Basics of

Analytical Chemistry

For

Second Year Students

2022

Course Name: Basics of Analytical Chemistry

Credit Hours: 1 hr.

Students: 2nd Year Science

Branch	Code
Biochemistry	chm201
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Contents

VOLUMETRIC ANALYSIS

1. Introduction

1.1. Some terms

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 **titrant** and the substance being titrated is termed the **titrand**.

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.

1.2. Classification of reactions in volumetric analysis

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

a) Reactions in which no change in valence occurs, these are dependent upon the combination of ions.

This type of reaction are divided into three main classes:

i- Neutralization reactions:

These include the titration of free bases or those formed from salts of weak acids by hydrolysis, with a standard acid (acidimetry) and the titration of free acid or those formed by the hydrolysis of salts of weak bases, with s standard base (alkalimetry). These reactions involve the combination of hydrogen and hydroxyl 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 collation of a cyanide with silver nitrate.

$$2 \ CN^- + Ag^+ \ \rightleftharpoons \ [Ag(CN)_2]^-$$
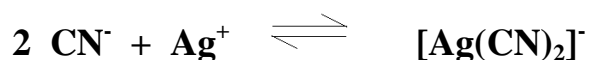
or of chloride ion with mercuric nitrate solution.

$$2 \ Cl^- + Hg^{++} \ \rightleftharpoons \ HgCl_2$$

Ethylenediaminetetraacetic acid (EDTA) is very important reagent for complex formation titrations.

$$Cu(H_2O)_4^{..} + 2 \ EDTA \ \rightarrow \ [Cu\text{-}(EDTA)_2]^{..} + 4 \ H_2O$$
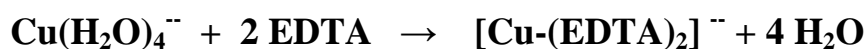
iii- Precipitations reactions:
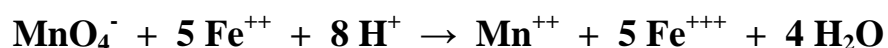
These depend upon the combination of ions, other than hydrogen or hydroxide ions, to form a simple precipitate as in the titration of silver ion with a solution of a chloride.

$$\text{Ag}^- + \text{NO}_3^- + \text{Na}^+ + \text{Cl} \rightarrow \text{AgCl} \downarrow \text{Na}^+ + \text{NO}_3^-$$
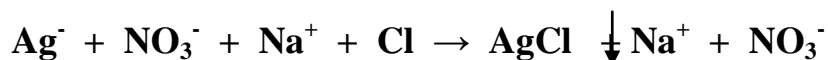
b- Oxidation-reduction reactions; those involve a change of valence or otherwise expressed, transfer of electrons.

For example:

$$\text{MnO}_4^- + 5\,\text{Fe}^{++} + 8\,\text{H}^+ \rightarrow \text{Mn}^{++} + 5\,\text{Fe}^{+++} + 4\,\text{H}_2\text{O}$$

1.3. 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 par unit weight of solvent. Thus, the nitrate solution just referred to will contain 25 g silver nitrate in 997.2 g of water at 20°C.

3) The physical chemist usually 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 **molal** 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. A **normal** solution is a solution which contains 1 gram equivalent of the active reagent dissolved in one liter of solution. For convenience,

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 results:

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 to the number of equivalents of the standard solution employed. We may write:

Normality (N) = <u>Number of gram-equivalents</u>
<u>Number of liters</u>

= **<u>Number of milligram equivalents</u>**
<u>Number of milliliters (ml)</u>

Hence, **Number of mg equivalents = Number of ml x N**

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

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

In practice V_A, V_B and normality N_A (of the standard solution) are known, hence normality N_B (of 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:

$$V_A \text{ x } N_A = V_B \text{ x } N_B$$
$$V_A = 0.2 = 25.0 \text{ X } 0.1$$

Then, $V_A = 12.5 \text{ ml}$

Example 2:

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

Solution:

A normal solution of $FeSO_4$ as a reluctant contain 1 mol per liter or 151.90 g per liter. Let the normality of the ferrous sulphate solution be N_1.

Then,　　　　　　　25 x N_1 = 30 x 0.125

　　　　　　　　　N_1 = 30 x 0.125/25 = 0.150 N

Hence the solution will contain

　N_1 x eq. Weight = 0.150 x 151.90 = 22.78 g $FeSO_4$ 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:

$$V_1 \ x \ N_1 \quad = \quad V_2 \ x \ N_2$$

$$V_1 \ x \ 2.127 \ = \ 1000 \ x \ 0.1$$

Then,　　　V_1 = (1000 x 0.1)/0.127 = 787.4 ml

1.4. Preparation of standard solutions:

If a reagent is available in the pure state, a solution of definite normality is prepared simply by weighing out an equivalent weight, or a definite fraction or multiple there of, dissolving it in the solvent, usually water, making up the solution to a known volume. It is not really essential to weigh out the equivalent weight. In practice it is often more convenient to prepare the solution a little more concentrated than is ultimately required, and then to dilute it with distilled water until the desired normality is obtained. If N_1 is the required normality, V_1 volumes after

dilution, N_2 the normality originally obtained and V_2 the original volume taken.

$$N_1 \, V_1 = N_2 \, V_2 \quad \text{or} \quad V_1 = (N_2 \, V_2)/N_1$$

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.

1.5. 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$^{\text{o}}$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.

2. Theory of acid-base titrations

2.1. Introduction

Acidimetry is the determination of acid substances by titration, and **Alkalimetry** 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.
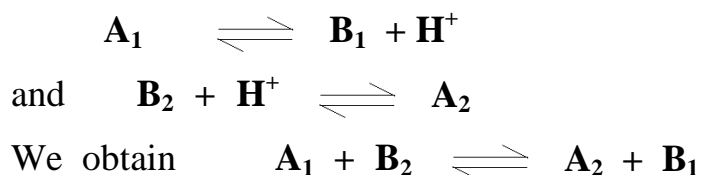
2.2. General conception of acids and bases (Bronsted theory):

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:

Acid $\rightleftharpoons$ proton + conjugate base

A $\rightleftharpoons$ H$^+$ + B
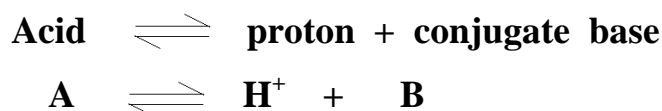
(It must be emphasized that the symbol H$^+$ represents the proton and not the "hydrogen ion").

Since the free proton cannot exist in solution in measurable concentration, reaction does not take place unless a base is added to concept the proton from the acid. By combining the equations.

A$_1$ $\rightleftharpoons$ B$_1$ + H$^+$

and **B$_2$ + H$^+$ $\rightleftharpoons$ A$_2$**

We obtain **A$_1$ + B$_2$ $\rightleftharpoons$ A$_2$ + B$_1$**

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

The stronger acid loses its proton more readily than the weaker, similarly, the stronger base accepts a proton more readily than does the weaker base. It is evident that the base or acid conjugate to a strong acid or strong base is always strong.

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

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

Acid$_1$ Base$_2$ Acid$_2$ Base$_1$
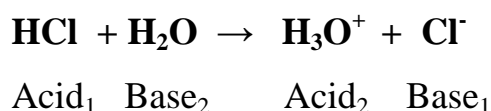
This process is essentially complete for al typical" strong" (i.e. highly ionized) acids. In marked contrast with "strong" acids, the reaction a typical "weak" or slightly ionized acid, such as acetic, proceeds only slightly to the right in the sense of the following:

$$HC_2H_2O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2$$

Acid$_1$ Base$_2$ Acid$_2$ Base$_1$
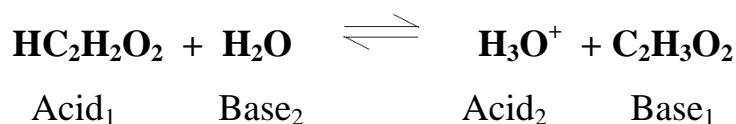
The conjugate base, in this theory, have strengths that vary inversely, as the strengths of the respective acids. The basic ionization constant of the conjugate base is given by the following equation;

$$K_B, conj. = K_W/K_A, conj.$$

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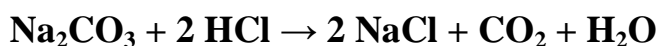
2.3. The Equivalent weight of an acid:

It is that weight of it which contains one g. atom of replaceable hydrogen, i.e. 1.008 g 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.

2.4. 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 1.008 g of hydrogen. The equivalent weights of sodium hydroxide and potassium hydroxide are 1 mol. Of calcium hydroxide; and barium hydroxide 1/2 mol.

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

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

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

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

2.5. Hydrogen-ion concentration and the pH scale:

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

$$[H_3O^+]\ [OH^-]/[H_2O]^2\ =\ K,\ \text{at constant temperature}$$

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

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

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

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

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

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

For example, in a solution that is 0.1 M in hydrogen ion.

$$[OH^-] = (10^{-14})/10^{-1} = 10^{-13} \text{ at room temperature}$$

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

$$[H^+] = 10^{-pH} \quad \text{or} \quad pH = \log(1/[H^+]) = -\log[H^+]$$

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

$$[OH^-] = 10^{-pOH} \quad \text{or} \quad pOH = \log(1/[OH^-]) = -\log[OH^-]$$

The following summary indicates the relationships

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

Acid   Neutral   Alkaline

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

pH < 7 < pOH   acidic reaction

pH = 7 = pOH   neutral reaction

pH > 7 > pOH   basic reaction

Examples:

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

$$pH = -\log[H^+] = -\log[4 \times 10^{-5}]$$
$$= 5.802 + -4.398 = 4.398$$

2) Find the hydrogen ion concentration corresponding to

$$pH = 5.643$$
$$pH = -\log[H^+] = 5.643 \qquad \log[H^+] = 5.643$$
$$= 6.365 = 2.28 \times 10^{-6}$$

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

Now $\log 1/25 = 0.97$.

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

2.5.1. The calculation of [H+] 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 winner

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

Where HB represents the un-ionized ion.

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

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

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

The course of $[H^+]$ or pH during a titration may be calculated for various intermediate points by substituting values for A and B into the

expression for the ionization constant. To calculate hydrogen ion concentration:

$$[H^+] = K_a [A]/[B]$$

$$= K_a [acid\ not\ yet\ titrated]/[salt\ already\ formed]$$

Concentrations are of course expressed in moles per liter. The molar 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.

$$pH = pK_a - log ([A]/[B])$$

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

2.6. 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 amounts of strong acids or bases or upon appreciable dilution. Typical mixtures are: acetic acid and mono potassium phosphate, plus ammonium chloride, boric acid and Borate, etc. The pH values of such mixtures will lie at point on the rather flat regions of the titration graphs, pH vs. milliters, for the various weak acids or bases Buffer action is readily understandable in terms of the mass action principle applied to the equilibrium

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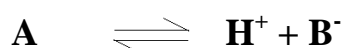
The acid A and the base B being conjugate, e.g.; NH_4^+ and NH_3, $HC_2H_3C_2$ and $C_2H_3O_2^-$, etc.

$$K_a = [H^+][B^-]/[A] \hspace{2cm} (1)$$

$$[H^+] \ = \ K_a \ [A]/[\ B^-] \qquad\qquad\qquad (2)$$

$$pH \ = \ pK_a - log \ ([A]/[B^-]) \ = \ pK_a - log \ [A] + log \ [B^-] \qquad (3)$$

Expression (3) shows the ratio of [A] to [B⁻] determines the pH rather than the absolute values of the concent-rations. 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 no ionized hydrogen acetate and thus diminishes the concentration of acetate ion slightly. Thus results in slightly lower pH because the ration $[HC_2H_3O_2]$, $[C_2H_3O_2^-]$ is only slightly changed. The addition of a small amount of sodium hydroxide produces the opposite effect.

Example:

Calculate the pH of the solution product by adding 10.0 ml of 1 M hydrochloric acid to 1 liter of a solution which is 0.1 M in acetic acid and 0.9 M in sodium acetate ($K_a = 1.82 \times 10^{-5}$).

pH $= pK_a + log$ [Salt]/[Acid] $= 4.74 - 0.09 = 4.65$

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

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

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

$[CH_3COOH] = 0.1 + 0.01 = 0.11$

pH = 4.74 + log 0.09/0.11 = 4.74 − 0.09 = 4.65

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

2.7. Acid-Base Indicators:

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

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

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

c) Development or disappearance of a fluorescence.

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

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

Basic Indicator: **InOH** $\rightleftharpoons$ **OH$^-$ + In$^+$** (2)
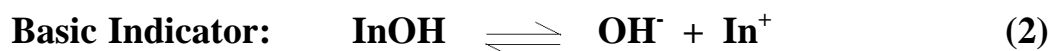
Where **HIn** is the unionized form of the acidic indictor which give the acid color and **In$^-$** is the ionized form, which produces the basic color. **InOH** is the unionized form of the basic indicator, which given the basic color and **In$^+$** is the ionized form, which produces the acid color.

