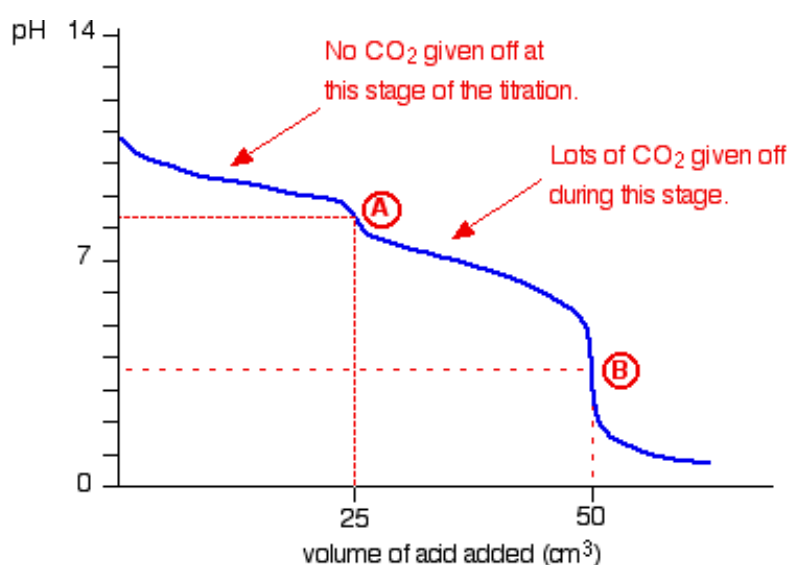
Or



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



The pH at the equivalence point is very approximately 3.9, and suitable indicators 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 is determined simply by 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- The stoichiometry :

Purity and definitions of composition of the precipitate may be affected by the adsorption of entrained 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- The rate of reaction:

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 of a more rapid precipitation in the reverse direction, i.e. to add a measured excess of titrant and back-titrate.

3- Although the solubility: 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- The lack of suitable indicators: for many precipitation titration imposes another limitations in such titrations.

Notwithstanding 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 argentometric

titrations, in particular are precise, simple and illustrative of almost all the important principles, and methods.

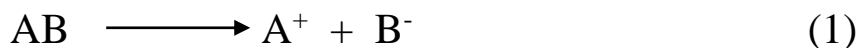
#### Limitations of Argent metric Titrations :

- 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  $\text{Fe}^{+3}$  form insoluble colored hydroxide in neutral or slightly acid medium (t). Some; such as  $\text{Al}^{+3}$ , hydrolyze to insoluble basic salts in neutral or slightly acid solution, showing a tendency to co precipitate chloride (c)  $\text{Hg}^{2+}$  form soluble complexes with halides of the type  $[\text{HgI}_4]^{2-}$ .

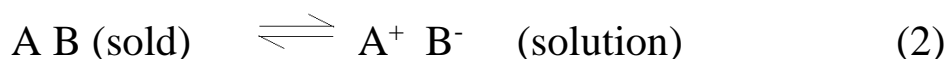
#### Solubility Product:

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 precip-itation 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 precip-itate 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<sup>+</sup> and B<sup>-</sup>. This reaction can be represented in its simplest form (i.e., without considering hydration of the ions) by the equation.



However, as the salt AB dissolves, more and more A<sup>+</sup> and B<sup>-</sup> 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.



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

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

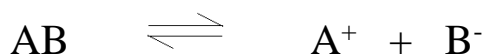
Since the concentration of AB is constant as long as the temperature remains constant and there is some solid AB in contact with the solution (in other words the solubility of AB is independent of the amount of AB present as long as some solid exists, which implies that the speed of the reaction represented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

$K \times \text{const} = [A^+][B^-] = S_{AB} = \text{Solubility product constant}$ . Let consider in the same way the saturated solution of the sparingly soluble salt X<sub>m</sub> Y<sub>n</sub> which dissociates into m action, X<sup>n+</sup> and n anions, Y<sup>m-</sup>. The equilibrium for this saturated solution can be represented by the equation.

