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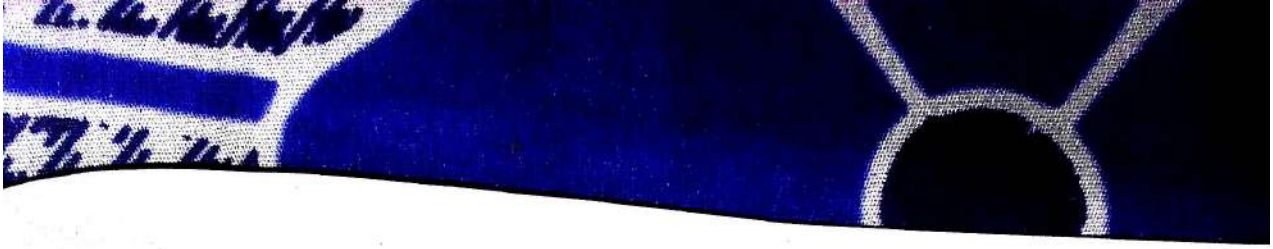


1 PHARMACEUTICAL ANALYSIS

INTRODUCTION

Concept of Pharmaceutical Analysis:-

Pharmaceutical Analysis is a branch of science, which deals with the qualitative, quantitative and semiquantitative estimation of given pharmaceutical sample.

Chemical analysis is the resolution of a chemical compound into its proximate or ultimate parts. In analytical chemistry, it is of prime importance to gain information about the qualitative and quantitative composition of substances and chemical species, that is, to find out what a substance is composed of and exactly how much. Broadly it is divided in three types;

Qualitative analysis:- It may be define as "which analyte present in the given sample". This has the goal to identify the various components present in the given sample on the basis of physical and chemical properties such as functional groups, elemental composition and melting point etc.

Quantitative analysis:- It may be define as "How much amount of analyte present in the given sample". This has the goal to determine the quantity of each component present in the given sample.

Semi-quantitative analysis:- It is the type of analysis which only describe whether the quantity of impurity present in given sample is below or above the specified limit such as limit tests.

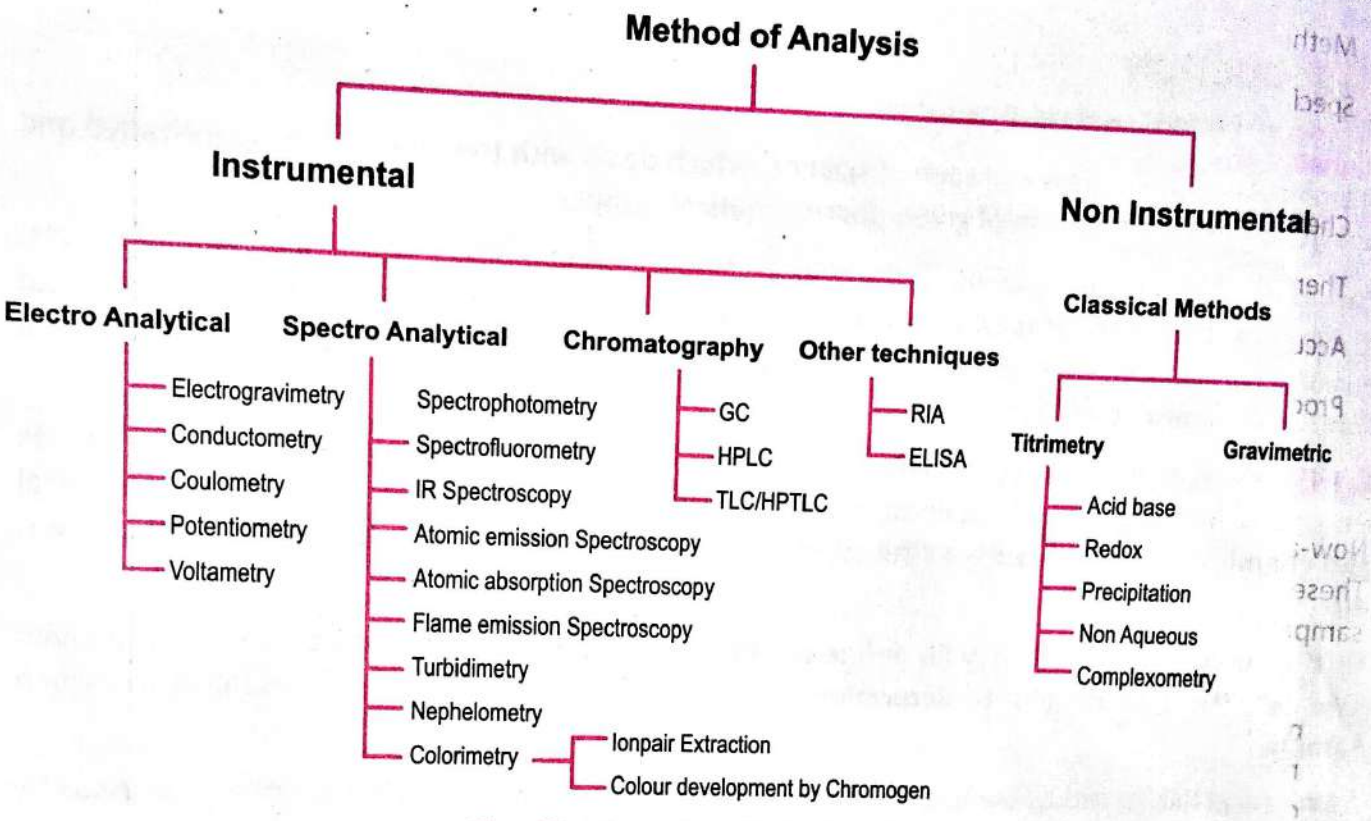
SCOPE OF ANALYSIS

The importance of analytical chemistry lies in the fact that it is the foundation pillar of the entire procedure of drug discovery, isolation, standardization and quality control. The basic importance of pharmaceutical analysis is its utility in standardization and quality control of medicines and drug substances to ensure the quality and stability of the final product. Now days the analytical techniques are popularly used in following fields:

1. Biological sample estimation.
2. Food determination.
3. Dairy product estimation.
4. Soil study.
5. Forensic determination.
6. Pesticide estimation in food and vegetable.
7. Environmental pollutant determination.

CLASSIFICATION OF ANALYTICAL METHODS

Analytical methods are often classified as being either classical or instrumental. This classification is largely historical with classical methods, sometimes called wet chemical methods preceding instrumental methods by a century or more.



Classification of analytical methods

1. CLASSICAL METHODS

In the early years of chemistry, most analyses were carried out by separating the components of interest (the analytes) in a sample by precipitation, extraction, or distillation. For qualitative analysis, the separated components were then treated with reagents then yielded products that could be recognized by their colour, their boiling or melting points, their solubility's in series of solvents, their odour, their optical character. Classical methods are also called wet chemical methods and are classified into two major types.

A. Gravimetric methods

B. Titrimetric methods

A. Gravimetric methods:- Gravimetric methods include determination of mass of analyte or some compounds produced from analyte.

B. Titrimetric methods:- Titrimetric methods include the determination of the volume or weight of standard reagent required to react completely with analyte. For example acid-base, oxidation-reduction, non-aqueous, complexometric and precipitation titrations.

Advantages of classical methods:-

1. Procedures are accurate and simple.
2. The equipment needed is cheap.
3. Methods are absolute.
4. Specialized training is usually not required.

Limitations of classical methods:-

1. Chemical environment is critical.
2. There is a lack of versatility.
3. Accuracy decreased with decreasing amounts.
4. Procedure is time consuming.