If the acid indicator is added to an acidic term on the right-hand side of equation (1) is increase and the ionization of the indicator is depressed by the common ion effect. The indictor is then predominate, in the unionised form of **HIn**; the acid color. If on the other hand, the

indicator is added to a basic solution, the $[H^+]$ is reduced by reaction of the acid indicator with the base, and reaction (1) proceeds to the right yielding more ionized indicator **[In⁻]** and the basic color predominates. The reverse is true for basic indicators, in acid solution the reaction (2) proceeds to the left and the basic color is prominent. In other words, the change in color of indicators is a process of automatism and the degree of ionization of indicators, as controlled by the pH, is the factor which determined tautomer predominates.

The nature of this process may be demonstrated in the case of the p-nitrophenol. In basic solutions, p-nitrophenol is present chiefly in the yellow ion, while in acid solution it is present as the color less nitro compound:

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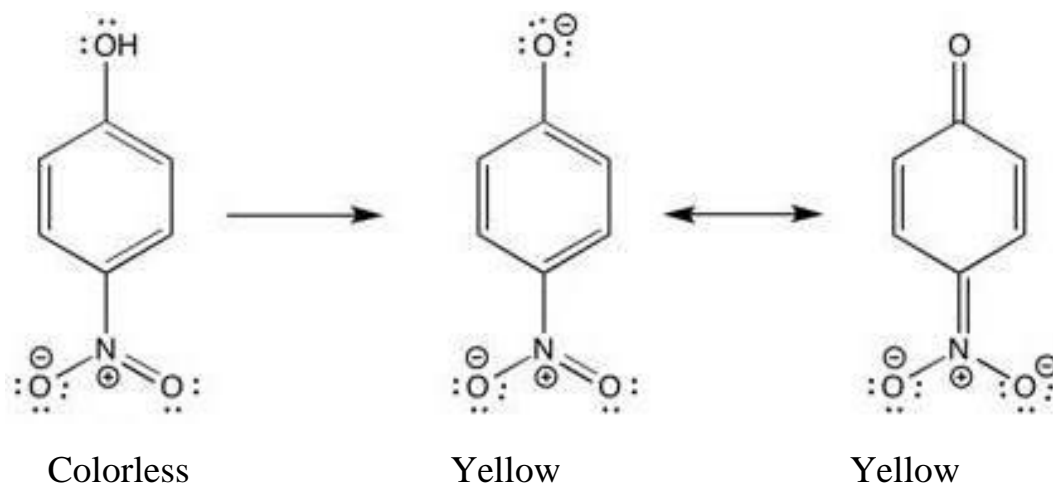
It should be noted that not all substances which show tautomeric properties can be used as indicators. the tautomeric change must be rapid, and must occupy a rather small range of pH. Therefore consideration of the tautomeric equilibrium modifies the Ostwald equation. If the formula **HIn** represents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

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

Considering the two equilibria separately

$$\textbf{[HIn'']/[HIn]} = \textbf{Keq} \quad and \quad \textbf{[H}^+\textbf{][In''}^-\textbf{]/[HIn'']} = \textbf{K}_a$$

Multiplying these two equations:

$$\textbf{[H}^+\textbf{][In''}^-\textbf{]/[HIn]} = \textbf{K}_{\textbf{Ind}}$$

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:

$$\textbf{pH} = \textbf{pK}_{\textbf{Ind}} \textbf{ - log[HIn]/[In''}^-\textbf{]} = \textbf{pK}_{\textbf{Ind}} + \textbf{log[In''}^-\textbf{]/[HIn]} \tag{1}$$

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

$$\textbf{[In''}^-\textbf{]/[HIn]} \qquad i.e. \qquad \textbf{[basic color]/[acid color]}$$

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

In case of indicators in which the colored ion is the cation and not the anion it is possible to derive a relation between color and pH , similar to the above relation
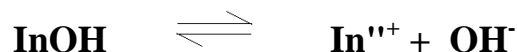
$$\textbf{InOH} \quad \rightleftharpoons \quad \textbf{In''}^+ + \textbf{OH}^-$$

$$\textbf{[OH}^-\textbf{][In''}^+\textbf{]/[InOH]} = \textbf{K}_{\textbf{Ind}}$$

and $\qquad \textbf{pOH} = \textbf{pK}_{\textbf{Ind}} \textbf{ - log [InOH]/[In''}^-\textbf{]}$

$$\textbf{pH} = \textbf{pK}_{\textbf{W}} \textbf{ - pOH}$$

$$= \textbf{pK}_{\textbf{W}} \textbf{ - (pK}_{\textbf{Ind}} \textbf{ - log [InOH]/[In''}^-\textbf{])}$$

$$\textbf{pH} = \textbf{pK}_{\textbf{W}} \textbf{ - pK}_{\textbf{Ind}} \textbf{ - log [In''}^-\textbf{]/[InOH]} \tag{2}$$

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

$$\textbf{[In''}^-\textbf{]/[InOH]} \qquad i.e. \qquad \textbf{[acid color]/[basic color]}$$

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

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

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

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

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

$$pH = pK_{Ind} + \log 10/1 = pK_{Ind} + 1$$

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

2.8. Mixed Indicators:

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

2.9. Screened Indicators:

Screened indicators increase the sharpness of the color change at the end point of a titration. A screened indictor is a mixture of an indicator and an inert dye whose color does not change with pH. The effect of the dye is to decrease the range of wavelengths transmitted by the solution, so that the light transmitted by the two colored forms of the indicator is not masked by light of other wave lengths. An example is the so-called

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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.

2.10. Turbidity Indicators:

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

2.11. Fluorescence Indicators:

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

Examples of fluorescent indicators are Eosin phioxin, chromo tropic acid, acridine orange etc.

3. 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.

3.1. 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 1 N HCl acid and the add drop wise of 1 N 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, $[H^+] = 1$ N

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

b) During the titration:

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

$$or \ pH \ = \ 0.48$$

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

$$\text{or pH} = 0.94$$

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

$$\text{or pH} = 1.3$$

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

$$\text{or pH} = 2.0$$

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

$$\text{or pH} = 2.3$$

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

$$\text{or pH} = 3.3$$

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.

$$\text{pH} + \text{pOH} = 14 \qquad \text{pH} = 7$$

d) Beyond the equivalence point :

The solution contains excess alkali.

With 100.1 ml of base $[H^+] = 0.1/200 = 5.0 \times 10^{-4}$,

$$\text{pOH} = 3.3 \text{ and pH} = 10.7$$

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

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

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 an pH 10.5 Phenolphthalein, methyl red, and methyl orange are most often used. (Fig. 1).
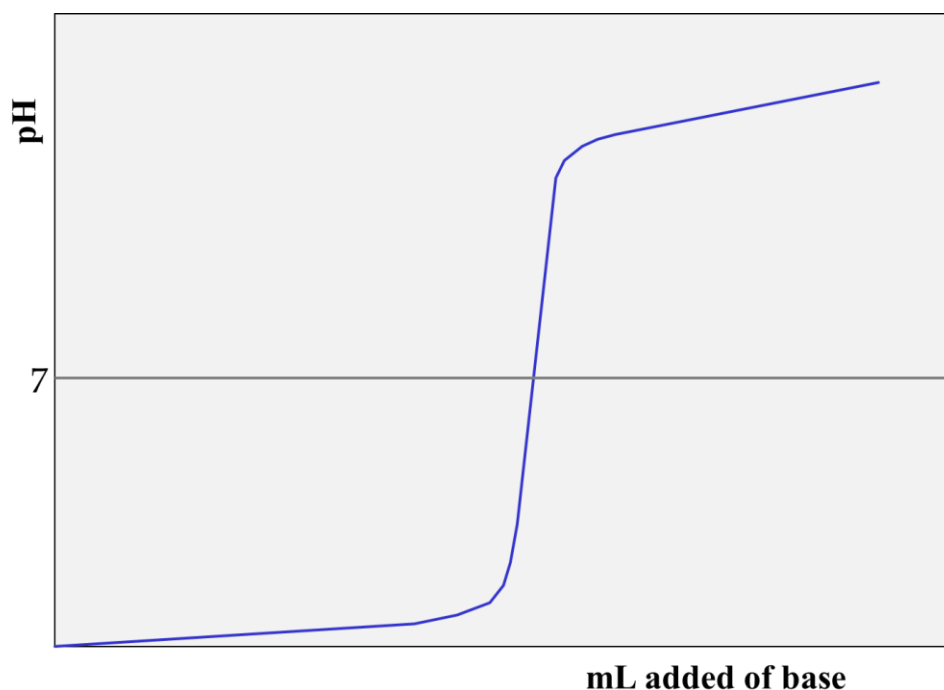
Figure 1 Titration curve of a strong acid with strong base.

3.2. 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. o.1 N acetic acid with 0.1 N NaOH .

a) At the beginning of titration:

In this case the hydrogen ion concentration at the first is less than before, since acetic acid is less ionized than hydrochloric acid. It can be calculated from the ionization constant of acetic acid which at 25^oC is 1.86×10^{-5} thus:
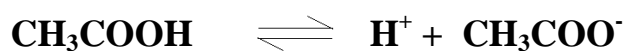
$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

$$[H^+][CH_3COO^-]/[CH_3COOH] = Ka = 1.86 \times 10^{-5}$$

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

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

$$[H^+] = (K_a [CH_3COOH])^{½}$$

$$[H^+] = (1.86 \times 10^{-5} \times 0.1)^{½} = 1.36 \times 10^{-3}$$

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

Hence, $pH = -\log 1.36 \times 10^{-3} = 2.87$

b) During the titrations:

The addition of NaOH to the acetic acid solution continually forms sodium acetate in solution and the acetate ions depress the ionization of the unneutralized acetic acid. The approximate hydrogen ion concentration at any point prior to the equivalence point can be found by substituting the relative concentration of acetate and undissocate acid in the ionization constant expression for acetic acid :

$$K_a = [CH_3COO^-][H^+]/[CH_3COOH]$$

$$[H^+] = K_a [CH_3COOH]/[CH_3COO^-]$$

$$pH = pK_a + \log [Salt]/[Acid]$$

When 50 ml of 0.1 N alkali have been added

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

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

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

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.

$$CH_3COO^- + H_2O \rightleftharpoons OH^- + CH_3COOH$$
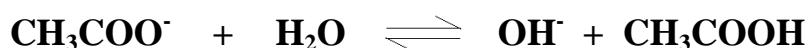
The equilibrium constant in this case is

$$K = [OH^-][CH_3COOH]/[CH_3COO^-] \qquad (1)$$

But the ionization constant of acetic acid .

$$K_a = [CH_3COO^-][H^+]/[CH_3COOH] \qquad (2)$$

The ion product constant of water:

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

The equation (1) is also obtained by dividing the ion product constant of water, by the ionization constant of acetic acid.

Hence $K = K_W/K_a = [OH^-][CH_3COOH]/[CH_3COO^-]$

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:

Therefore $[OH^-]^2/[CH_3COO^-] = K_W/K_a$

$$[OH^-] = (K_W/K_a\, C)^{1/2}$$

and since $[H^+] = K_W/[OH^-]$

$[H^+] = K_W/\{(K_W/K_a)\, C\}^{1/2} = K_W^{1/2}K_a^{1/2}/C^{1/2}$

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

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

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

(Where $pK_W = - \log K_W$ and $pK_a = - \log K_a$)

In the sample under consideration,

$K_W = 1 \times 10^{-14}$, $pK_W = 14$, $K_a = 1.86 \times 10^{-5}$, $pK_a = 4.74$ and $C = 0.05$

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

$= 7 + 2.37 - 0.54 = 8.83$

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:

$pOH = -\log (0.1 \times 0.1/200.1) = 4.3$

$pH = 14 - 4.3 = 9.7$

The preceding pH values and other values in the titration are depicted graphically in Fig. 2. The common indicator suitable for this titration is

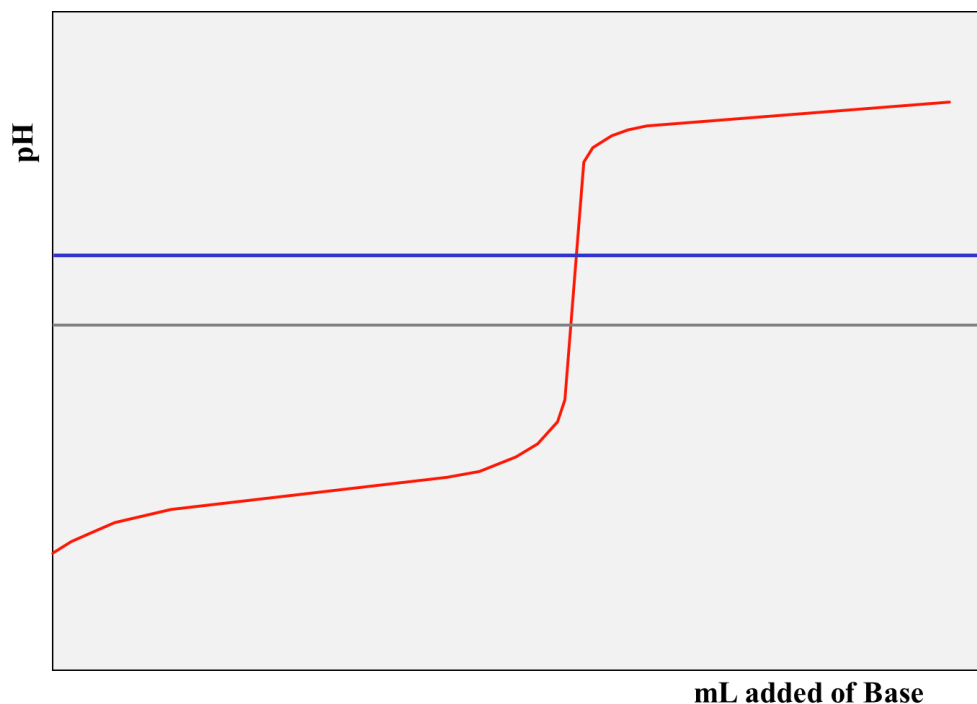phenolphalein, and the use of an indictor like methyl red or methyl orange would lead to erroneous results.

mL added of Base

Figure 2 Titration curve of a weak acid with strong base.