$$[X^{n+}]^m [Y^{m-}]^n = S_{X_m Y_n}$$



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



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

$$V_2 = K_2 \times [Ag^+] [Cl^-]$$

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

$$K_1 = K_2 \times [Ag^+] [Cl^-]$$

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

#### 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- At the start the Titration :

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

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

### 2- During the titration :

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

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

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

$$\text{or } p\text{Ag}^+ + p\text{Cl}^- = 9.92 = p\text{AgCl}$$

in the last calculation  $p\text{Cl}^- = 1.48$  , hence  $p\text{Ag}^+ = 9.92 -$

$1.48 = 8.44$ . In this manner the various concentrations of chloride and silver ion can be computed up to the equiv-alence point.

### 3- At the equivalence point:

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  $K_5$  .

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

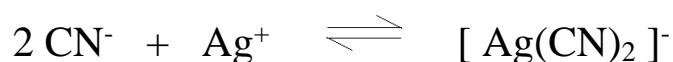
$$p\text{Ag}^+ = p\text{Cl}^- = 1/2 p\text{AgCl} = 9.92/2 = 4.96.$$

### 4- Beyond the end point:

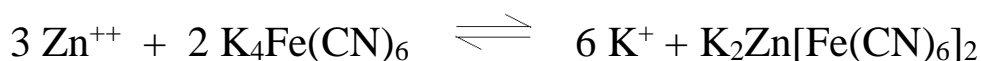
With 100.1 ml of silver nitrate solution  $[Ag^+] = 0.1 \times 0.1 / 200.1 = 5 \times 10^{-5}$  or  $pAg^+ = 4.30$ , hence  $pCl^- = pAgCl - pAg^+ = 9.92 - 4.30 = 5.62$ . The results calculated as illustrations as well as some additional points are shown graphically in Fig.9. This illustrates clearly the change in  $pCl^-$  or  $pAg^+$  at vicinity of the equivalence point.

### 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 equiv-alent of KCN in the titration with silver ions is 2 mols, since the reaction is :



In the titration of zinc ion with potassium ferrocyanide solution:



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.  $1.7 \times 10^{-12}$ ). 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 hence silver chloride will be precipitated.

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

$$\begin{aligned} [Ag^+] \times [Cl^-] &= S_{AgCl} = 1.2 \times 10^{-10} \\ [Ag^+]^2 \times [CrO_4^{--}] &= S_{Ag_2CrO_4} = 1.7 \times 10^{-12} \\ [Ag^+] &= \frac{S_{AgCl}}{[Cl^-]} = \frac{S_{AgCrO_4}}{\sqrt{[CrO_4^{--}]}} \\ &= \frac{[Cl^-]}{\sqrt{[CrO_4^{--}]}} = \frac{S_{AgCl}}{\sqrt{[Ag_2CrO_4^{--}]}} = \frac{1.2 \times 10^{-10}}{\sqrt{1.7 \times 10^{-12}}} = 9.2 \times 10^{-5} \end{aligned}$$

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

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

$$[\text{CrO}_4^{2-}] = \left[ \frac{\text{Cl}^-}{9.2 \times 10^{-5}} \right]^2 = \left[ \frac{1.1 \times 10^{-5}}{9.2 \times 10^{-5}} \right]^2 = 1.4 \times 10^{-2}$$

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 if  $[ \text{CrO}_4^{2-} ] = 0.003$  silver chromate will be precipitated when :

$$[\text{Ag}^+] = \frac{S_{\text{Ag}_2\text{CrO}_4}}{\sqrt{\text{CrO}_4^{2-}}} = \frac{1.7 \times 10^{-12}}{\sqrt{3 \times 10^{-3}}} = 2.4 \times 10^{-5}$$

if the theoretical concentration of indicator is used :

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

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  $1.3 \times 10^{-5} \times 150/0.1 = 0.02$  ml of 0.1  $\text{AgNO}_3$ . 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  $\text{CrO}_4^{2-}$  concentration is greatly decreased: being converted to the slightly ionized  $\text{HCrO}_4^-$ . The decrease in  $\text{CrO}_4^{2-}$  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.