2. INSTRUMENTAL METHODS

Now-a-days instrumental methods of analysis are widely accepted over the classical methods. These methods are extremely sensitive, providing precise and detailed information from small sample of material. Instrumental methods can be classified into following types.

A. Electro analytical methods:- Electro analytical methods are the modification of chemical methods in which the reaction progress and endpoint are determined by an electric measurement. Major electro analytical methods used for analysis are electrogravimetry, conductometry, coulometry, potentiometry, voltametry etc.

B. Spectroanalytical methods:- Spectroanalytical methods are widely used for qualitative as well as quantitative analysis. They give results in the form of an interpretable spectrum therefore are called spectroanalytical or spectroscopic methods. For example spectrophotometry, infrared spectrophotometry, atomic emission spectroscopy, atomic absorption spectroscopy, flame emission spectroscopy, turbidimetry, nephelometry, colorimetry etc.

C. Chromatographic methods:- Chromatographic methods are mainly used for the determination of complex mixtures or mixture of components by separating then into individuals. For example Gas chromatography, HPLC, TLC/HPTLC.

D. Other methods:- Beside above methods there are much more instrumental analytical methods which are used in analysis depending upon the type of analyte such as RIA, ELISA etc.

Advantages of instrumental methods:-

1. Small amount of samples are required for analysis.
2. High sensitivity is obtained.

3. Measurements obtained are reliable.
4. The determination is very fast.
5. Even complex samples can be handled easily.

Limitations of instrumental methods:-

1. An initial calibration is needed.
2. Final accuracy is often in the region of ± 5%.
3. Initial cost and upkeep of complex equipment is high.
4. Concentration range is limited.
5. Sizeable space is usually required.
6. Specialized training is needed.

METHODS OF EXPRESSING CONCENTRATION

Concentration of an analyte in a solution can be expressed by more than one method depending upon the type of analysis carried out. Major methods for expressing concentration are:-

1. Molarity
2. Normality
3. Molality
4. Mole fraction
5. Formality

1. Molarity:- Molarity can be defined as the number of moles of solute dissolved in 1000 ml of solution. It is denoted by 'M'. We need two pieces of information to calculate the molarity of a solute in a solution:-

The moles of solute present in the solution.

The volume of solution (in litres) containing the solute.

To calculate molarity we uses following equation:-

$$\text{Molarity (M)} = \frac{\text{number of moles of solute (X)}}{\text{volume of solution in litres (V)}}$$

If molarity is given, weight of the substance can be determined by using following equation:-

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

Molarity is calculated by:-

$M_1V_1 = M_2V_2$

Where,

M_1 = molarity of known solution.

V_1 = volume of known solution.

M_2 = molarity of unknown solution.

V_2 = volume of unknown solution.

2. Normality:- Normality of a solution can be defined as the number of gram equivalents of solute dissolved in 1000 ml of solution. It is denoted by 'N'.

$$\text{Normality (N)} = \frac{\text{number of gram equivalents of solute (X)}}{\text{volume of solution in litres (V)}}$$

Normality is calculated by:-

$N_1V_1 = N_2V_2$

Where,

N_1 = normality of known solution.

V_1 = volume of known solution.

N_2 = normality of unknown solution.

V_2 = volume of unknown solution.

Normality calculation from a concentrated solution:-

$$\text{Volume of concentrated solution required} = \frac{E \times NR \times 100}{C \times SG}$$

Where,

E = equivalent weight.

NR = normality required.

C= concentration of given solution (given on container).

SG = specific gravity.

Equivalent weight:- It is the ratio between molecular weight and basicity or acidity of acid and base.

Calculation of equivalent weight of substances:-

1. Equivalent weight of an acid:- it is the ratio of molecular weight to its basicity.

$$\text{Equivalent weight of acid} = \frac{\text{molecular weight}}{\text{basicity}}$$

Basicity is the number of replaceable hydrogen atoms present in an acid.

a. Example:- Equivalent weight of hydrochloric acid is:-

$$\text{Equivalent weight of hydrochloric acid} = \frac{36.5}{\text{basicity}} = \frac{36.5}{1} = 36.5$$

b. Example:- Equivalent weight of sulphuric acid is:-

$$\text{Equivalent weight of sulphuric acid} = \frac{98}{\text{basicity}} = \frac{98}{2} = 49$$

2. Equivalent weight of a base:- It is the ratio of molecular weight to its acidity.

$$\text{Equivalent weight of base} = \frac{\text{molecular weight}}{\text{acidity}}$$

Acidity is the number of replaceable hydroxyl groups of the base.

a. Example:- Equivalent weight of sodium hydroxide is:-

$$\text{Equivalent weight of sodium hydroxide} = \frac{40}{\text{acidity}} = \frac{40}{1} = 40$$

b. Example:- Equivalent weight of calcium hydroxide is:-

$$\text{Equivalent weight of calcium hydroxide} = \frac{74}{\text{basicity}} = \frac{74}{2} = 37$$

3. Equivalent weight of a salt:- It is the ratio of molecular weight to valence.

$$\text{Equivalent weight of salt} = \frac{\text{molecular weight}}{\text{valence}}$$

a. Example:- Equivalent weight of sodium carbonate is:-

$$\text{Equivalent weight of sodium carbonate} = \frac{106}{\text{valence}} = \frac{106}{2} = 53$$

b. Example:- Equivalent weight of sodium bicarbonate is:-

$$\text{Equivalent weight of sodium bicarbonate} = \frac{84}{\text{valence}} = \frac{84}{1} = 84$$

3. Molality: It is defined as the number of moles of solute dissolved in 1 kilogram of solvent.

We need two pieces of information to calculate the molality of a solute in a solution:-

The moles of solute present in the solution.

The mass of solvent (in kilograms) in the solution.

To calculate molality following equation is used:-

$$\text{Molality} = \frac{\text{number of moles of solute}}{\text{mass of solvent in kilograms}}$$

4. Mole fraction:- The mole fraction (X) of an analyte in a solution is the ratio of the number of moles of analyte in the total number of moles of all components in the solution.

To calculate mole fraction, we need to know the number of moles of each component present in the solution.

The mole fraction of A, in a solution consisting of A, B, C, ... is calculated using the equation:-

$$\text{Mole fraction of A} = \frac{\text{moles of A}}{(\text{moles of A} + \text{moles of B} + \text{moles of C} + \ldots)}$$

To calculate the mole fraction of B,

$$\text{Mole fraction of B} = \frac{\text{moles of B}}{(\text{moles of A} + \text{moles of B} + \text{moles of C} + \ldots)}$$

5. Formality:- Formality of a solution may be defined as the number of gram formula masses of the ionic solute dissolved in per litre of the solution. It is denoted by F. Commonly, the term formality is used to express the concentration of the ionic solids which do not exist as molecules but exist as network of ions. A solution containing one gram formula mass of solute per litre of the solution has formality equal to one and is called formal solution. The formality of a solution changes with change in temperature.

$$\text{Formality} = \frac{\text{number of gram formula masses of solute}}{\text{volume of solution in litres}}$$

or

$$\text{Formality} = \frac{\text{mass of ionic solute in grams}}{\text{gram formula mass of solute} \times \text{volume of solution in litres}}$$

STANDARDIZATION

Standardization means, determination of strength of a given sample solution and can be determined by reacting the solution quantitatively with a standard solution.