3.3. Neutralization of weak base with a strong acid:

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

a) At the beginning or titration:

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

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

$$[NH_4^+][OH^-]/[NH_4OH] = K_b = 1.75 \times 10^{-5}$$

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

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

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

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

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

pH $= 14 - 2.287 = 11.13$

b) pH during titration :

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

$$K_b = [NH_4^+][OH^-]/[NH_4OH]$$

$$[OH^-] = K_b [NH_4OH]/[NH_4^+]$$

$$[H^+] = K_w/[OH^-] = K_w/\{K_b [NH_4OH]/[NH_4^+]\}$$

$$pH = pK_w - pK_b - \log [Salt]/[Base]$$

OR $pOH = pK_b + \log [salt]/[base]$ (Henderson-Hasselbalch equation)

$pH = pk_w - pOH$ then, $pH = pk_w - pK_b - \log [salt]/[base]$

For 50 ml of base

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

$pH = 14 - 4.76 - \log (3.33 \times 10^{-2}/3.33 \times 10^{-2}) = 9.24$

Similarly, the other points can be calculated.

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:

$$\textbf{NH}_4\textbf{Cl} + \textbf{H}_2\textbf{O} \rightleftharpoons \textbf{H}^+ + \textbf{Cl}^- + \textbf{NH}_4\textbf{OH} \qquad \textbf{(1)}$$

For which

$$K_H = [NH_4OH][H^+]/[NH_4^+] = K_w/K_b$$

K_H is the hydrolysis constant, $K_w = [H^+] [OH^-]$ and

$K_b = [NH_4^+][OH^-]/[NH_4 OH]$

Let $[H^+] = [NH_4OH]$, because for each mole of NH_4OH produced, one mole of H^+ is formed. Let the concentration of the ammonium ion

concentration approximately equal to the concentration C , of the salt at the equivalence point.

Therefore $\underline{[\,H^+\,]^2}$ = $\underline{K_w}$

$\quad\quad\quad\quad$ C $\quad\quad$ K_b

$\quad$ $[\,H^+\,]$ = $\dfrac{K_w\ C}{\sqrt{K_b}}$

pH = 1/2 pK_w - 1/2 pK_b - 1/2 log C

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

d- <u>pH beyond equivalence point</u>:

After the equivalence point has been reached, the solution contains excess of H^+ ions, hydrolysis changes may be assumed, with sufficient accuracy for our purpose, to be those due to the excess of acid present pH = - log [H^+]. The values completed in the above manner are represented graphically in Fig 3. The common indicator suitable for this titration is methyl red, or methyl orange.
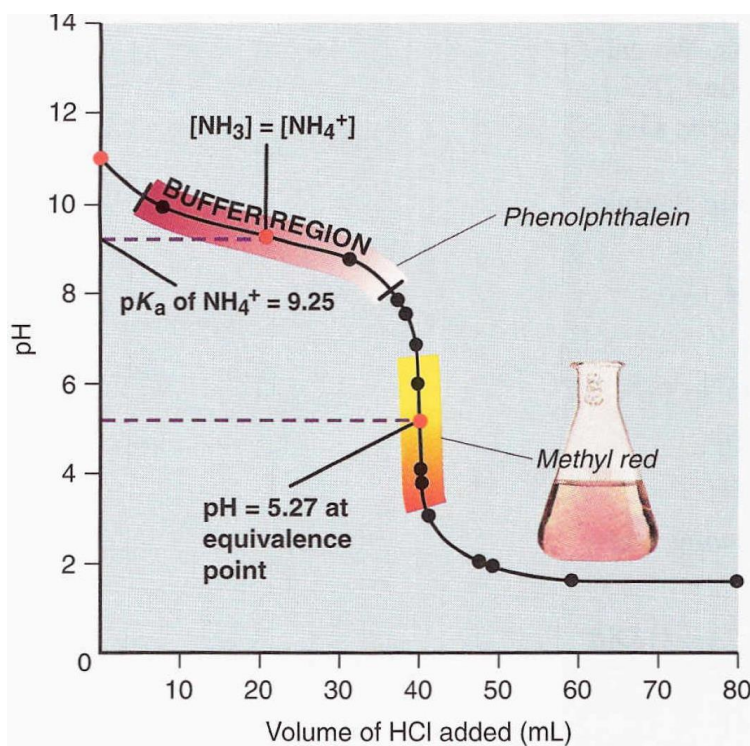

Fig (3) Titration curve of a weak base with strong acid.

3.4 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 (E)(C): the diagram of Fig. 4 . The (F) (F). Such titrations are of little practical value 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.
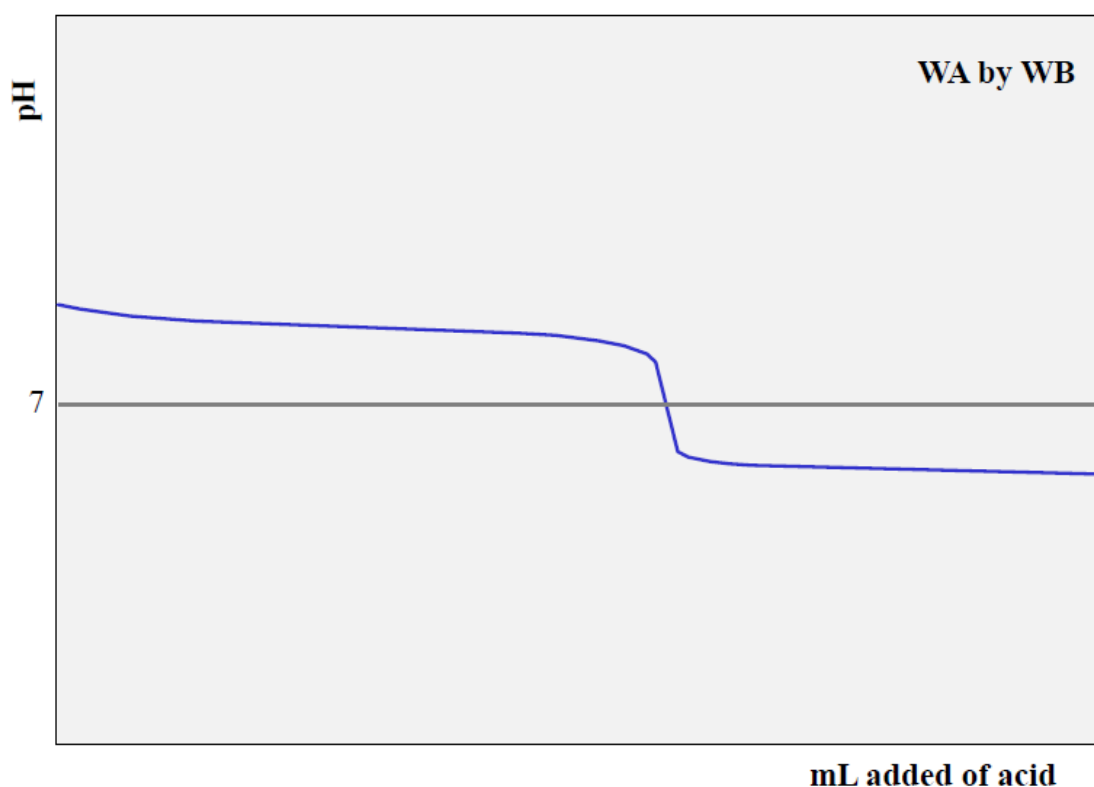

Fig. 4 Titration curve of a weak base with weak acid.

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

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

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$$pH = - 1/2 \log K_w - 1/2 \log K_a + 1/2 \log K_b$$
$$pH = 1/2\, pK_w + 1/2\, pK_a = 1/2\, pK_b$$

3.5 Titration of polybasic acids with strong base:

a- <u>Ionization polybasic acids</u> :

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

$$H_2A \;\rightleftharpoons\; H^+ + HA^- \quad \dots\dots\dots\dots\dots \quad (1)$$

$$H\ A \;\rightleftharpoons\; H^+ + A \quad \dots\dots\dots\dots\dots \quad (2)$$

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

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

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

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

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

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

$$H_2A^- \;\rightleftharpoons\; H^+ + HA^{--}$$
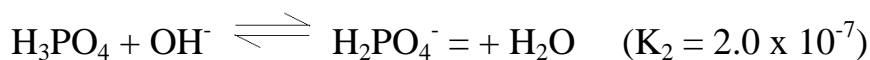
28

$$HA^{--} \rightleftharpoons H^+ + A^{---}$$
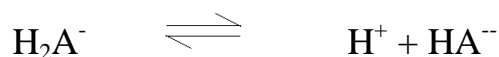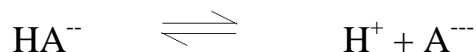
b- **Example :**

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

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

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

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

There is no third inflection, for the ionization constant $HPO_4^{=}$ is extremely small (3.6×10^{-13}). The graph shows that H_3PO_4 can be accurately titrated to $H_2PO_4^-$. If methyl orange is used as the indicator the $H_2PO_4^-$ can be titrated to $HPO_4^{=}$ with fair precision if phenolphthalein is used as the indicator and that H_3PO_4 cannot be titrated according to the equation:
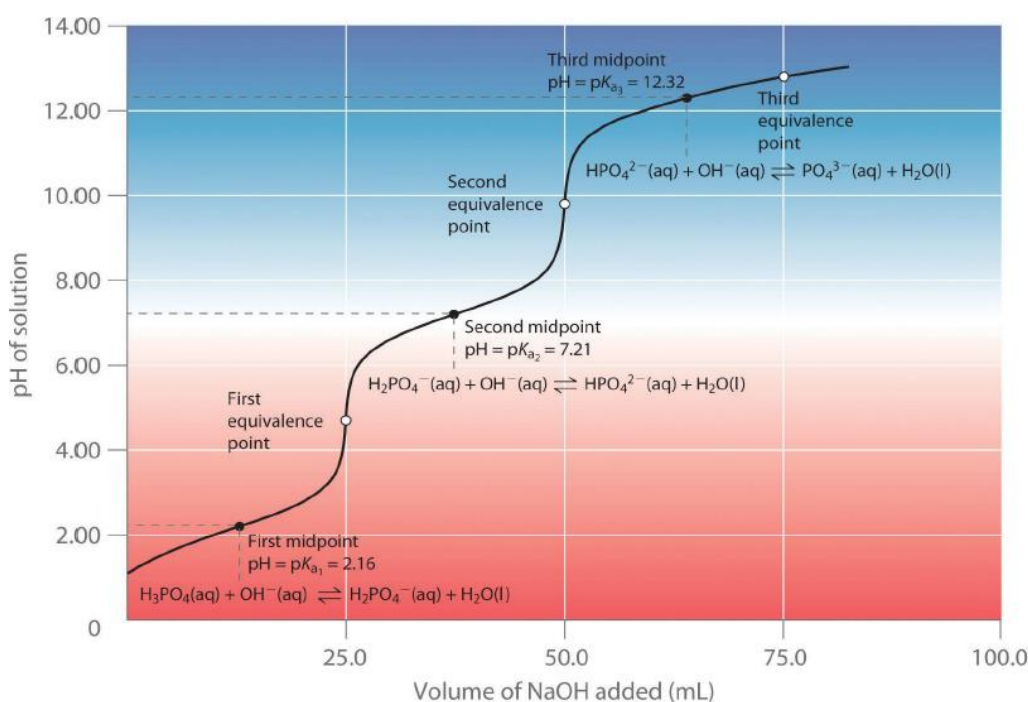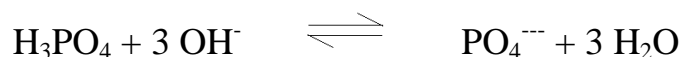
$$H_3PO_4 + 3\,OH^- \rightleftharpoons PO_4^{---} + 3\,H_2O$$

Fig. 5 Titration curve of H_3PO_4 with NaOH.

c- Calculation of the pH of each inflection :

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

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

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

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

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

or pH = 1/2 (pK_1 + pK_2)

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

$$[H^+] = \sqrt{2.0 \times 10^{-3} \times 7.0 \times 10^{-8}} = 2.2 \times 10^{-5}$$
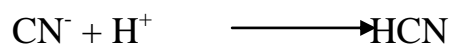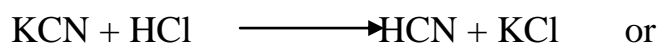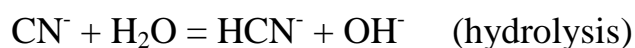
Or pH = 1/2 (2.16 + 7.17) = 4.66

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

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

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

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

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

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

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

KCN + HCl $\longrightarrow$ HCN + KCl   or

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

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

A few examples encountered in practice will not be considered:

1- Titration of cyanide with strong acid :

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

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

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

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

If 100.1 ml. of HCl acid are added, the pH will be 4, with 100.2 ml., the pH will be 3.7 with 101 ml. the pH will be 3, etc. There will be a fairly abrupt decrease of pH in the neighborhood of the equivalence point. If the titration error is not to exceed 0.2 percent, any indicator covering the pH range 3.7 - 5.1, may be used. Suitable indicators are promo cresol green methyl orange, bromo-phenol blue and methyl red.