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:



This interferes with the titration, the silver oxide may even precipitate before silver chromate especially where the solubility product of  $\text{Ag}_2\text{O}$  is exceeded. If ammonium salts are present, the  $\text{P}^{\text{H}}$  of the solution must not exceed pH 8 otherwise free ammonia will be produced and dissolve the silver chloride precipitate. Therefore, the saline solution should be neutralized before titration if necessary, by adding  $\text{NaHCO}_3$  or dilute  $\text{HNO}_3$ , as the case may be.

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

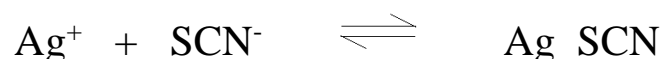
3- The reverse titration of silver ion with chloride ion using chromate as indicator is not feasible, the flocculated  $\text{Ag}_2\text{CrO}_4$  formed initially, reacts

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 .

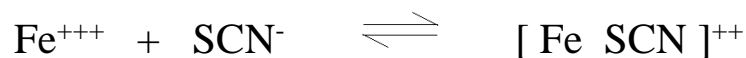
4- Titration of iodide; and of thiocyanate is not successful because silver iodide and silver thio-cyanate adsorb chromate ions so strongly that a false and somewhat indistinct end point is obtained.

B- Formation of a soluble colored compound:

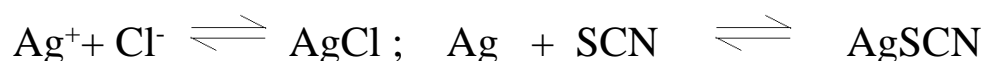
This procedure is exemplified by the method of Volhard for the titration silver in the presence of free nitric acid with standard potassium or ammonium thiocyanate solution. The indicator is a solution of ferric nitrate or of ferric ammonium alum. The addition of the thiocyanate solution produces first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



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



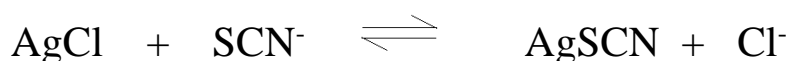
This method may be applied to the determination of chlorides, bromides and iodides in acid solution. Excess of standard silver nitrate solution is added, and the excess is back-titrated with standard thiocyanate solution. For the chloride estimation, we have the following two equilibria during the titration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



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

$$\frac{[ \text{Cl}^- ]}{[ \text{SCN}^- ]} = \frac{S_{\text{AgCl}}}{S_{\text{AgSCN}}} = \frac{1.2 \times 10^{-10}}{7.1 \times 10^{-13}} = 170$$

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  $[ \text{Cl}^- ] / [ \text{SCN}^- ]$  in the solution is 170 .



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:

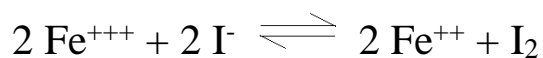
- i - The silver chloride is filtered off before back titration.
- ii - After the addition of the silver nitrate, potassium nitrate is added as coagulant, the suspension is boiled for about 3 minutes, cooled and then titrated immediately.
- iii- An immiscible liquid is added to "coat" the silver chloride particles and thereby protect them 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:

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

The titration error is small, and no difficulties arise in the determination of the end point. Silver iodide (S.P.  $1.7 \times 10^{-16}$  ) 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.



### C - Use of adsorption indications:

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 .

The theory of the action of these indicators 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 ,

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 takes 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 then be converted into silver chloride, which will then primarily adsorb 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 be small and the color change far from sharp with certain indicators.
- ii- The indicator ion must be of opposite charge to the ion of the precipitating agent.
- iii- The indicator ion should not be adsorbed by the particular compound has been completely precipitated but it should be strongly adsorbed immediately after the equivalence point.