Standard may be of two types:-

1. Primary standard:- Primary standard is a solution of known strength made from the substance of high purity, which satisfy following conditions:-

1. It should be highly stable.
2. It should be obtained in pure state.
3. It should have high molecular weight.
4. It should be of high solubility i.e. readily soluble in water.

Examples of primary standards used for titration of acids are:-

Sodium carbonate:- Na_2CO_3, mol wt. = 105.99 g/mol

Tris-(hydroxymethyl)aminomethane (THAM):- $(CH_2OH)_3CNH_2$, mol wt. = 121.14 g/mol

Examples of primary standards for titration of bases are:-

Potassium hydrogen phthalate (KHP):- $KHC_8H_4O_4$, mol wt. = 204.23 g/mol

Potassium hydrogen iodate:- $KH(IO_3)_2$, mol wt. = 389.92 g/mol

Oxalic acid:- $C_2H_2O_4$, mol wt. = 90.03488 g/mol

Examples of primary standards for redox titrations are:-

Potassium dichromate:- $K_2Cr_2O_7$, mol wt. = 294.19 g/mol

Sodium oxalate:- $Na_2C_2O_4$, mol wt. = 134.00 g/mol

2. Secondary standard:- Secondary standard is a solution of known strength which is previously standardized by a primary standard. For example:- Standard solution of 0.1 M sodium hydroxide, standard solution of 0.1 N sulphuric acid etc.

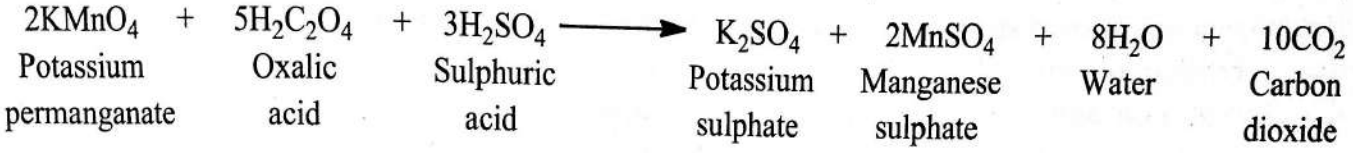
PREPARATION AND STADARDIZATION OF SOLUTIONS

In volumetric analysis, solutions are needed to be accurately prepared to minimize errors in results. Preparation and standardization of some commonly used solutions in volumetric analysis is described here under:-

1. PREPARATION OF OXALIC ACID (0.1 N):- Weigh accurately about 6.3 mg of oxalic acid and dissolve in 1000 ml of distilled water. Oxalic acid is a primary standard therefore there is no need to standardize it.

2. PREPARATION AND STANDARDIZATION OF POTASSIUM PERMANGANATE SOLUTION (0.1N):-

Principle:- In redox titrations, strength of an oxidizing agent is estimated by titrating it with a reducing agent and vice-versa. Potassium permanganate acts as an strong oxidizing agent in acidic medium that oxidizes oxalic acid into carbon dioxide. Known strength of oxalic acid is titrated directly with potassium permanganate. End point can be detected with appearance of permanent pink colour, potassium permanganate acts as self indicator. Reaction involved in this titration is as follows.



Preparation of potassium permanganate solution (0.1 N):- Weigh accurately about 3.2 g of potassium permanganate and dissolve in 1000 ml of distilled water, then heat on water-bath for 1 hour, allow to stand for 2 days and filter it through a funnel containing plug of glass wool.

NOTE:- Store the prepared solution in dark coloured bottle i.e. protected from light.

Standardization of potassium permanganate solution (0.1 N)

1. Clean and dry all glassware as per standard laboratory procedure.
2. Take 500 ml of unknown stock solution of potassium permanganate in a clean and dry beaker.
3. Rinse the burette with distilled water. Then, pre-rinse it with a portion of the potassium permanganate solution before you fill it up for the titration. Pre-rinsing is necessary to ensure that all of the solution in the burette is the desired solution, not a diluted or contaminated solution.

   To do this, add about 10 ml of the potassium permanganate solution to the clean burette. Carefully turn the burette on its side so the liquid slowly runs out the top. Rotate the burette on its axis during this time to make sure the solution wets the sides all the way to the top. Pour the rinse from the burette into a waste beaker. Repeat the rinsing process with a second portion of the potassium permanganate solution.
4. Take 20 ml of prepared oxalic acid solution in a conical flask.
5. Add 5 ml of sulphuric acid.
6. Warm the mixture to about 70°C.
7. Then fill the burette with potassium permanganate solution.
8. Start titration with the potassium permanganate solution until reach the endpoint. The approach of the endpoint is suggested by the temporary appearance of a pink colour that fades when the solution is swirled for upto 10 seconds. A pink colour that persists for more than 30 seconds signals the actual endpoint.

Note:- The solution may lose its colour after 30 seconds or more, but it is not considered.

9. Record the reading of burette.
10. Repeat the titration three times to get precise readings.
11. Take mean of them and calculate normality of potassium permanganate solution.

3. PREPARATION OF SODIUM THIOSULPHATE (0.1 N):-

Principle:- When known strength of potassium iodate is reacted with excess potassium iodide in acidic condition, results in liberation of iodine. Liberated iodine is titrated directly with sodium thiosulphate. End point can be detected with disappearance of permanent blue colour due to conversion of iodine into sodium iodide. Reaction involved in this titration is as follows.

$$\underset{\text{Potassium iodate}}{KIO_3} + \underset{\text{Potassium iodide}}{5KI} + \underset{\text{Sulphuric acid}}{3H_2SO_4} \longrightarrow \underset{\text{Potassium sulphate}}{3K_2SO_4} + \underset{\text{Iodine}}{3I_2} + \underset{\text{Water}}{3H_2O}$$

$$\underset{\text{Iodine}}{I_2} + \underset{\text{Sodium thiosulphate}}{2Na_2S_2O_3} \longrightarrow \underset{\text{Sodium tetrathionate}}{Na_2S_4O_6} + \underset{\text{Sodium iodide}}{2NaI}$$

Preparation of sodium thiosulphate (0.1 N):- Weigh accurately about 24.8 g of sodium thiosulphate ($Na_2S_2O_3.5H_2O$) and dissolve it in 200 ml of freshly boiled and cooled water. Shake the content for 2 minutes and make up the volume upto 1000 ml.

Standardization of sodium thiosulphate (0.1 N)

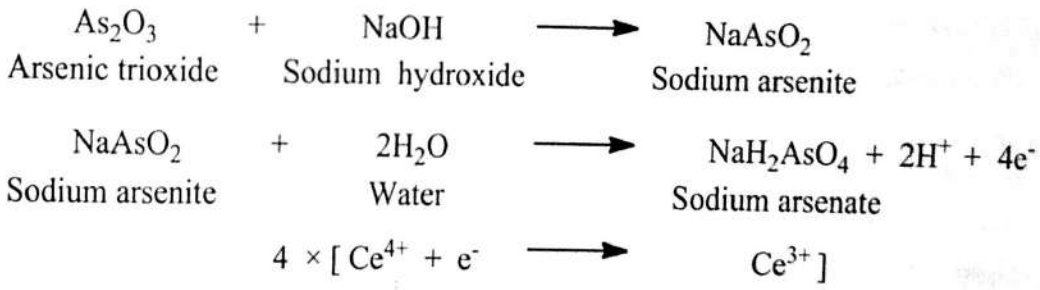
1. Clean and dry all glassware as per standard laboratory procedure.
2. Take 500 ml of unknown stock solution of sodium thiosulphate in a clean and dry beaker.
3. Rinse the burette with distilled water. Then, pre-rinse it with a portion of the sodium thiosulphate solution before you fill it up for the titration. Pre-rinsing is necessary to ensure that all of the solution in the burette is the desired solution, not a diluted or contaminated solution.