2- Titration of borate ion with a strong acid:

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

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

Or $B_4O_7^-$ + 2 H^+ + 5 H_2O $\rightleftharpoons$ 4 H_3BO_3
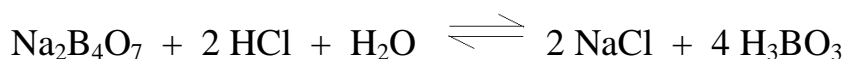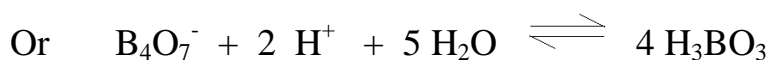
Boric acid behaves as a weak monobasic acid with a dissociation constant of 6.4 x 10^{-10} . The pH at the equivalence point in the titration of 0.2 N borax with 0.2 N hydrochloric acid is that due to 0.1 N boric acid, i.e. 5.1 further addition of hydrochloric acid will cause a sharp decrease of pH as in the case of potassium cyanide. Similar indicators may therefore be used.

3- 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:

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

or CO_3^{--} + H^+ $\rightleftharpoons$ HCO_3^-
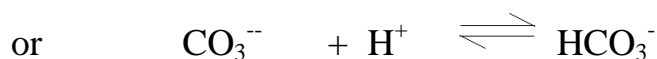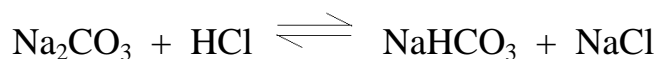
The equivalence point for the primary stage of ionization of carbonic acid is at pH (1/2 pK_1 + 1/2 pK_2 = 8.3,) and we have seen that thymol blue and, less satisfactorily phenolphthalein may be employed to detect the end point .

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

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

Or CO_3^{--} + $2H^+$ = H_2CO_3
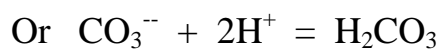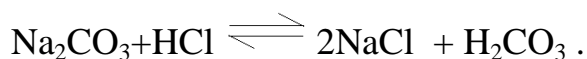
The same end point is reached by titrating sodium bicarbonate solution with HCl acid :

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

or HCO_3^- + H^+ $\rightleftharpoons$ H_2CO_3
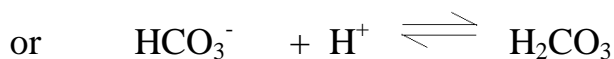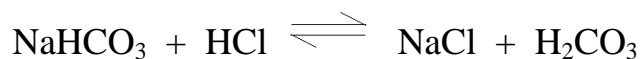
The pH at the equivalence point is very approximately 3.9, and suitable indictors are therefore methyl yellow, methyl orange and congo red.
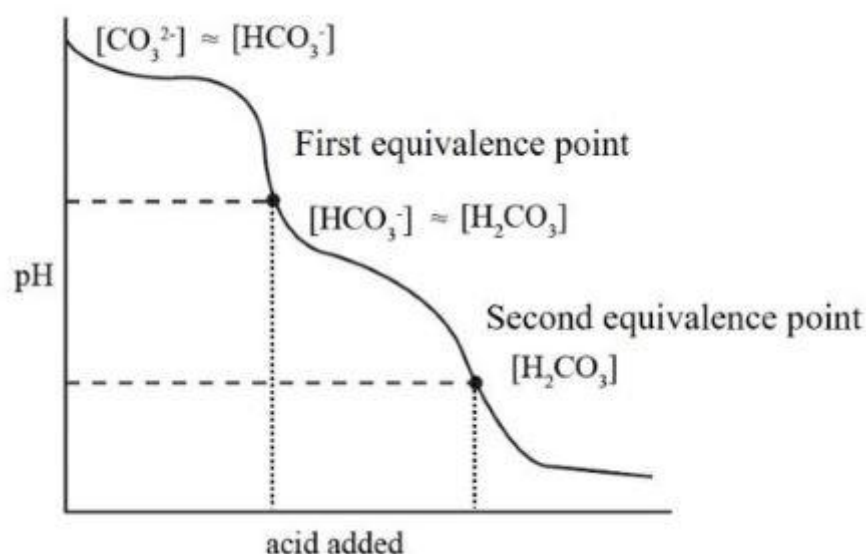
Fig. 6 Titration of Na_2CO_3 with HCl.

VOLUMETRIC PRECIPITATION TITRATIONS (PRECIPITIMETRY)

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

Limitations of volumetric precipitation titrations:

Volumetric precipitation reactions have several limitations combining those of the titrimetric methods in general, and some of those of the gravimetric methods. In particular, few points need here be stressed in comparing volumetric precipitation reactions with the other volumetric reactions, where no precipitates form.

1- The stoichiometry :

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

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

3- Although the solubility: of the precipitate may be depress-ed 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 experi-mental 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 thiocynate and few mercury, lead and zinc salts are the most important compounds involved in precipitation titrations. The argent metric titrations, in particular are precise, simple and illustrative of almost all the important principles, and methods.

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

Solubility Product:

Ionic reactions are usually complete when any change occurs that lowers the concentrations of ions to very small values. The factor

governing the completeness of a precipitation reaction is the solubility of the precipitate formed. The more insoluble l the precipitate, the more complete is the reaction at the equivalence point of the titration, and the larger is the change in concentration of the reacting ions. The equilibrium concentration of the reacting ions. The equilibrium constant expressing the solubility of a precipitate is the familiar solubility product constant.

Let us consider what happens when the sparingly soluble salt AB comes in contact with water. Some of the salt dissolves in water and assuming this compound to be an ionic solid, dissociated into its ions A^+ and B^- This reaction can be represented in its simplest form (i.e., without considering hydration of the ions) by the equation.

$$AB \longrightarrow A^+ + B^- \qquad\qquad (1)$$
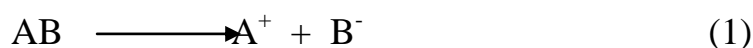
However, as the salt AB dissolves, more and more A^+ and B^- are in solution, with the net result that the change of their recombining to form AB increases; that is, the equilibrium represented simply by equation 2.

$$A B \text{ (sold)} \rightleftharpoons A^+ B^- \text{ (solution)} \qquad\qquad (2)$$
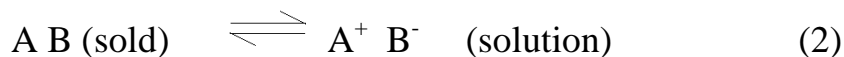
for a saturated solution is established. The equilibrium constant for this reactions is :

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

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

$K \times const = [A^+][B^-] = S_{AB} =$ Solubility product constant. Let consider in the same way the saturated solution of the sparingly soluble salt $X_m Y_n$

which dissociates into m cation, X^{n+} and n anions, Y^{m-}. The equilibrium for this saturated solution can be represented by the equation.

$$[X^{n+}]^m [Y^{m-}]^n = SX_m Y_n$$
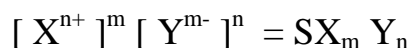
A more deduction of the solubility product principle can be obtained along the following lines. For simplicity, we shall consider a binary electrolytes

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$
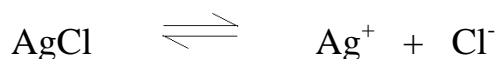
The velocity of the forward reaction depends, only upon the temperature and at any given temperature:

$$V_1 = K_1$$

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

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

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

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

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

Course of ion concentration during a precipitation:

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

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

1- At the start the titration :

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

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

2- 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 l because of increase in volume of solution. Since the total volume of solution is now 150 ml. the

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

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

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

in the last calculation $pCl^- = 1.48$, hence $pAg^+ = 9.92 -$

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

3- 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 .

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

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

4- Beyond the end point:

With 100.1 ml of silver nitrate solution $[Ag^+] = 0.1 \times 0.1/ 200.1 = 5 \times 10^{-5}$ 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.
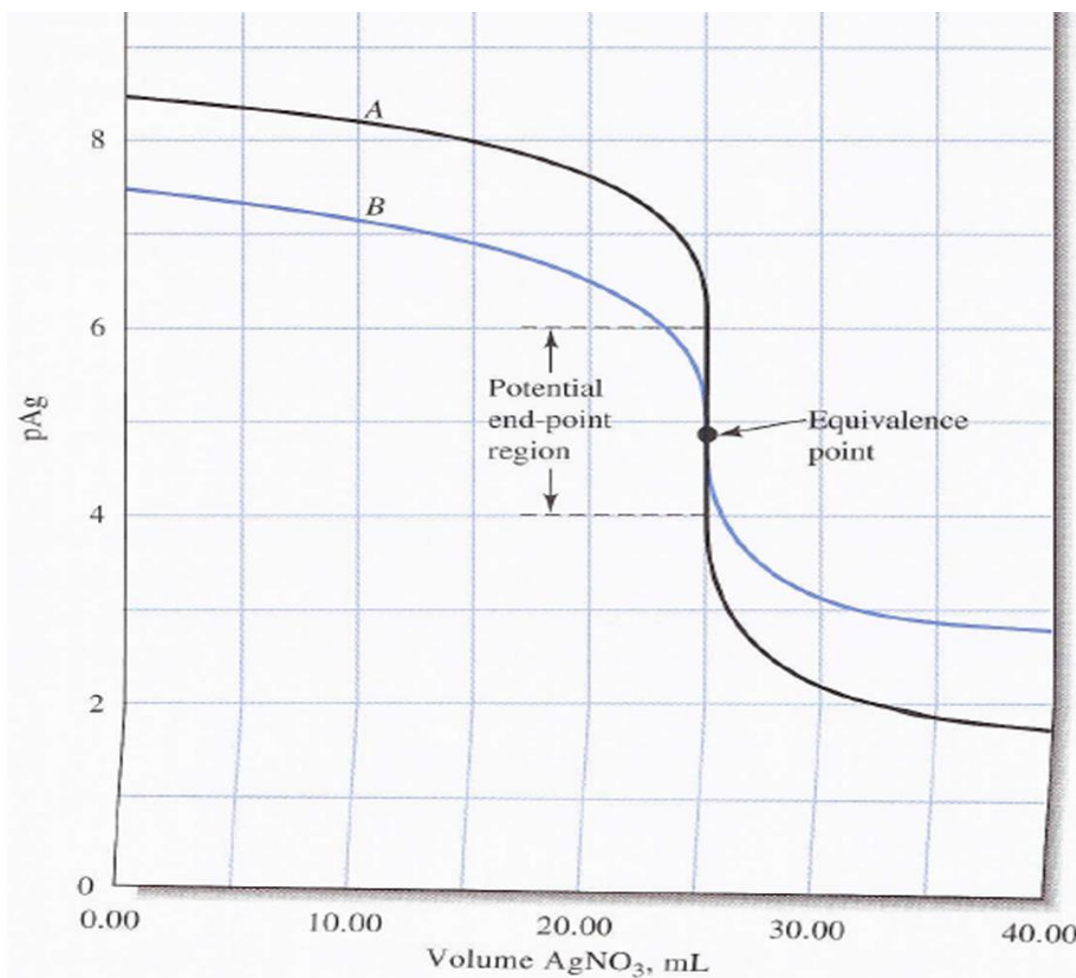
**Fig . 7** Titration of 0.1 N sodium chloride with 0.1 N AgNO$_3$.