Some Adsorption Indicators and Their Applications:

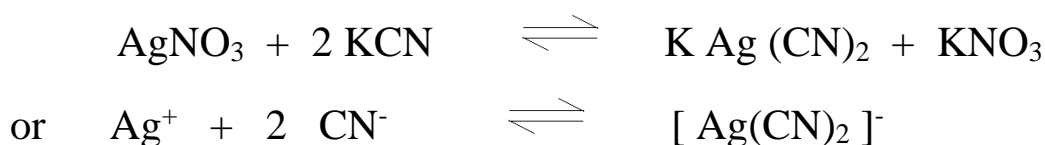
1- Fluorescein: For the titration of chlorides fluorescein may be used. This is a very weak acid (  $K_a = \text{Ca.}1 \times 10^{-8}$  ) hence even a small amount of other acids reduces the already minute ionization, thus rendering the detection of the end point (which depends essentially upon the adsorption 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 may 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,  $\text{Br}^-$ ,  $\text{I}^-$  and  $\text{SCN}^-$ , the competition is not serious and a very sharp end point is obtained in the titration of bromide, iodide and thiocyanate even in dilute solutions. Rose Bengal (dichloro tetraiodofluorescein) and dimethyl di-iodo-fluorescein have been recommended 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 the indicator action is not noticeably adsorbed by silver bromide. 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- Turbidity method:

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

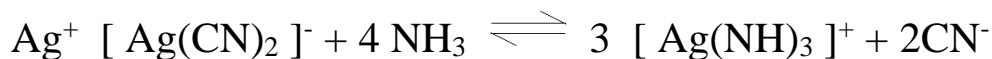


When the above reaction is complete, further addition silver nitrate solution yields the insoluble silver argent cyanide.

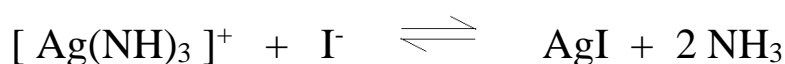


The end point of the reaction is therefore indicated by the formation of permanent turbidity. The only difficulty in obtaining a sharp end point lies in the fact that silver cyanide, precipitated by local excess concentration of silver ion somewhat prior to the equivalence point, is very slow to redissolve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

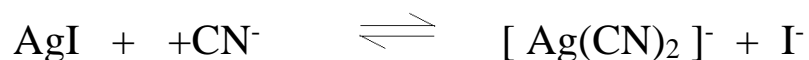
In Denige modification of Liebig method . iodide ion is used as indicator and aqueous ammonia is introduced to solubilise the silver cyanide:



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.



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:



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 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  $[\text{Ag}(\text{CN})_2]^-$  ion, the excess of cyanide may be determined by the Liebig-Deniges method.

## 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 operation .

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

### Precipitation Methods:

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.  $\text{Ag}^+ \text{NaCl}$      $\text{AgCl}$  filtered    washed to  
soluble salts remove

dried at    weighed as  
150-150°C    silver chloride

Frequently the constituent being estimated is weighed in a form other than that in which it was precipitated. Thus magnesium is precipitated, as ammonium magnesium phosphate  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , but is weighed, after ignition as the pyrophosphate  $\text{Mg}_2\text{P}_2\text{O}_7$

#### Choice of precipitant:

One of the important considerations in 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 been realised. Reagents are mostly selective, i.e. react with a group of compounds. However selectivity can be improved by adjusting the conditions of the experiment e.g. Reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  prevents its 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 remaining in solution does not exceed the minimum detectable by ordinary 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 tenacious because:

a- they are retained readily by 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. absor-ption of water or CO<sub>2</sub> form air.
- 3) Finally, the content of the element being determined in the precipitate should be as low as possible.

\* Gravimetric factor (chemical factor ):

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<sub>2</sub>O<sub>3</sub>x.H<sub>2</sub>O. The preci-pitate is littered washed, and ignited to Fe<sub>2</sub>O<sub>3</sub>, which is found to weigh 0.2481 gm. Calculate the percentage of iron (Fe) in the sample .