   To do this, add about 10 ml of the sodium thiosulphate solution to the clean burette. Carefully turn the burette on its side so the liquid slowly runs out the top. Rotate the burette on its axis during this time to make sure the solution wets the sides all the way to the top. Pour the rinse from the burette into a waste beaker. Repeat the rinsing process with a second portion of the sodium thiosulphate solution.
4. Take 10 ml of prepared potassium iodate solution in an iodine flask.
5. Add 2 g of potassium iodide and 5 ml of dilute sulphuric acid in it.
6. Keep the flask in dark for 10 minutes.

7. Add 2 to 3 drops of starch indicator.
8. Then fill the burette with sodium thiosulphate solution.
9. Start titration with the sodium thiosulphate solution until reach the endpoint. The approach of the endpoint is suggested by the change of a blue colour to colourless.
10. Record the reading of burette.
11. Repeat the titration three times to get precise readings.
12. Take mean of them and calculate normality of sodium thiosulphate solution.

4. PREPARATION AND STANDARDIZATION OF CERIC AMMONIUM SULPHATE (0.1 M):-

Principle:- Ceric ammonium sulphate solution is titrated with primary standard arsenic trioxide in the presence of sulphuric and osmic acid using ferroin sulphate as an indicator. End point can be detected by change in colour from pink to very pale blue. Reaction involved in this titration is as follows.



Preparation of ceric ammonium sulphate (0.1 M):- Weigh accurately about 65 g of ceric ammonium sulphate $[Ce(NH_4)_4(SO_4)_4.2H_2O]$ and dissolve it in a mixture of 30 ml sulphuric acid and 500 ml water with gentle heat. Cool and filter the solution, then make up the volume upto 1000 ml.

Standardization of ceric ammonium sulphate (0.1 M):-

1. Clean and dry all glassware as per standard laboratory procedure.
2. Take 500 ml of unknown stock solution of ceric ammonium sulphate in a clean and dry beaker.
3. Rinse the burette with distilled water. Then, pre-rinse it with a portion of the ceric ammonium sulphate solution before you fill it up for the titration. Pre-rinsing is necessary to ensure that all of the solution in the burette is the desired solution, not a diluted or contaminated solution.

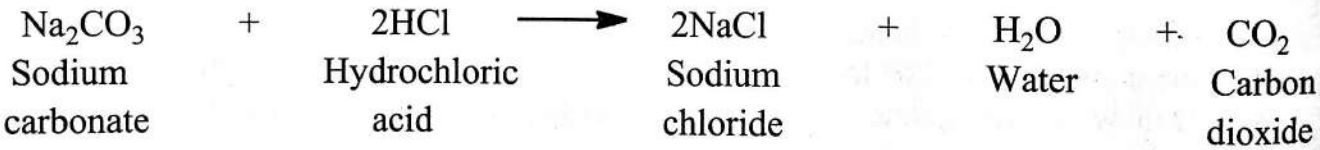
   To do this, add about 10 ml of the ceric ammonium sulphate solution to the clean burette. Carefully turn the burette on its side so the liquid slowly runs out the top. Rotate the

burette on its axis during this time to make sure the solution wets the sides all the way to the top. Pour the rinse from the burette into a waste beaker. Repeat the rinsing process with a second portion of the ceric ammonium sulphate solution.

4. Weigh accurately about 0.2 g of arsenic trioxide (previously dried at 105°C for 1 hour) and transfer it to 500 ml conical flask.
5. Add 25 ml of sodium hydroxide solution (8.0% w/v) in it and swirl to dissolve.
6. Add 100 ml distilled water and mix properly.
7. Add 30 ml dilute sulphuric acid, 0.5ml osmic acid solution and ferroin sulphate solution and mix properly.
8. Then fill the burette with ceric ammonium sulphate solution.
9. Start titration with the ceric ammonium sulphate solution until reach the endpoint. The approach of the endpoint is suggested by the change of a pink colour to very pale blue.
10. Record the reading of burette.
11. Repeat the titration three times to get precise readings.
12. Take mean of them and calculate molarity of ceric ammonium sulphate solution.
13. Equivalent factor of Arsenic trioxide for 0.1 M ceric ammonium sulphate is 0.004946.

5. PREPARATION AND STANDARDIZATION OF HYDROCHLORIC ACID (0.1M):-

Principle:- Known strength of sodium carbonate is titrated directly with hydrochloric acid. End point can be detected by using methyl orange or methyl red as an indicator. Reaction involved in this titration is as follows.



Preparation of HCl (0.1 M):- Take 8.5 ml of Hydrochloric acid and dilute upto 1000 ml with distilled water.

Standardization of hydrochloric acid (0.1 M):-

1. Clean and dry all glassware as per standard laboratory procedure.
2. Take 500 ml unknown stock solution of HCl in a clean and dry beaker.
3. Rinse the burette with distilled water. Then, pre-rinse it with a portion of the HCl solution before you fill it up for the titration. Pre-rinsing is necessary to ensure that all of the solution in the burette is the desired solution, not a diluted or contaminated solution.

   To do this, add about 10 ml of the HCl solution to the clean burette. Carefully turn the burette on its side so the liquid slowly runs out the top. Rotate the burette on its axis during this time to make sure the solution wets the sides all the way to the top. Pour the rinse from

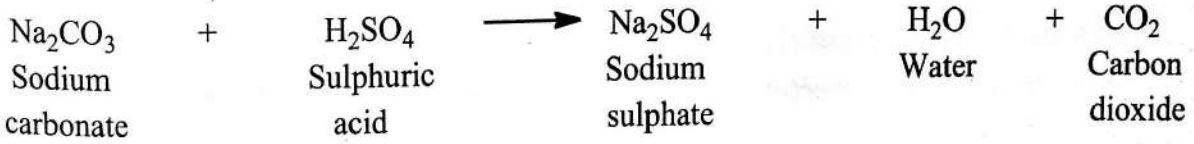
the burette into a waste beaker. Repeat the rinsing process with a second portion of the HCl solution.

4. Weigh accurately about 0.3 g of anhydrous sodium carbonate heated previously at 270°C for 1 hour and transfer it in a conical flask.
5. Add 20 ml distilled water and shake well or sonicate it on sonicator for 5 minutes or until dissolve properly.
6. Add 2 drops of methyl orange or methyl red indicator.
7. Then fill the burette with unknown stock solution of HCl.
8. Start titration with the HCl until reach the endpoint. The first titration should be performed by adding 0.50 ml portions of HCl solution from burette, with swirling. The approach of the endpoint is suggested by the temporary appearance of a pink colour that fades when heat the solution to boiling. Cool and continue the titration until pink colour appears that persists for more than 30 seconds and is no longer affected by continued boiling which signals the actual endpoint.

   Note:- The solution may lose its colour after 30 seconds or more, but it is not considered.
9. The first titration gives a rough idea of the amount of HCl needed to neutralize the anhydrous sodium carbonate.
10. Heat the solution to boiling and observe for 30 seconds, if pink colour fades away continue the titration further by adding more acid in flask.
11. Record the reading of burette.
12. Repeat the titration three times to get precise readings. For this we can add about 70% of the needed HCl quickly and then, near the end, add HCl one drop at a time until the endpoint is observed.
13. Take mean of them and calculate molarity of HCl.
14. Equivalent factor of sodium carbonate for 0.1 M HCl is 0.00529.