Equivalent weights:

Here the equivalent weight is the weight of the substance which contains or reacts with 1 g. atom of a univalent action M$^+$ (which is equivalent to 1.009 g. of hydrogen) 1/2 g. atom of a bivalent action M^{2+}, 1/3 g atom of a trivalent action M^{3+}, etc. For the action, the equivalent weight is the atomic weight divided by the valence. For a reagent which reacts with this action, the equivalent weight is the weight of it which reacts with one equivalent of the action. The equivalent weight of a salt in precipitation reactions is the gram molecular weight of the salt divided by the total valence of the reacting ion) Thus the equivalent weight of silver

nitrate in the titration of chloride ion is its molecular weight. In a complex formation reaction the equivalent weight is most simply deduced by writing down the ionic equation of the reaction. For example, the equivalent of KCN in the titration with silver ions is 2 moles , since the reaction is :

$$2\,CN^- \;+\; Ag^+ \;\rightleftharpoons\; [\,Ag(CN)_2\,]^-$$
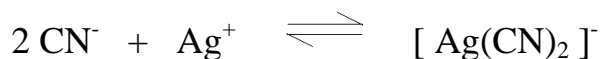
In the titration of zinc ion with potassium ferrocyanide solution:

$$3\,Zn^{++} \;+\; 2\,K_4Fe(CN)_6 \;\rightleftharpoons\; 6\,K^+ + K_2Zn[Fe(CN)_6]_2$$
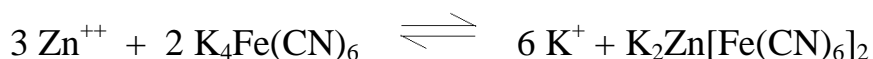
the equivalent weight of the ferrosyanide is one third of the formula weight.

Determination of end points in precipitation reaction:

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

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

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

<u>**The theory of the action**</u> of these indictors is based open the properties of colloids. When a chloride solution is titrated with a solution of silver nitrate, the precipitated silver chloride adsorbs chloride ions (a precipitate

has a tendency to adsorb its own ions); this may be termed the primarily adsorbed layer, and it will bold by secondary adsorption oppositely charged ions present in solution (shown diagrammatically in Fig. 8a). 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).
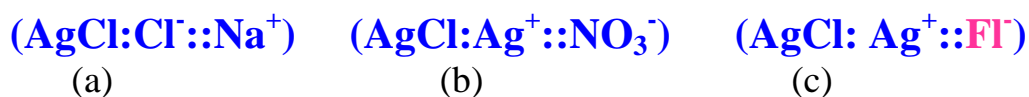
$(AgCl:Cl^-::Na^+)$ $(AgCl:Ag^+::NO_3^-)$ $(AgCl: Ag^+::Fl^-)$
(a)   (b)   (c)

Fig. (8)

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 adsorbed chloride ions. The fluorescent ions secondarily adsorbed will pass back into solution, to which they impart a greenish-yellow color.

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

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

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

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

Some adsorption indicators and their applications:

1- Fluorescein: For the titration of chlorides fluorescein may be used. This is a very weak acid ($K_a = Ca.1 \times 10^{-8}$) 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 my be utilized in slightly acid solution of pH greater than 4.4 this indicator has the further advantage that is applicable in very dilute solutions.

3- Eosin (tetrabromofluorescein): is a stronger acid and can be used down to a pH of 1.2. The color change is sharpest in an acetic acid solution. Eosin is so strongly adsorbed on silver halides that it can be used for chloride ion before the equivalence point and thereby gives a premature indication of the end point. With the more strongly adsorbing ions, Br^-, I^- and SCN^-, the competition is not serious and a very sharp end point is obtained in the titration of bromide, iodide and thiocyanat even in dilute solutions.

4- Rose Bengal (dichlorotetraiodofluorescein) and dimethyl diiodofluorescein have been recommend for the titration of iodides. rhodamine 6 G: The hydrochloride of a basic dye (0.05 per cent aqueous solution), is a good indicator for the titration of silver ions with a standard bromide solution in dilute nitric acid solution (the acidity should not exceed 0.5 N). As long as silver ions are present is express the indicator action is not noticeably adsorbed by silver bromine. At the equivalence point or after a very slight excess of bromine has been added, the precipitate adsorbs the dye strongly and acquires a blue violet color.

B- 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

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

or $$Ag^+ + 2 CN^- \rightleftharpoons [Ag(CN)_2]^-$$
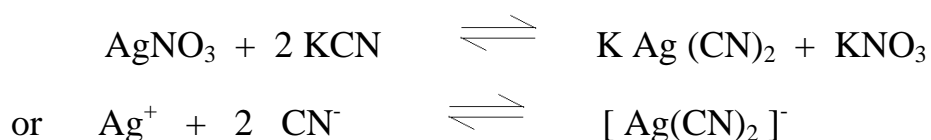
When the above reaction is complete, further addition silver nitrate solution wields the insoluble silver argent cyanide.

$$Ag^+ + [Ag(CN)_2]^- \rightleftharpoons [Ag(CN)_2]$$
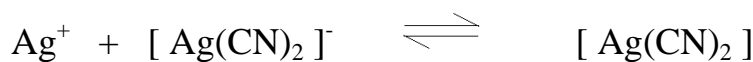
The end point of the reaction is therefore indicated by the formation of permanent turbidity. The only difficulty in obtaining a sharp end point lies in the fact that silver cyanide, precipitated by local excess concentration of silver ion somewhat prior to the equivalence point, is very slow to redissolve and the titration is time–consuming.

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

$$Ag^+ + [Ag(CN)_2]^- + 4NH_3 \rightleftharpoons 3[Ag(NH)_3]^+ + 2CN^-$$
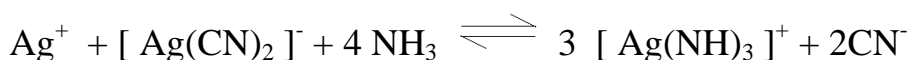
The iodide ion and ammonia solution are added before the titration is commenced, the formation of silver iodide (as turbidity) will indicate the end point.

$$[Ag(NH)_3]^+ + I^- \rightleftharpoons AgI + 2NH_3$$
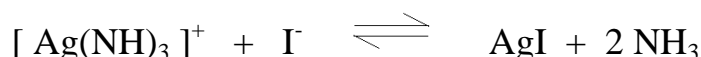
During the titration any silver iodide which would be formed will be kept in solution by the excess of cyanide ion always present until the equivalence point is reached:

$$AgI + CN^- \rightleftharpoons [Ag(CN)_2]^- + I^-$$
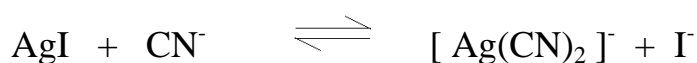
The method may also be applied to the analysis of silver halides by dissolution in excess of cyanide solution and back-titration with standard silver nitrate. It can also be utilized indirectly for the determination of several metals, notably nickel, cobalt, and zinc, which form stable stoichiometric some complexes with cyanide ion. Thus if a Ni (II) salt in ammoniacal solution is heated with excess of cyanide ion, the Ni ion is formed quantitatively, since it is more stable than Ag $[(CN_2)]^-$ ion, the excess of cyanide may be determined by the Liebig-Deniges method.

COMPLEX FORMATIONS TITRATIONS (COMPLEXIMETRY)

Introduction:

Titrations that cause the formation of a stable complex ion or a slightly dissociated molecule will be considered complex forming titrations. Although there are numerous reactions that fall into these two categories, actually only a few are suitable for analytical determinations. This is due to the fact that the equilibrium constant for many complex forming reactions is to

small to permit the accurate detection of the equivalence point. Furthermore, a number of complex ions of different composition may be formed during the same titration. Finally, indicators for the detection of the equivalence point of complex forming reactions are not as easily found as for precipitation reaction, even though the requirements for an indicator in both types of reactions are similar. Only three complex – forming action that have been developed into titrimetric method will be discussed in this chapter. These examples illustrate the various types of reactions that are suitable for analytical methods and probably represent some of the most practiced of these methods.

A- <u>Argentimetric titration of cyanide:</u>

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

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

$$Ag^+ \; + \; [Ag(CN)_2]^- \; \rightleftharpoons \; Ag\,[Ag(CN)_2]\downarrow$$
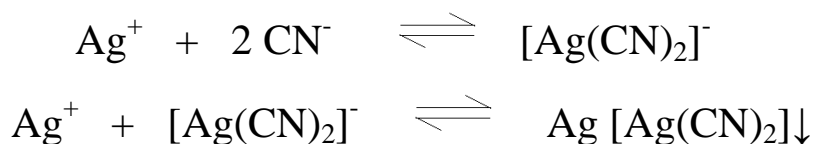
The chloride, bromide, iodide ions, etc., do not interfere. The only difficulty in obtaining a sharp end-point lies in that silver cyanide, precipitated by local concentration of silver ion somewhat prior to the equivalence point, precipitating in a cruddy form which is slow to redissolve in the excess cyanide.

The formation of silver cyanide can be prevented by addition of ammonia which complexes the silver ion and dissolve the precipitate.

$$Ag\,[Ag(CN)_2] + 4NH_3 \rightleftharpoons 2[Ag(NH_3)_2]^+ + 2CN^-$$
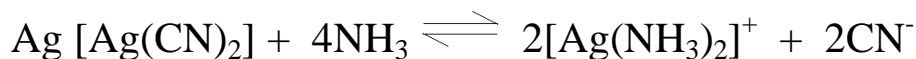
If now iodide ion, usually as a solution of potassium iodide is added to the solution before the titration is started, formation of silver iodide will indicate the end-point.

$$[Ag(NH_3)_2]^+ + I^- \rightleftharpoons AgI\downarrow + 2\,NH_3$$
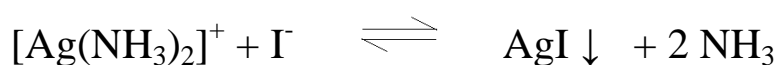
During the titration any silver iodide would have a tendency to form will be kept in solution by excess cyanide always present until the end-point is reached.

$$AgI + 2\,CN^- \rightleftharpoons Ag(CN)_2^- + I^-$$
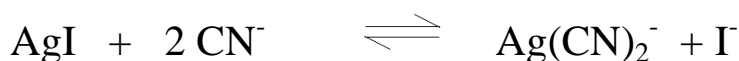
When the last of the cyanide has been removed from the solution at the equivalence point, an opalescence caused by the iodide will appear. This is due to the fact that the first addition of the silver nitrate in excess will react with the iodide to form AgI. The cyanide in which this precipitate was soluble through out the titration is no longer present to keep it in solution, and it does not dissolve in. When viewed against a black, this end-point is easily seen and the method gives excellent results.

Determination of cyanide and halide in admixture:

By a combination of Liebig and Volhard methods. it is possible to determine cyanide and halide in admixture. The solution containing cyanide and halide is titrated with standard silver nitrate solution until the first turbidity which marks the

completion of the precipitation of cyanide (Liebig method). An additional amount to the standard silver nitrate is then added, in excess of the amount required for the complete precipitation of both cyanide and halide .

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

$$Cl^- + Ag^+ \rightleftharpoons AgCl$$
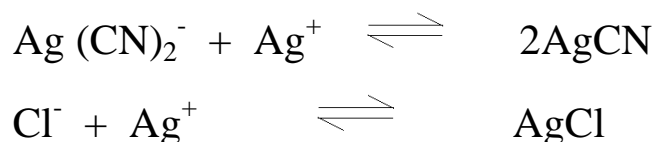
The precipitates are filtered off, washed, and the excess silver ion in the filtrate and washings is back titrated with standard thiocyanate solution, using ferric alum indicator (Volhard method). If the halide is bromide, no filtration required .