The reaction are  $2\text{Fe}^{3+} \longrightarrow \text{Fe}_2\text{O}_3 \times \text{H}_2\text{O} \longrightarrow \text{Fe}_2\text{O}_3(\text{S})$

Since 2 mol of Fe<sup>3+</sup> produce 1 mol of Fe<sub>2</sub>O<sub>3</sub>, mol Fe = 2 mol Fe<sub>2</sub>O<sub>3</sub> .

$$\frac{\text{gm}}{55.85 \text{ gm/mol}} = 2 \times \frac{0.2481 \text{ gm.}}{159.69 \text{ gm/mol}}$$
$$\text{gm} - 0.2481 \text{ gm.} \times \frac{2 \times 5589 \text{ gm/mol}}{159.69} = 0.1755 \text{ gm}$$



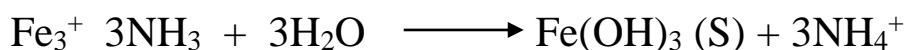
$$159.63 \text{ gm/mol}$$

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

\* Note that in calculating the weight of Fe in the precipitate, the weight of precipitate, 0.2481 gm., is multiplied by the factor (  $2 \times 55.85 / 159.69$  ) 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  $\text{Fe}_2\text{O}_3$ . thus the gravimetric factor for Fe in  $\text{Fe}_2\text{O}_3$  is commonly written  $2 \text{ Fe}/\text{Fe}_2\text{O}_3$ , where Fe in  $\text{Fe}_3\text{O}_4$  is  $3 \text{ Fe}/\text{Fe}_3\text{O}_4$ , and MgO in  $\text{Mg}_2\text{P}_2\text{O}_7$  is  $2 \text{ MgO}/\text{Mg}_2\text{P}_2\text{O}_7$ .

Example: Calculate the number of milliliters of ammonia, density 0.99 g/ml., 23 % by weight  $\text{NH}_3$ , which will be required to precipitate as  $\text{Fe}(\text{OH})_3$ , the ion in a 0.70 gm sample that contains 25 %  $\text{Fe}_2\text{O}_3$

The precipitation reaction is :



and  $3 \text{ X mol Fe}^{3+} = \text{mol NH}_3$

$$\text{mol Fe}_2\text{O}_3 \text{ in sample} = \frac{0.0 \times 0.25}{15969} = 0.011$$

$$\text{mol Fe}^{3+} = 2 \times \text{mol Fe}_2\text{O}_3 = 2 \times 0.011 = 0.0022$$

$$M_{\text{NH}_3} = \frac{0.99 \text{ gm/mol} \times 1000 \text{ ml/liter} \times 0.025}{1903 \text{ gm/mol}}$$

$$M_{\text{NH}_3} = 134 \text{ mol/liter}$$

$$\text{mol NH}_3 - V \times M \quad \text{where } V = \text{liters of NH}_3$$

Hence

$$3 \times 0.0022 = V \times M = -V \times 1.34$$

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

\* The purity of the precipitate:

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 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 0.1  $\mu$ ) as a consequence of which certain characteristic properties

Become apparent . Ordinary filter papers will retain particles up to a diameter of 10  $\mu$  , 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 or 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 a light 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  $\text{Ag}^+$  and  $\text{Cl}^-$  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  $\text{Na}^+$  ,  $\text{Cl}^-$  and  $\text{NO}_3^-$  ions (as well as  $\text{H}^+$  and  $\text{OH}^-$ ). The surface  $\text{Ag}^+$  ions attract  $\text{Cl}^-$  and  $\text{NO}_3^-$  ions, and the surface  $\text{Cl}^-$  ions attract  $\text{Na}^+$  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. If 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. Thus the surface of the particle acquires a layer of chloride ions and the particles become negatively charged. The process

is represented schematically in Figure.  $\text{Cl}^-$  ions are said to form a primary layer, they in turn attract  $\text{Na}^+$  ions  $\text{Na}^+$  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 an electrical double layer which imparts a degree of stability to the colloidal dispersion.