6. PREPARATION AND STANDARDIZATION OF SULPHURIC ACID (0.1M):-

Principle:- Known strength of sodium carbonate is titrated directly with sulphuric acid. End point can be detected by using methyl orange or methyl red as an indicator. Reaction involved in this titration is as follows.



Preparation of sulphuric acid (0.1 M):- Take 5.4 ml of Sulphuric acid and dilute upto 1000 ml with distilled water.

Standardization of sulphuric acid (0.1 M):-

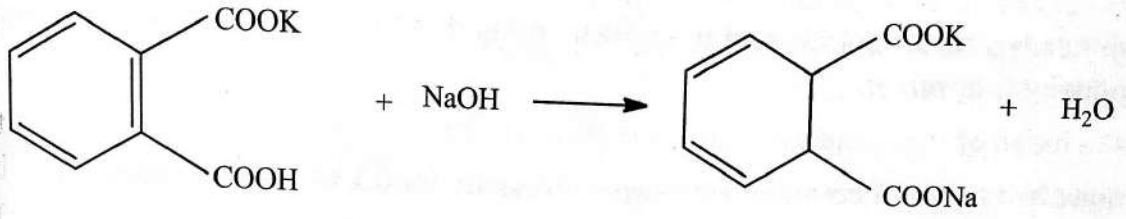
1. Clean and dry all glassware as per standard laboratory procedure.
2. Take 500 ml of unknown stock solution of H_2SO_4 solution in a clean and dry beaker.
3. Rinse the burette with distilled water. Then, pre-rinse it with a portion of the H_2SO_4 solution before you fill it up for the titration. Pre-rinsing is necessary to ensure that all of the solution in the burette is the desired solution, not a diluted or contaminated solution.

   To do this, add about 10 ml of the H_2SO_4 solution to the clean burette. Carefully turn the burette on its side so the liquid slowly runs out the top. Rotate the burette on its axis during this time to make sure the solution wets the sides all the way to the top. Pour the rinse from the burette into a waste beaker. Repeat the rinsing process with a second portion of the H_2SO_4 solution.
4. Weigh accurately about 0.3 g of anhydrous sodium carbonate heated previously at 270°C for 1 hour and transfer it in a conical flask.
5. Add 20 ml distilled water and sonicate it on sonicator for 5 minutes to dissolve properly.
6. Add 2 drops of methyl orange or methyl red indicator.
7. Then fill the burette with unknown stock of H_2SO_4 solution.
8. Start titration with the H_2SO_4 until reach the endpoint. The first titration should be performed by adding 0.50 ml portions of H_2SO_4 solution from burette, with swirling. The approach of the endpoint is suggested by the temporary appearance of a pink colour that fades when heat the solution to boiling. Cool and continue the titration until pink colour appears that persists for more than 30 seconds and is no longer affected by continued boiling, which signals the actual endpoint.

   Note:- The solution may lose its colour after 30 seconds or more but it is not considered.
9. The first titration gives a rough idea of the amount of H_2SO_4 needed to neutralize the anhydrous sodium carbonate.
10. Heat the solution to boiling and observe for 30 seconds, if pink colour fades away continue the titration further by adding more acid in flask.
11. Record the reading of burette.
12. Repeat the titration three times to get precise readings. For this we can add about 70% of the needed H_2SO_4 quickly and then, near the end, add H_2SO_4 one drop at a time until the endpoint is observed.
13. Take mean of them and calculate molarity of H_2SO_4.
14. Equivalent factor of sodium carbonate for 0.1 M H_2SO_4 is 0.01059.

7. PREPARATION AND STANDARDIZATION OF SODIUM HYDROXIDE (0.1 M):-

Principle:- Known strength of potassium hydrogen phthalate is titrated directly with sodium hydroxide. End point can be detected by using phenolphthalein as an indicator. Reaction involved in this titration is as follows.



Potassium hydrogen phthalate	Sodium hydroxide	Potassium sodium phthalate	Water

Preparation of sodium hydroxide (0.1 M):- Dissolve 4 g of sodium hydroxide in 1000 ml distilled water.

Standardization of sodium hydroxide (0.1 M):-

1. Clean and dry all glassware as per standard laboratory procedure.
2. Take 500 ml of unknown stock solution of NaOH in a clean and dry beaker.
3. Rinse the burette with distilled water. Then, pre-rinse it with a portion of the NaOH solution before you fill it up for the titration. Pre-rinsing is necessary to ensure that all of the solution in the burette is the desired solution, not a diluted or contaminated solution.

   To do this, add about 10 ml of the NaOH solution to the clean burette. Carefully turn the burette on its side so the liquid slowly runs out the top. Rotate the burette on its axis during this time to make sure the solution wets the sides all the way to the top. Pour the rinse from the burette into a waste beaker. Repeat the rinsing process with a second portion of the NaOH solution.
4. Weigh accurately about 1 g of potassium hydrogen phthalate powdered and heated previously at 120°C for 2 hour and transfer it in a conical flask.
5. Add 15 ml distilled water and sonicate it on sonicator for 5 minutes to dissolve properly.
6. Add 2 drops of phenolphthalein indicator.
7. Then fill the burette with unknown stock of NaOH solution.
8. Start titration with the NaOH until reach the endpoint. The first titration should be performed by adding 0.50 ml portions of NaOH solution from burette, with swirling. The approach of the endpoint is suggested by the temporary appearance of a pink colour that fades when the solution is swirled for upto 10 seconds. A pink colour that persists for more than 30 seconds, signals the actual endpoint.

   Note:- The solution may lose its colour after 30 seconds or more, but it is not considered.

9. The first titration gives a rough idea of the amount of NaOH needed to neutralize the potassium hydrogen phthalate.
10. Record the reading of burette.
11. Repeat the titration three times to get precise readings. For this we can add about 70% of the needed NaOH quickly and then, near the end, add NaOH *one drop* at a time until the endpoint is observed.
12. Take mean of them and calculate molarity of NaOH.
13. Equivalent factor of potassium hydrogen phthalate for 0.1 M NaOH is 0.020422.

MULTIPLE CHOICE QUESTIONS

Q.1 ..... may be defined as an essential or distinctive characteristic, property or attribute.

a. Purity
b. Quantity
c. Quality
d. None of these

Q.2 API stands for

a. Active Pharmacy Interpretation
b. Acute Pulmonary Interaction
c. Active Pharmaceutical ion
d. Active Pharmaceutical Ingredient

Q.3 Which analytical technique is used for determine the amount of oxidizing agents?

a. Oxidation-reduction titration
b. Bromometry
c. Complexometry
d. None of these

Q.4 Given the following which is the widely used quantitative analytical method.

a. Non-aqueous Titration
b. Aqueous Titration
c. Acid Base Titration
d. Volumetric Analysis

Q.5 %w/w express the ..... .

a. Number of gm of solute in 1000 gm of product
b. Number of gm of solute in 100 gm of product
c. Number of ml of solute in 100 ml of product
d. Number of gm of solute in 100 ml of product

Q.6 Given the following all are the role of analytical chemistry except

a. Geographical Assay
b. Applied Research
C. Clinical and biological Studies
d. All of these

Q.7 %w/v express

a. Number of ml of solute in 100 gm of product.
b. Number of ml of solute in 100 ml of product
c. Number of gm of solute in 100 ml of product
d. None of these.

FILL IN THE BLANKS

1. ..... study of separation, identification, and quantification of the chemical components.
2. Redox titration is based on the reaction between ..... and ..... .
3. ..... is the determination of the amount of a particular element, species or compound present in a sample.