Determination of Nickel or Copper:

In additional to the reaction between silver, and cyanide ions, a standard cyanide solution can be used to determine nickel or copper. If the cyanide solution is added to an ammonical solution of nickel ion containing a small of silver iodide, the nickel cyanide complex, $Ni(CN)_4^{2-}$, formed followed by the disappearance of the insoluble silver iodide. The disappearance of the precipitate indicates the end point, the following reaction takes place.

$$Ni (NH_3)_4^{++} + 4 CN^- \longrightarrow Ni(CN)_4^{2-} + 4 NH_3$$
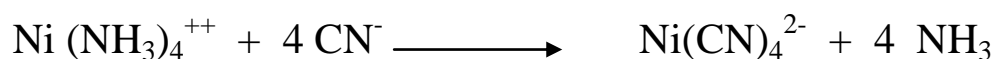
Since iron does not interfere and is kept in solution by the addition of citrate, this method is widely used for the rapid determination of nickel in steel .
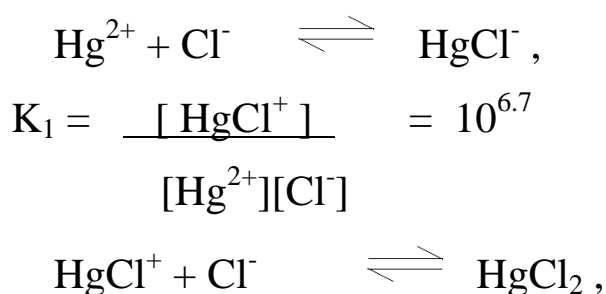
Cyanide ions react with ammoniacal cupric solutions in a rather unexpected way to produce cuprous cyanide $Cu(CN)_3^{2-}$ and a cyanate according to the equation:

$$2\ Cu(NH_3)_4^{++} + 7\ CN^- + H_2O \longrightarrow$$
$$2\ Cu(CN)_3^{2-} + CNO^- + 4\ NH_4^+ + 6\ NH_3$$
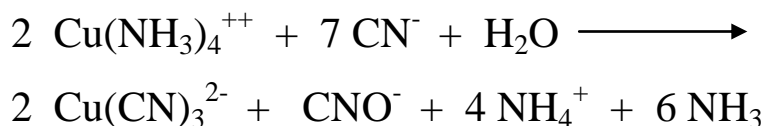
The disappearance of the blue copper ammonia complex marks end point of the titration, Because this titration does not always proceed stoichiometrically according to the equation and due to the difficulty of detecting the last trace of blue color the method is not very accurate for this determination.
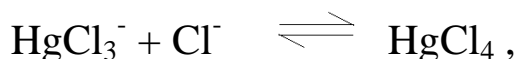
B- Mecurimetric titrations:

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

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

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

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

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

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

$$K_3 = \frac{[\,HgCl_3^-\,]}{[HgCl_2][Cl^-]} = 10^{1.9}$$

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

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

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

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

$$Fe(CN)_5NO^{2-} \; + \; Hg^{2+} \; \rightleftharpoons \; HgFe(CN)_5NO$$
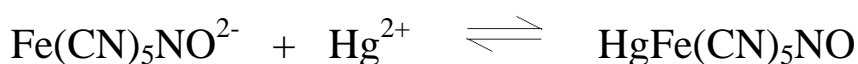
The pH at the equivalence point of the titration is not as low as might be expected from the consumption of mercuric is in the following reaction:

$$Hg^{2+} \; + \; HgCl_2 \; \rightleftharpoons \; 2\,HgCl^+ \qquad\qquad (1)$$
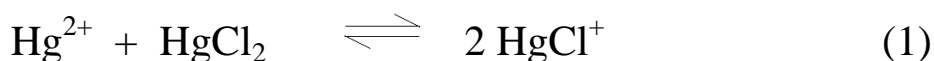
$$K = \; K_1/K_2 = \; 1.8$$

Actually, the mercuric nitroprusside precipitate is first so somewhat after the equivalence point, and a correction must be applied. The correction is not really the same an indicator blank

run with distilled water, because the above reaction (1) does not then take place appreciably. The correction depends upon the final concentration of mercuric chloride and hence varies with the quantity of the sample and the final volume. An advantage of this mercurimetric method over Mohr method, is that the titration may be performed in solutions which are quite acidic and fairly, dilute, e.g. at levels of chloride which frequently occur in natural water. But some cations e.g. Cd^{2+}, Cu^{2+}, etc. interfere by forming slightly soluble nitroprussides. Certain organic compounds which form colored complexes with mercuric ions have also been used as indicators for the mercuimetric titration of chloride. The best known is diphenylcarbazone (orange) which gives intense violet mercuric complex:
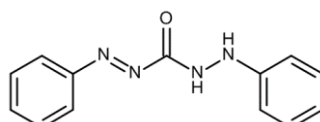

Good results are obtained at a pH of about 3.3, as adjusted by the acid-base indicator bromophenol blue whose greenish yellow color change at the end-point of the titration.

C- <u>Titrations with multidentate complexes</u>:

Multidentate complexes also called chelating agents are suitable metal-ion titrations, because the chelating involves very few steps that differ widely in stability constants. Certain

chelating agents such as ethylenediaminetetraacetic acid, possess enough legends.

To fill the whole coordination sphere of metal ions in one-step chelating reactions. The formula (I) is preferred to (II). Since it has been shown from measurements of the dissociation constants that two hydrogen atoms are probably held in the form of Zwitter ion. The value of pK are respectively $pK_1 = 2.0$, $pK_2 = 2.7$. $pK_3 = 2.6$ and $pK_4 = 10.3$ at 20 ^{o}C, these values suggest that it behaves as a bicaroxylic acid with two strongly acidic groups end that there are two protons of which the first ionizes in the pH region of about 6.3 and the second at a pH of about 11.5.
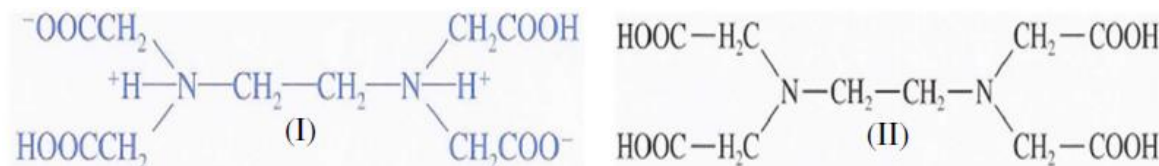
Various trivial names are used for ethylenediaminetetracetic acid and its sodium salts, and these include. Trilon B, complexone III, Sequestrane, Verseme, and Chelaton 3. The disodium salt is most widely employed in titrimetric analysis. To avoid the constant use of the long name, the abbreviation EDTA will be utilized for the di sodium salt when describing its use in titrations. Other complexing agents (complexiones) which are sometimes used include nitrilotriacetic acid (III) or NTA or complexone I, this has $pK_1 = 1.9$, $pK_2 = 2.5$, and $pK_3 = 9.7$)

and 1.2-diamino cyclohexane- N,N,N',N' tetra acetic acid (IV), this should presumably be formulated as a Zwitter ion structure like (I), it is probably the trans- form; the abbreviated here is DCYTA or DCTA or complexon (IV).
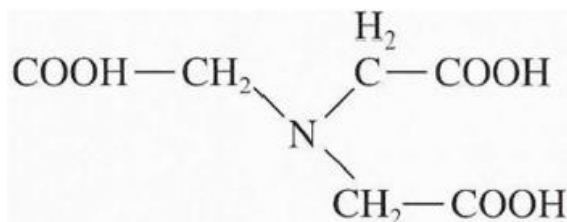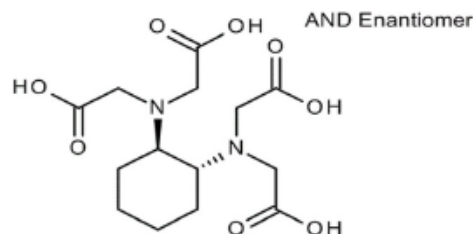
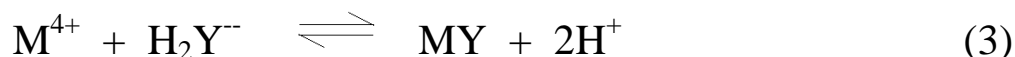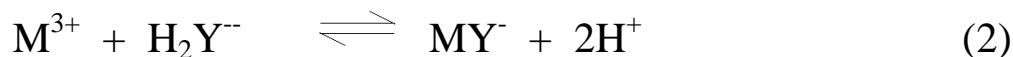(III)   (IV)

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

To simplify the following discussion ethylene diaminetetracetic acid will be assigned the formula H_4Y the disodium salt is therefore Na_2H_2Y and affords the complex forming ion H_2Y^{--} in aqueous solution. The usefulness of EDTA as a titrant is due to the presence of four or six atoms which are available for coordination to a metal cation in such a way that five member rings are produced, 1:1 complexes are usually

formed and these are the most important. The reactions with cations, e.g. M^{++}, may be written as:

$$M^{2+} + H_2Y^{--} \rightleftharpoons MY^{--} + 2H^+ \qquad (1)$$

For other cations, the reaction may be expressed as:

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

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

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

One gram ion of the complex forming H_2Y^{--} reacts in all cases with one gram ion of the metal and in each case, also two gram ions of hydrogen ion are formed. The resulting complexes have similar structures but differ from one another in the charge that they carry. One such structure, suggested for the complex with a divalent metal is shown in Fig 9.
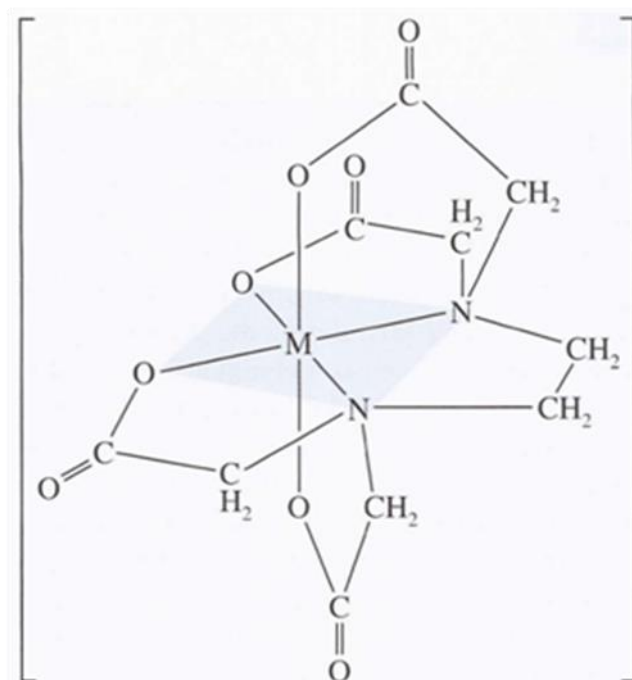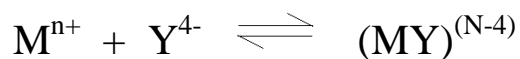

Fig. 9

Stability constants:

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

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

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

The apparent, or conditional stability constant (or complex formation constant) at a particular pH may be calculated from the relationship K/α, where α is the fraction of EDTA present as Y^{4-} only and not as the other ions formed by the ionization of H_4Y. The efficiency of complex formation with EDTA is affected by the variation of the pH of the solution. A decrease in pH will reduce the concentration of the complexing species, hence EDTA forms complexes with metal ions best in basic solutions. In special cases, the complexing efficiency does not decrease appreciably unit the pH of the solution is relatively low. Thus, copper is almost complexed at pH 3.5. For magnesium and calcium a slight reduction in complexing efficiency occurs when the pH falls below 7.5. With increase in pH of the solution, the tendency to form slightly soluble metallic hydroxides in enhanced. This can be expressed:

$$(MY)^{(n-4)} + nOH^- \rightleftharpoons M(OH)_n + Y^{4-}$$
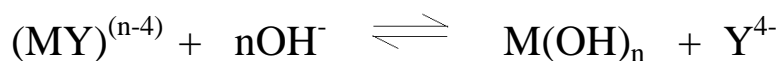
The extent of hydrolysis of $(MY)^{(n-4)}$ depends upon the characteristics of the metallic ion and is largely controlled by the solubility product of the hydroxide and, of course by its solubility constant, thus iron (III) (S.P. 1×10^{-36}) is precipitated

as the hydroxide in basic solution but nickel (S.P. 5.6×10^{-18}) remains complexed. The use of excess of EDTA reduces the influence of hydrolysis in basic solution.