These layers cause colloidal particles to repel one another, and the particles therefore resist combination to form larger particles which will settle from 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  $\text{AgCl}$ , coagulation can be achieved by further addition of  $\text{AgNO}_3$  until equivalent amounts of silver and  $\text{Cl}^-$  ions are present. Since  $\text{Ag}^+$  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 material which are sufficiently large to settle from the solution i.e. If a small amount of electrolyte is added to a colloidal solution, particles coagulate into larger aggregates. The coagulation effect is explained simply 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 nuclei 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.

#### \*Amorphous precipitates have:

- 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  $\text{BaSO}_4$  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  $\text{BaSO}_4$ , 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 (espe-cially 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 thought to be determined by the relative rates of two processes, (1) the formation of nuclei called 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 conditions 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 term, the greater the number of nuclei formed 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  $\text{CaC}_2\text{C}_4$  and  $\text{ZnS}$ , 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  $\text{Fe}(\text{OH})_3$  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 saturation 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 .

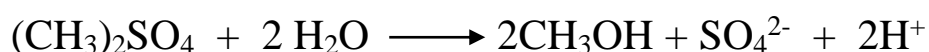
$H_2N$



$H_2N$

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

Barium ions have also been precipitated homogeneously as crystalline  $\text{BaSO}_4$  by slow hydrolysis of dimethyl sulphate according to the following equation



#### Washing of precipitates:

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 possess 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  $250^\circ\text{C}$ .

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  $\text{Fe}(\text{OH})_3$  is first dried at 100°C – 105°C, then ignited to the pure dry  $\text{Fe}_2\text{O}_3$ .

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

a) Incineration 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  $\text{BaSO}_4$  which is reduced to  $\text{BaS}$  or  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$ , etc. For this, the precipitate after drying is separated from filter paper by friction, the filter paper is first incrimented 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) Incineration 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.,  $\text{Al}_2\text{O}_3$

#### 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 down together. For example, on precipitation of  $\text{Ba}^{2+}$  ions as  $\text{BaSO}_4$  from a solution containing  $\text{Pb}^{2+}$  ions, the precipitate will be contaminated by  $\text{PbSO}_4$ . Similarly, aluminum and/or chromium ions if present during the precipitation of  $\text{Fe}^{3+}$  ions as  $\text{Fe}(\text{OH})_3$ , 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, impurities are retained on the surface of the precipitated particles by the adsorption power.

Adsorption is a reversible process, it is accompanied by an opposite process which is known as desorption, 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 equilibrium 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 its own ions e.g.,  $\text{BaSO}_4$  precipitate preferentially adsorbs its own ions,  $\text{Ba}^{2+}$  and  $\text{SO}_4^{2-}$ , dependent on which is present in the solution in excess. Among extraneous ions,  $\text{NO}_3^-$  ions are adsorbed more than  $\text{Cl}^-$  ions because  $\text{Ba}(\text{NO}_3)_2$  is less soluble than  $\text{BaCl}_2$ .

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 be 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 recrystallization 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 recrystallization.

## 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 of 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  $\text{BaSO}_4$  by drop wise addition of sulphuric acid solution to  $\text{BaCl}_2$  solution. The  $\text{BaSO}_4$  crystals grow in a medium containing  $\text{Ba}^{2+}$  ions in excess, Barium ions become adsorbed as primary layer and  $\text{Cl}^-$  ions are hold as counter ions (secondary layer). As more precipitant ( $\text{H}_2\text{SO}_4$ ) is added,  $\text{Cl}^-$  counter ions are displaced by  $\text{SO}_4^{2-}$  ions which are common to the precipitate. Since this displacement is incomplete, the precipitate occludes some  $\text{Cl}^-$  ions. In other words, we obtain a  $\text{BaSO}_4$  precipitate contaminated with a small amount of  $\text{BaCl}_2$ . The situation is different if the order of precipitation is reversed i.e, if  $\text{BaCl}_2$  solution is added drop wise to  $\text{H}_2\text{SO}_4$  acid solution.  $\text{BaSO}_4$  crystals grow in a medium containing  $\text{SO}_4^{2-}$  ions in excess. Sulphate ions form the primary layer while  $\text{H}^+$  (or  $\text{Na}^+$  or  $\text{K}^+$  present in solution) are the counter ions. This means that as a result of occlusion, the precipitate contains an admixture of  $\text{H}_2\text{SO}_4$  or of various sulphates such as  $\text{K}_2\text{SO}_4$  or  $\text{Na}_2\text{SO}_4$ .