VERY SHORT ANSWER QUESTIONS

Q.1 Define Pharmaceutical Chemistry.

Q.2 Define Quality.

Q.3 Give the name of different techniques of pharmaceutical analysis.

Q.4 What do you understand by Analytical Chemistry?

LONG ANSWER QUESTIONS

Q.1 Explain in detail about the role of Quality Control in Pharmacy.

Q.2 Define analytical chemistry and explain the role of analytical chemistry.

ANSWERS

MULTIPLE CHOICE QUESTIONS

1. c 2. d 3. d 4. d 5.b 6. a 7. c

FILL IN THE BLANKS

1. Analytical chemistry 2. Analyte, titrant 3. Quantitative analysis

2 ERRORS

INTRODUCTION

In pharmaceutical analysis, the aim if an analyst that is performing analytical operation/experiment in analytical laboratory must be that he or she must obtain a true result by performing an analytical procedure correctly as required. But in reality, an analyst which have knowledge about the various aspects of analytical operations knows very well that the true or theoretical value of result is very rare and he/she should only try to get his/her results close to the true value. How much close is the result to the true value depends upon the knowledge of analyst towards the chemistry or principle of operation, possible interferences in operation i.e. from other ions, elements and compounds as well as hands-on experience about the statistical distribution of values.

ERROR

The term error refers to the difference between the measured and true value in the results of any analytical operation.

However, it is not possible to eliminate error from any measurement, even the person performing the operation is expert, performing operation in best conditions and performing on best quality instrument. One should only made attempts to minimize errors and get results which are close to the true value at best possible.

To check the error analyst must know the true value of particular experiment's results but term "true value" is never ever known in reality. Analyst have to make use of a standard value instead of true value which can be obtained by two methods:-

1. Absolute method:- The sample which is to be analyzed can be synthesized/prepared using known quantities of constituents in known conditions to get a primary standard. In this primary standard the true values of constituents are known. Then it is analyzed by some suitable method and value obtained is recorded and considered as standard value. Now the sample is analyzed by same method in same conditions and observed value is recorded. From above two values error can be calculated for that method.

2. Comparative method:- Sometimes it is not possible to synthesize/prepare a sample under analysis. In that case, the analytical data provided by some standard agency is regarded as absolutely true. From that the error can be calculated.

SOURCES OF ERRORS

Errors in the results in an analysis can be resulted from various sources. Some major sources of errors in pharmaceutical analysis are described here under.

1. **Human source:-** The qualification and experience of an analyst performing the analysis has major impact on error in results. If an experiment is performed by inexperienced person the chances of error are more as compared to same experiment performed by the experienced analyst.
2. **Instrumental, apparatus and glassware:-** If the instrument, glassware as well as apparatus used in analysis is of low quality and uncallibrated the chances of error are increased at significant extent.
3. **Experimental conditions:-** If the analysis is carried out in the conditions which are unfavourable for particular experiment or analysis the desirable result will not obtained.
4. **Constituents used in analysis:-** If various constituents like standard, solvents, reagents etc used in analysis are not of desired quality and purity the results will be obtained with errors.
5. **Procedure:-** If the analytical procedure used in analysis is not validated and if validated but not followed carefully the errors in the results will obtained.

TYPES OF ERRORS

Errors occurs in analysis can be majorly classified into two types:-

1. **Systemic errors:-** Systemic errors is also known as determinate errors. These are the errors whose source or cause as well as magnitude is known and can be avoided or minimized by following proper procedure carefully and taking necessary precautions. Systemic errors can be classified as follows:-

a. **Personal errors:-** For these errors the person carrying operation or experiment is responsibly. These errors occurs when the procedure is not properly followed or done carefully. These errors are common when analyst not personally doing operation but connected to the procedure as observer. Some of the examples of personal errors are:-

i. Person carrying titration cannot able to detect endpoint by colour change clearly and always add some more amount of titrant that actually required which result in positive error i.e. measured value is always bit more than standard value.

ii. Person is not washing precipitate properly in gravimetric determinations that result's error in final result.

iii. Person performing assay has not free hand in making dilutions and add more or less solvent in dilution preparations that directly give error in results.

iv. Person carrying titrations is unable to read burette properly and always note incorrect values that also cause error in results.

b. **Instrumental errors:-** Instrumental errors are seen when the instrument used in the operation doesn't give accurate measurement which it needed to be give. These are due to

use of uncalibrated or improperly calibrated glassware's like pipette, burette etc and instruments like spectrometers, pH meters, potentiometers etc.

c. Reagent errors:- Reagent errors are due to the reagents used in analysis. These errors are seen when contaminated reagents are employed in analysis or the reagents attacks on the apparatus or glassware and introduce impurities in analyte sample under analysis.

d. Method errors:- These errors are not easy to detect which are usually occurs when the analytical method is not performed properly or is unsuitable for particular analysis. Some examples of method errors are:-

i. Calculations in chemical reactions are made on the completion of reaction at specific time as per procedure. But sometimes due to slight variability in experimental conditions the reaction is not completed i.e. only 97% completed and calculations are made. This results error in measurement.

ii. In U.V. spectrophotometric analysis, the use of different absorption maxima from that of specific for the analyte cause poor absorption and cause error in results.

iii. When pH of solvent is not adjusted properly it also give inaccurate response in HPLC and give error in final results.

iv. In gravimetric analysis, another substance present in the sample is also get precipitated along with desired substance which give error in results.

e. Additive errors:- These errors are independent of the amount of substances present in the sample. For example, Loss in the weight of crucible during the incineration of precipitate gives error in final results.

f. Proportional error:- The magnitude of proportional error depends upon the amount of sample. Proportional error is usually due to the materials that interferes the analytical procedure. For example, use of impure NaOH in titration of HCl give error in results and concentration of NaOH is proportional to the error in results.

g. Constant error:- The constant error is independent of the magnitude of measured amount but become less significant as the magnitude increased. For example, In titrations addition of 0.1 ml more titrant in 10 ml titrand to see colour change clearly at the endpoint gives error of 0.1ml. Similarly for 20 ml titrand 0.1 ml more titrant is added it also give same 0.1 ml error even on double the size of sample. Therefore as the amount of titrand increases the significance of constant error decreases.

2. Random error:- Random error is also known as indeterminate error. The cause of random error is usually not known therefore cannot eliminated by careful working or taking precautions during analysis. For example a person performing titration by same method in same conditions for same sample, the results are not identical. The error observed in that condition is called random error.

METHODS OF MINIMIZNG ERRORS

As we know the error is an indifferentiate part of any analytical operation. Analyst try his best to minimize the error as much as possible. Errors can be minimized by applying following methods during analysis:-

1. **Proper callibration of instruments, apparatus and applying corretions:-** By callibration of instruments like U.V. spetrophotometer, pH meter, potentiometer etc and glasswares like burette, measuring cylinder etc before performing analysis one can eliminate errors to very much extent. Errors can also be minimized by applying necessary corrections if the source of error is known.

2. **By running control determination:-** By running a control determination parallerly to the sample by taking standard under same experimental conditions the error can be reduced at very possible extent. However, a standard should contain same weight of the constituent present in unknown sample. The weight of the constituent of unknown sample can be calculated as follows.

$$\frac{\text{result for standard}}{\text{result for unknown}} = \frac{\text{weight of constituent in standard}}{x}$$

Where,

x = weight of constituent in unknown sample.