Titration curves:

If, in the titration of a strong acid, pH is plotted against the volume of solution of the strong base added .A point of inflexion occurs at the equivalence similarly in the EDTA titration, if pM (negative logarithm the free metal ion concentrations: ($pM = -Log [M^{n+}]$) is plot against the volume of EDTA solution added, a point of inflexion occurs at the equivalence point; in some instances this sudden increase may exceed 10 pH units. The general shape of titration curves obtained by titrating 10.0 ml of a 0.01 M solution of a metal ion M with a 0.01 MEDTA solution is shown in Fig. 10. The stability constants of various metal EDTA complexes are indicated at the extreme right of the curves. It is evident that the greater the stability constant, the sharper is the end point provided the pH maintained constant.
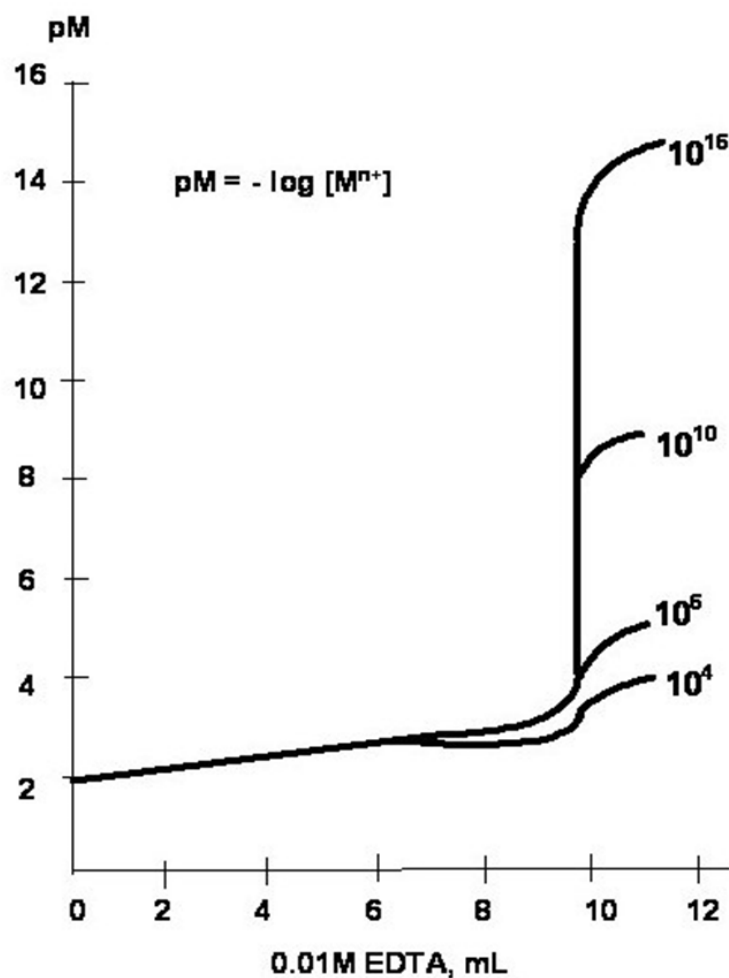
Fig. 10 Titration of metal ion with EDTA

Calculation the change of pM during the titration:

The calculations involved in obtaining chemometric curve may be illustrated by the reaction between magnesium ion and EDTA. Consider the titration of 50.0 ml of a 0.1 M solution of Mg^{2+} (buffered at pH 10) with 0.10 M EDTA solution. In calculating the Mg^{2+} concentrations during the titration the effect of hydrolysis will be neglected.

1- pMg before the addition of titrant:

Since the Mg^{2+} ion concentration is given as 0.1 M, the

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

2- pMg during titration:

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

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

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

3- pMg at the equivalence point:

At this point, 50.0 ml. of 0.1 M EDTA have been added. The reaction :

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

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

$$K_{stab.} = \frac{[MgY^{2-}]}{[Mg^{2+}][Y^{4-}]} = 5.0 \times 10^8 \qquad (2)$$

At the equivalence point

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

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

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

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

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

4- pMg after the equivalence point :

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

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

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

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

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

$$\frac{5 \times 110}{110 \times a \times 1} = 5.0 \times 10^8$$

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

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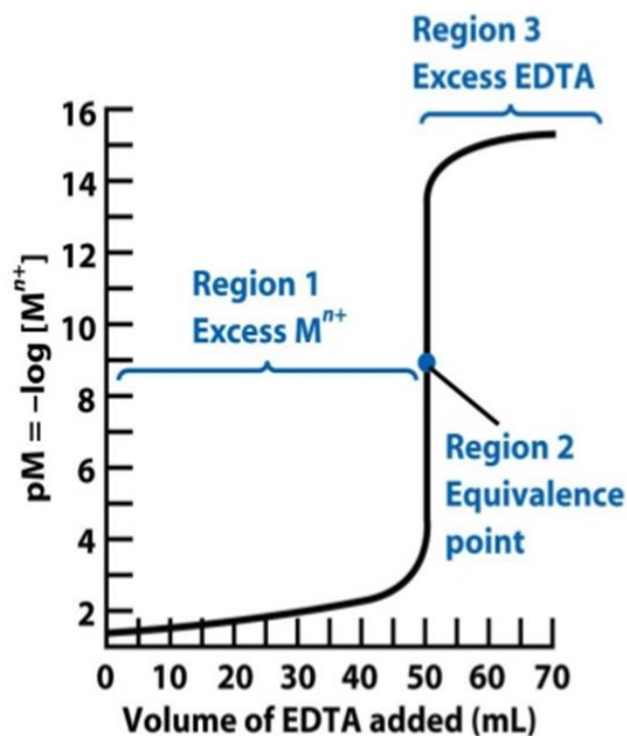
Fig. 11 Titration of Mg With EDTA

Types of EDTA titrations:

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

1- Direct titration:

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

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

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

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

## 3- <u>Replacement or substitution titrations</u>:

Substitution titrations may be used for metal ions that do not react (or react unsatisfactorily) with a metal indicator or for metal ions which form EDTA complexes that are more stable than those of other metal such as magnesium and calcium. The metal cation M^{n+} to be treated with to magnesium complex of EDTA, when the following reaction occurs:

$$Mn^{n+} + MgY^{--} \rightleftharpoons (MY)^{(n-4)+} + Mg^{++}$$
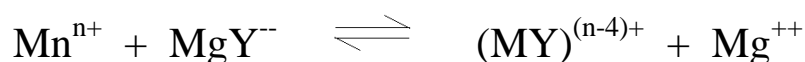
The amount of magnesium ion set free is equivalent to the action present and can be titrated with a standard solution of EDTA and a suitable metal indicator.

4- Alkalimetric titration :

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

$$Mn^{n+} + H_2Y^{--} \rightleftharpoons (MY)^{(n-4)+} + 2H^+$$
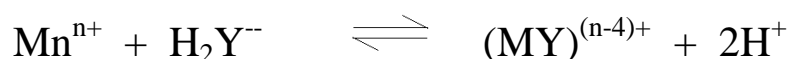
The hydrogen ions thus set free can be titrated with a standard solution of sodium hydroxide using an acid-base indicator or a potentiomtric end point; alternatively, an iodate iodide mixture is added as well as the EDTA solution and liberated iodine is titrated with a standard thiosulphate solution.

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

5- Miscellaneous Methods:

Change reactions between the nickel cyanide ion [Ni $(CN)_4]^{2-}$ the potassium salt is readily prepared and the element to be determined. whereby nickel ions are set free have a limited application. Thus silver, palladium, and gold which themselves

cannot be titrated complex metrically can be determined in this way.

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

$$[Ni(CN)_4]^{--} + 2Pd^{++} \rightleftharpoons 2[Pd(CN)_2]^{--} + Ni^{++}$$
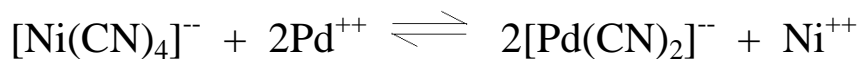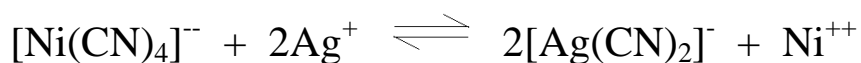
These reactions take place with sparingly soluble silver salt, and hence provide a method for the determination of the halide ions Cl^-, Br^-, I^- and the thiocyanate ion SCN. The anion is first precipitated as the silver salt, the latter dissolved in a solution of $[Ni(CN)_4]^{--}$, and the equivalence amount of nickel thereby set free is determined by rapid titration with EDTA using an appropriate indicator (Murexide, Bromopyrogalol Red, or Eriochrome Red B).

Sulphate may be determined by precipitation as barium sulphate or as lead sulphate, the precipitate is dissolved in an excess of standard EDTA solution, and the excess of EDTA is back-titrated with a standard magnesium or zinc solution Eriochrome Black T as indicator. Phosphate may be determined by precipitating as: $Mg(NH_4)PO_4.6H_2O$ dissolving the precipitate in dilute hydrochloric acid, adding an excess of standard EDTA solution, buffering at pH = 10, and back–titrating with standard magnesium ion solution in the presence of Eriochrome Black T.


Titration of mixtures (Masking and demasking agents):

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

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

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

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

$$M^{++} + CN^- \rightleftharpoons [M(CN)_4]^{2-}$$
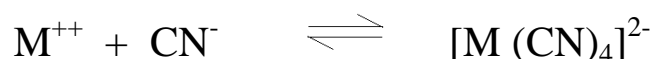
It is therefore possible to determine such actions as those of Ca, Mg, Pb, and Mn in the presence of the above-mentioned metals by masking with an excess of potassium or sodium cyanide. A small amount of iron may be marked by cyanide if it is first reduces to be ferrous state by the addition of ascorbic acid. Titration (IV), iron (III), and aluminum can be masked with triethanolamine, mercury with iodide ions, and aluminum, ion (III), titanium (IV), and beryllium with ammonium fluoride actions of the alkaline earth metals yield slightly soluble fluorides.

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

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

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

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

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

iii- Add excess of chloral hydrate (or of formaldehyde acetic acid solution, 3 :1) to the titrated solution in to liberate the Zn from the cyanide complex, and titrate until the indicator turns

blue. This gives the Zn only. The Cu content may then be found by difference.

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

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

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

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

Metal ion indicators:

Principally, metal ion indicators are organic dyes with acid-base indicator properties, that undergo color change when a proton is transferred to, or from dye molecule. In addition, the dye molecule also contains chelating group which includes the

transferable proton, and which is joined to the conjugated system responsible for the color.

The electrochemical series of the metals is obtained. The greater the negative value of the potential, the greater is tendency of the metal to pass into the ionic state. A metal will formally displace any other metal below it in the series from solutions of its salts. Thus magnesium, aluminum, zinc, or iron will displace copper from solutions of its salts, lead will displace copper, mercury or silver, copper will displace silver. The standard electrode potential is a quantitative measure of the readiness of the element to lose electrons. It is therefore a measure of the strength of the element as a reducing agent in aqueous solution the more negative the potential of the element, the more powerful is its action as a reductant.
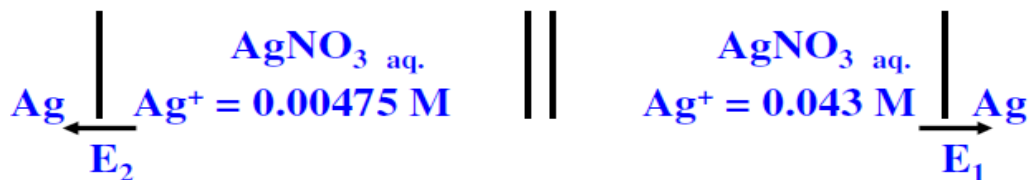
REDOX TITRATIONS

Concentration cells:

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

$$E = \underline{0.59} \log C_1 + E_o - (\underline{0.059} \log C_2 + E_o)$$

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

$$\text{Ag} \underset{E_2}{\overset{\longleftarrow}{\Big|}} \begin{array}{c} \text{AgNO}_3 \text{ aq.} \\ \text{Ag}^+ = 0.00475 \text{ M} \end{array} \Big|\Big| \begin{array}{c} \text{AgNO}_3 \text{ aq.} \\ \text{Ag}^+ = 0.043 \text{ M} \end{array} \underset{E_1}{\overset{\longrightarrow}{\Big|}} \text{Ag}$$

Assuming, there is no potential difference at the liquid junction.
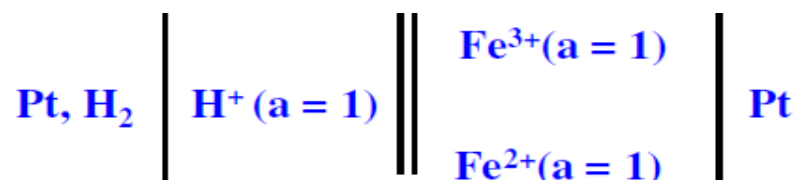
$$E \ = \ E_1 \ - \ E_2 \ = \ \frac{0.059}{1} \ \log \ \frac{0.043}{0.00475} \ = \ 0.056 \ \text{volt}$$

Oxidation-reduction cells:

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

difference between the platinum and the solution relative to a standard as reference. Thus for a ferric-ferrous,

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

$$\text{Pt, H}_2 \left| \text{H}^+ (a = 1) \right\| \begin{array}{c} Fe^{3+}(a = 1) \\ \\ Fe^{2+}(a = 1) \end{array} \left| \text{Pt} \right.$$

The potential measured in this way is called the standard (reduction) potential. The standard potentials enable us to predict which ions will oxidize or reduce other ions an unit activity (or molar concentration). Thus permanganate ion can oxidize Cl^-, Br^-, I^-, Fe^{2+} and $(Fe(CN)_6)^{4-}$; ferric ion must be emphasized that for many oxidant's the pH of the medium is of great importance, since they are generally used in acidic media. Thus in measuring the standard potential of the MnO_4^{--} - Mn^{2+} system it is necessary to state that the hydrogen-ion activity is unity, this leads to $E^o = +1.52$ volts. Similarly the value of E^o for $Cr_2O_7^{2-}$ -- Cr^{3+} electrode is 1.33 volts. This means that the MnO^{4-} - Mn^{2+} system is a better oxidizing agent than the $Cr_2O_7^{2-}$ - Cr^{3+} system. Since the standard potentials for Cl_2 - $2Cl^-$ and Fe^{3+} - Fe^{2+} electrodes - 1.14 and 0.77 volt respectively permanganate and dichromate will oxidize ferrous ion but only permanganate will oxidize chloride ion; this explain, why dichromate but not permanganate can be used for the titration of ferrous ion hydrochloric acid solution.