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 Å units respectively. It is evident that while  $K^+$  ions can replace  $Ba^{2+}$  ions in  $BaSO_4$  crystals,  $Na^+$  ions cannot, 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  $SO_4^{2-}$  ions in  $BaSO_4$ .
- 4) The co-precipitation of  $KMnO_4$  and  $BaSO_4$ , in this case a pair of ions ( $Ba^{2+}$  and  $SO_4^{2-}$ ) is replaced by another pair ( $K^+$  and  $MnO_4^-$ ), comparable in size to the 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.

Organic precipitant can be classified into:

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



OH

OH

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 subsistent (R) and by adjusting the pH .

NO<sub>2</sub>

NO<sub>2</sub>

ii) Dipicrylamine: O<sub>2</sub>N- NH--- NO<sub>2</sub>

NO<sub>2</sub>

NO<sub>2</sub>

It gives sparingly soluble salt with K<sup>+</sup>. It is used for its separation. Interfering actions should be removed first e.g., NH<sub>4</sub><sup>+</sup>

iii) Oxalic acid:

Nearly all oxalates are insoluble in water except alkali metals and ammonium oxalate. It is extensively used for precipitating Ca<sup>2+</sup> from alkaline solutions as Ca oxalate H<sub>2</sub>O

b) Anionic precipitants:

These are organic basic compounds which form insoluble salts with certain anions.

i) Benzidine

H<sub>2</sub>N

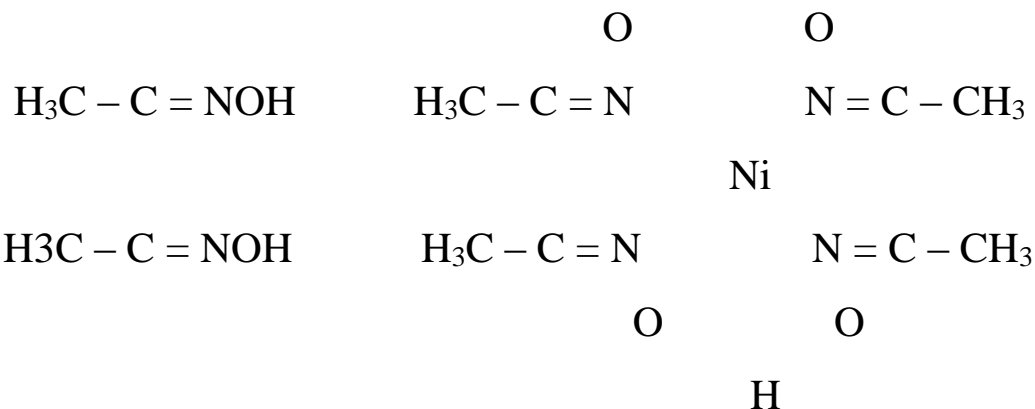
NH<sub>2</sub>

forms insoluble salts with SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup>. It precipitate with sulphate is more insoluble in water than BaSO<sub>4</sub>.

\* Chelate forming reagents:

i) Dimethylgluoxime

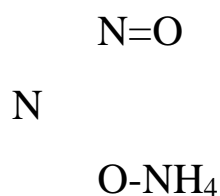
N



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 .



This reagent was originally proposed from precipitation of copper and iron, that is why it was given the short name cupferron. It is now also used for precipitation of vanadium, zirconium, titanium, tin, tantalum etc.

Precipitation is always can be 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<sub>2</sub>SO<sub>4</sub>, but not HNO<sub>3</sub> acid since oxidizing agents destroy the reagent.

iii) -hydroxy quinoline, oxin :

Although hydroxyquinolin 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.