3. **By running blank determination:-** Blank determination is the determination under same experimental conditions which are used for sample analysis but in this case the sample is excluded. The aim of blank determination is know the effect of impurities introduced by reagents on results. From the readings obtained from blank determination one can eliminate the error at very much extent.

4. **By comparing results of independent methods:-** In that case, the analysis of same sample by totally different methods is performed and the results obtained from both methods are compared. If they are identical than they are considered as reliable. For example:- Determination of strength of HCl solution is performed by titration with standard NaOH and also by precipitation titration method with Analytical as $AgCl_2$ and results obtained from both methods are compared. Another example is of hardness of water, in this case the concentrations of magnesium and calcium is determined by both atomic absorption spectroscopy and EDTA titrations and results are compared.

5. **By using standard addition:-** In this method, small amount of standard of constituent present in sample is added and sample is analyzed for the total amount of constituent present. The difference in the results from sample with and without added standard is calculated. Satisfactory recovery gives the confidence of accuracy of result.

6. **By using internal standard:-** In this method, the fixed amount of a reference material is added to a series of known concentrations of material to be analyzed. The ratios of values obtained for the internal standard and series of known concentrations are plotted against concentration on a graph which gives a straight line. Same amount of internal standard is

then added to the unknown concentration and determined by same method and ratio obtained is plotted on graph to calculate exact concentration.

ACCURACY

The term "accuracy" refers to the concordance between the measured and true value or in other word it refers that how much close the measured value is to the true value. It also reffers as "correctness of measurement". In relation to error accuracy is inversely proportional to it i.e. more the accuracy less will be the error or vice-versa.

$$\text{Accuracy} = \frac{1}{\text{error}}$$

For analytical method, accuracy can be calculated by two methods which are:-

1. Absolute method:- In this method, the analysis is carried out by a specific method on the standard sample of high purity which can be obtained from a standard source or synthesized by analyst in laboratory with rigorous purification and values of results are noted down. Using same method the analysis of same sample is carried out but this time possible interferences are added to the sample and values of results are noted down. From the values obtained from standard and standard sample with added interferences the accuracy of the method in the absence and presence of interferences can be determined.

2. Comparative method:- Comparative method is useful when primary standard can be unavailable and impossible to prepare in laboratory by analyst i.e. mineral, ore, alloy etc. In that case results from a standard source with same method is correlated to get confidence of accuracy. Sometimes secondary standards are used for analysis.

Another approach include two fundamentally different methods are employed in analysis of same sample and their results are correlated for accuracy determination.

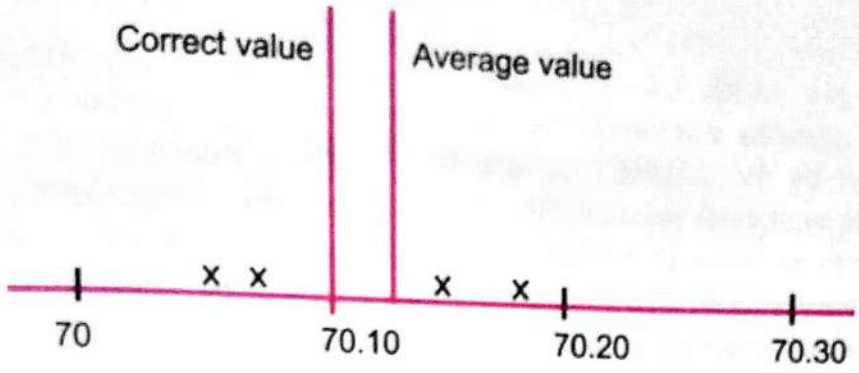
PRECISION

Precision refers to the degree of closeness between the several measurement of same quantity of sample by same method.

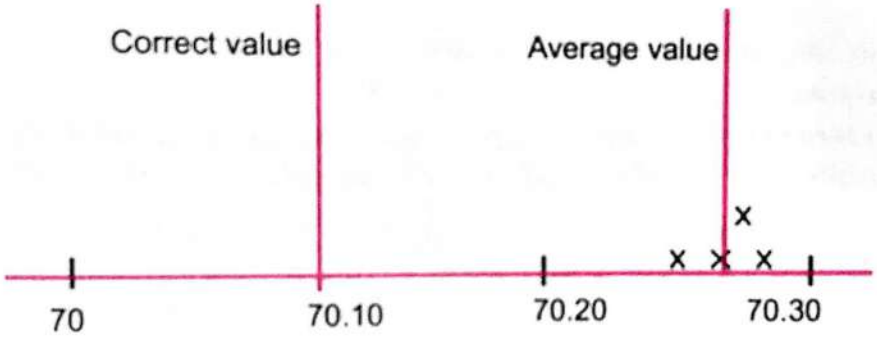
Precision and accuracy are correlated to each other. Accuracy represents correctness of measurements while precision represents reproducibility. Precision always represent accuracy but higher degree of accuracy doesn't necessarily represent that the method is precise.

For example:- Two analysts performed analysis on a sample that contain 70.10% ± 0.04% of a constituent. The results obtained by them are as follows:-

Results of analyst A are 70.07, 70.18, 70.14, 70.08 and average value is 70.12



Results of analyst B are 70.27, 70.28, 70.26. 70.28 and average value is 70.27



Here we can see that the values of results obtained by analyst A are accurate but not precise as compared to analyst B while on the other hand values obtain by analyst B are precise but not accurate. Therefore, precision accompanies accuracy but higher degree of precision doesn't.

Above example also shows that the results of analyst are close to the correct value and are pointed either sides of the correct value which represents random error while results of analyst B are away from the correct value and are very precise which represents constant error.

Precision can be classified into three main types which are:-

1. Repeatability:- In this the same analysis is performed for several times in same conditions and same time (same day).
2. Intermediate precision:- In this the same analysis is performed by changing analyst, lot of chemical, instrument or time interval (separate days).
3. Reproducibility:- In this same analysis is performed in different laboratory or place by same method.

SIGNIFICANT FIGURES

Significant figures are digits which are necessary to express the results. Accuracy of a measurement is depends upon the number of significant figures used to represent it. More the significant figures more will be the accuracy. For example, a sample Analytical 71.2 in a rough balance and 71.2932 in an analytical balance. Here in rough balance measurement there are only three significant figures while in analytical balance there are six and each value give the precision of respective measurement. In 71.2932 the figures 71.293 are known with certainty while sixth digit with some uncertainty i.e. less than ±1. Significant figures are independent of decimal point placement for example, 7.12, 71.2, 0.712 all contain three significant figures. Some rules about the significant figures are:-

1. Uncertain figure is only one and is independent of number of significant figures present in the result.
2. Significance of digit zero depends upon its position. For example:- In number 70.01 all the figures including zeroes are significant but in case of 0.07001 zero before decimal point is not significant and zero before 7 is also not significant because its purpose is only to indicate the position of decimal point therefore it has only four significant figures.
3. For the correction of significant numbers, rounding off the quantities is made by adding 1 to the last figure if the rejected figure is 5 or above. For example, if we need only first three digits from these two figures i.e. 1.257 and 1.253 after round off we get 1.26 and 1.25.
4. In case of addition or subtraction, each value should contain same number of significant figures. For example if we want to add these three numbers i.e. 1.268, 1.24, 1.04 after correction numbers will be 1.27 + 1.24 + 1.04 = 3.55.
5. In case of multiplication or division, the result is reported in such way that it contain least number of significant figures which depends upon the least number figure in the problem. For example in multiplication of 1.27, 1.249, 1.5796, 1.23 the result is round off to get only three significant figures because least significant figure number in the problem contain is 3 significant figures.