Calculation of the standard (reduction) potential:

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

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

or $\text{Ox} \quad + \text{ ne} \quad \rightleftharpoons \quad \text{Red}$
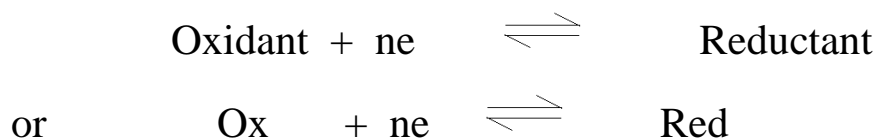
The electrode potential which is established when an inert or unattackable electrode is immersed in a solution containing both oxidant and reductant is given by the expression:

$$E_T = E^o + (RT/nF)\ln(a_{Ox}/a_{Red})$$

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

Since activities are often difficult to determine directly they may be replaced by concentrations: the error thereby introduced is usually of no great importance. The equation becomes: $E_T = E^o + (RT/nF)\ln(C_{Ox}/C_{Red})$

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

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

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

Equilibrium constants of oxidation-reduction reactions:

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

$$a\ OX_1\ -\ b\ Red_2 \rightleftharpoons b\ Ox_2\ +\ a\ Red_1$$
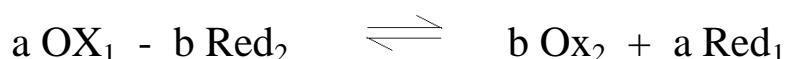
The complete reaction may be regarded as combine of two oxidation-reduction electrodes. $a\ Ox_1$, $a\ Red_1$ and $B\ Ox_{11}$, $b\ Red_{11}$, combined together into a cell; at equilibrium, the potentials of both electrodes are the same

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

$$E_2 = E_2^o + \frac{0.059}{n} \log \frac{[\ Ox_2\ ]^b}{[\ Red_2]^b}$$

At equilibrium, $E_1 = E_2$ hence

$$E_1^o + \frac{0.059}{n} \log \frac{[\ Ox_1\ ]^a}{[\ Red_1]^a} = E_2^o + \frac{0.059}{n} \log \frac{[Ox_2\ ]^b}{[Red_2]^b}$$

$$\text{or} \ \ \log \frac{[Ox_2]^b}{[Red_1]^a} / \frac{[\ Red_2]^b}{[\ Ox_1]^a} = \log k = \frac{n}{0.059} (E_1^o - E_2^o)$$

This equation may be employed to compute the equilibrium constant of any redox reaction provided the two standard potentials E_1^o are known; from the value of K thus obtained the feasibility of the reaction in analysis may be ascertained. Let us consider the simple reaction:
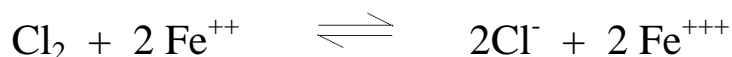
$$Cl_2 + 2\, Fe^{++} \rightleftharpoons 2Cl^- + 2\, Fe^{+++}$$

The equilibrium constant is given by:

$$\frac{[\,Cl^-\,]^2 \times [\,Fe^{+++}\,]^2}{[\,Cl_2\,] \times [\,Fe^{++}\,]^2} = K$$

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

$$E^o_{Cl2,\,2\,Cl^-} + \frac{0.059}{2} \log \frac{[Cl_2]}{[Cl^-]^2} = E_{lCl2\,,\,Cl^-}$$

$$E^o_{Fe3+,\,Fe2+} + \frac{0.059}{1} \log \frac{[Fe^{3+}]}{[Fe^{2+}]} = E_{2Fe3+/Fe+2}$$

Now $E^o Cl_2, 2Cl^- = 1.36$ volts and $E^o\, Fe^{3+}, Fe^{2+} = 0.75$ volts hence,

$$Log\ \frac{[Fe^{+++}]^2\,[Cl^-]^2}{[Fe^{++}]^2\,[Cl_2]} = (2/0.059)0.61 = 20.68 = \log\ K$$

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

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

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

$$Ce^{++++} + Fe^{++} \rightleftharpoons Ce^{+++} + Fe^{+++}$$
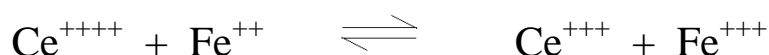
For (1) at $25^{o}C$

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

For (2) at $25^{o}C$

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

The equilibrium constant of the reaction is given by:

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

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

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

The reaction it therefore virtually complete. during the addition of ceric solution at: the equivalence point, its only

effect will be the exist the ferrous iron (since K is large) and consequently change the ratios $[Fe^{3+}]/[Fe^{2+}]$ when 10 ml of the oxidizing agent have been added, $[Fe^{3+}]/[Fe^{2+}]$ = 10/90 (approx.), and $E_1 = 0.75 - 0.059x \log 110/90 = 0.75 - 1.59 = 0.69$ volt.

with 50 ml of the oxidizing agent, $E_1 = E_1^o = 0.75$ volt.

with 90 ml $E_1 = 0.75 - 0.0591 \log 90/10 = 0.81$ volt.

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

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

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

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

The subsequent addition of the ceric solution will merely increase the ratios $[Ce^{4+}]/[Ce^{3+}]$.

Thus: with 100.1 ml , $E_1 = 1.45 + 0.0591 \log 0.1/100 = 1.27$ volts

with 101 ml, $E_1 = 1.45 + 0.591 \log 1/100 = 1.33$ volts

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

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

These results are plotted graphically in Fig. 12. It is of interest to calculate the ferrous-ion concentration in the neighborhood of the equivalence point. When 99.9 ml. of the Ceric solution have been added

$[Fe^{2+}] = 0.1 \times 0.1/199.9 = 5 \times 10^{-5}$ or p $Fe^{2+} = 4.3$.

The concentration at the equivalence point is given by:

0.1 N ceric sulphate added ml.

$$[Fe^{3+}]/[Fe^{2+}] = K = 7 \times 10^{11} = 8.5 \times 10^5$$

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

$$[Fe^{2+}] = 5 \times 10^{-2} / 8.5 \times 10^5 = 6 \times 10^{-8} \text{ N}, \text{ or } pFe^{2+} = 7.2$$

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

From the equations :

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

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

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

Thus pFe^{2+} changes from 4.3 to 1.0 between 0.1 percent before and 0.1 per cent after the stoichiometric end point.
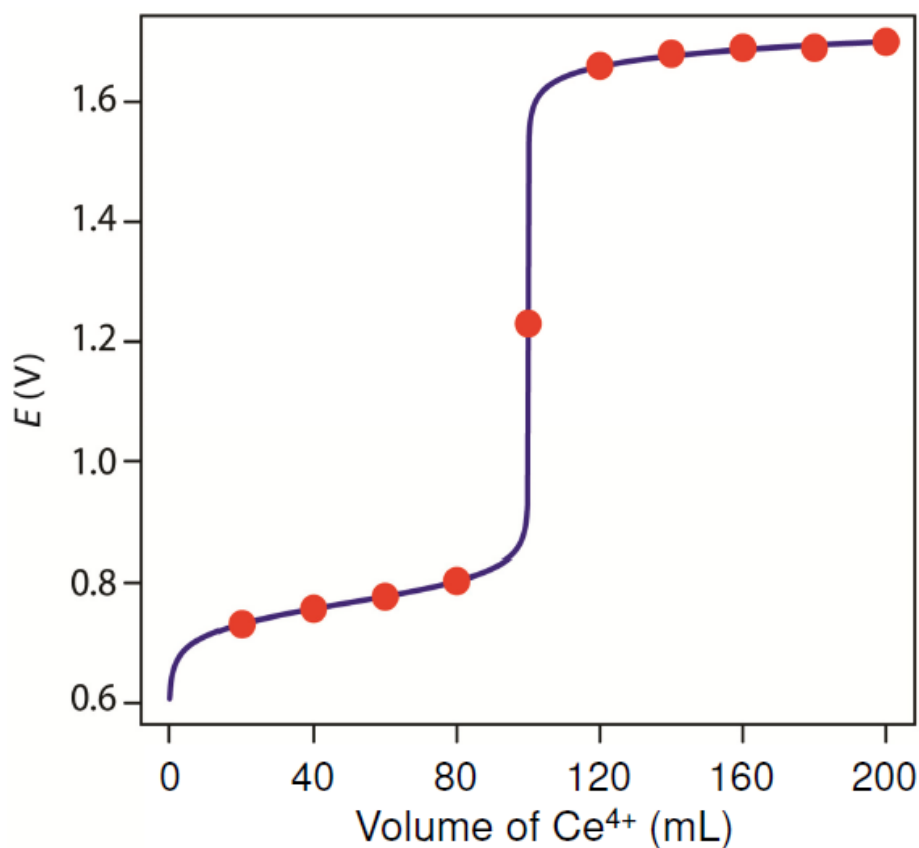
Fig. 12 Titration curve of ferrous iron with ceric cerium

Detection of the end point in redox titrations

1- The reagent may serves as its own indicator:

This is well illustrated by potassium permanganate. One drop (0.05 ml.) of excess of say, 0.1 N-potassium permanganate will impart a visible pink coloration to several hundred ml. of solution, even in the presence of slightly colored ions, such as ferric ions. This method has the drawback that an excess of oxidizing agent is always present at the end point; for wok of the highest accuracy, the indicator blank may be determined and allowed for, or the error may be considerable reduced by

performing the standardization and determination under similar experimental conditions.

b- **External indicators:**

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

c- **Internal oxidation-reduction indicators:**

The oxidation reduction indicator should mark the sudden change in the oxidation potential in the neighbor-hood of the equivalence point in an oxidation reduction titration. The ideal oxidation-reduction indicator will be one with an oxidation potential intermediate between that of the solution titrated and that of the titrant, and which exhibits a sharp readily detectable color change. An oxidation- reduction indictor (redox indicator) is a compound which exhibits different colors in the oxidized and reduced forms:

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

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

$$E \;=\; E^{o}_{In} \;-\; RT/nF \; \ln \frac{[In_{Ox}]}{[In_{Red}]}$$

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

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

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

diphenylamine (colourless)

E < 0.73 V

diphenylbenzidine (colourless)

+ 2H$^+$ + 2e

+ 2e

diphenylbenzidine (violet)
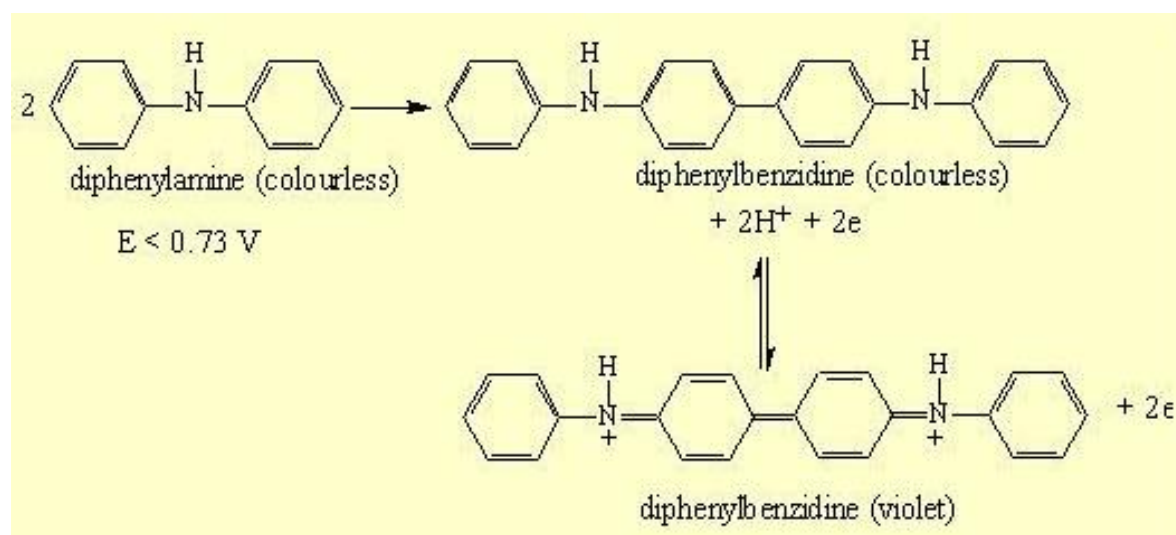
d- **Potentiometric methods:**

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