REVIEW QUESTIONS

MULTIPLE CHOICE QUESTIONS

Q.1 Absolute error is the difference between ..... & ..... .

a. Experimental mean, Measured Value

b. Measured Value, True Value

c. Experimental Value, True Value

d. None of These

Q.2 Give the following are the type of systemic error except

a. Error of methods

b. Instrumental method

c. Personal error

d. Random error

Q.3 ..... relates to the quality of a result.

a. Precision

b. Accuracy

c. Standard deviation

d. Significant figure

Q.4 Random error is also known as

a. Accidental error

b. Indeterminate error

c. Determinate error

d. Both a and b

Q.5 Given the numerical figure having how many significant figures?

a. Two

b. Four

c. Three

d. None of these

FILL IN THE BLANKS

1. ..... result from the carelessness, inattention, or personal limitations of the experimenter.
2. ..... eliminates most instrumental systematic errors.
3. ..... refers to the value found by dividing the absolute error by the true value.
4. The ..... is constant with sample size, but the ..... varies when sample size is changed.

SHORT ANSWER QUESTIONS

Q.1 Explain the following terminologies:

a. Titration b. Indicator

c. Standard deviation d. Mean (Average Deviation)

Q.2 What do you understand by precision?

Q.3 Define error.

Q.4 Give the difference between the accuracy and precision.

LONG ANSWER QUESTIONS

Q.1 Explain the various commonly used methods of expressing concentrations.

Q.2 Explain in brief about the significant figure.

Q.3 Define systemic error and explain in brief the types of systemic error.

Q.4 Describe accuracy and precision and give the relation between the accuracy and precision.

ANSWERS

MULTIPLE CHOICE QUESTIONS

1.c 2.d 3.b 4.d 5. B

FILL IN THE BLANKS

1.Personal error 2. Calibration

3. Relative error 4. absolute error, relative error

3 ACID BASE TITRATIONS

INTRODUCTION

Acid base titration is based upon the neutralization reaction between acid and base. Therefore it is also called neutralization titration. In acid base titrations, the standard solution having known concentration of acid is titrated against the unknown concentration of base or vice-versa. The point at which the moles of acid exactly cancel out the moles of base present in the solution is known as stoichiometric point or end point of the titration.

CONCEPT OF ACID BASE

The concept of acid base may be understand by three major theories proposed for acid and base and these are.

1. Arrhenius acid base theory
2. Bronsted-lowry proton theory
3. Lewis electron theory

1. Arrhenius acid base theory:- Arrhenius suggested his theory in 1884. According to Arrhenius,

Acid is a substance which gives rise to hydrogen ions when dissolved in water. These hydrogen ions form hydronium ions in association with solvent.

$$HA \leftrightarrow H^+ + A^-$$

$$H^+ + H_2O \leftrightarrow H_3O^+$$

A base is defined as a substance which ionizes to give hydroxyl ions when dissolved in water

$$BOH \leftrightarrow B^+ + OH^-$$

There are some substances which do not contain hydroxyl ions themselves but increases OH^- ion concentration of the solution e.g. Amines. This behavior is explained on the basis of hydrolysis or reaction with water. These substances are called pseudo base.

$$B + H2O \leftrightarrow BH^+ + OH^-$$

Arrhenius theory explained the acid base behavior in aqueous solvent but failed to explain the acid base behavior in non-aqueous solvents.

2. Bronsted-lowry proton theory:- This theory was put forward by Bronsted in 1923. Similar theory was also proposed by Lowry independently. According to Bronsted theory,

An acid is a substance which can donate protons. For Example:

$$B + H^+ \leftrightarrow BH^+$$

The cation BH^+ acts as an acid as it donates proton

A base is a substance that can accept protons. For example:

$$HA \leftrightarrow H^+ + A^-$$

In this equation, anion A^- acts as a base as it accepts a proton

In the above reaction, the acid and base pairs are called as conjugate acid base pair i.e the base is the conjugate base of the acid and the acid is the conjugate acid of the base.

$$Acid \leftrightarrow Base + H^+$$

For the acid-base reaction to take place, it is necessary to have two conjugate acid-base systems as it involves proton transfer from one system to the other.

Bronsted theory is able to explain acid-base behavior in non aqueous solvents.

The conjugate acid-base system is a necessity for a reaction to take place. This reaction can be deemed to be proton transfer from one system to another.

Example:

$$\underset{\text{Acid}}{CH_3COOH} \leftrightarrow \underset{\text{Base}}{CH_3COO^- + H^+}$$

Water can act as both acid and base i.e. it is amphoteric in nature.

For example:

$$\underset{\text{Acid 1}}{H_2O} + \underset{\text{Base 1}}{H_2O} \leftrightarrow \underset{\text{Acid 2}}{H_3O^+} + \underset{\text{Base 2}}{OH^-}$$

3. Lewis electron theory:- Lewis suggested this theory in 1923. According to this theory,

An acid is a species that can accept an electron pair and a base is a species that can donate an electron pair. In following example, BF_3 is an acid and NH_3 is a base. They form acid base complex or adduct or co-ordination complex.

$$\underset{\text{Acid}}{BF_3} + \underset{\text{Base}}{NH_3} \rightarrow \underset{\text{Co-ordinate complex}}{BF_3{-}NH_3}$$

Lewis theory is useful to explain indicator colour change in non-protonic systems showing acid-base reaction.

THEORIES OF ACID BASE INDICATORS

There are two major theories for acid base indicators.

1. Ostwald's theory
2. Quinonoid theory

Indicators are the substances which produce some readily seen change at the equivalence point of the titration.

Accuracy of any titration mainly depend on the accuracy in detection of end point. At end point the moles of acid exactly neutralize the moles of base in the solution and this point is detected by some indicator.

In acid base titrations, when an indicator show colour change is called endpoint of the titration. In ideal conditions, the endpoint and equivalence point coincide with each other but practically there is always a small difference between them which is called titration or endpoint error.

Acid base indicators are the indicators which give different colour with the change in hydrogen ion concentrations of the solution. They give different colour at different pH conditions. The colour which is given by an indicator in an acid solution is called acid colour while the colour which is given in alkali solution is called alkaline colour of an indicator. However, this colour change is not sudden or abrupt, it takes small interval of pH to change usually two pH units and this interval is called **colour change interval** of an indicator.

1. Ostwald's theory:- This theory of indicator action was suggested by W. Ostwald. He suggest that most of the acid base indicators are very weak organic acids or bases and colour change of the indicator is due to the ionization of indicator. The unionized indicator has different colour than ionized indicator.

Consider that 'HInd' is a weak organic acid indicator and in aqueous solution it is well dissociated as follows:-

$$\underset{\text{Undissociated indicator}}{HInd} \leftrightarrow H^+ + \underset{\text{dissociated indicator}}{In^-}\ \text{(poorly dissociated)}$$

In above reaction, dissociated indicator have different colour than undissociated indicator. But as in acid base titrations, if that indicator is placed in an acidic solution of acid HA following equilibrium exist:-

$$HInd \leftrightarrow \boxed{H^+} + In^-\ \text{(Dissociation decreased)}$$

$$HA \leftrightarrow \boxed{H^+} + A^-$$

Common ion

HIn is a weak acid therefore it poorly dissociates and due to common ion effect its dissociation further decreased. The equilibrium is shifts towards the left hand side. Therefore in the presence acid the dissociation of HIn is almost negligible and indicator is mostly in undissociated form that show undissociated indicator colour.

But if the same indicator is added in an alkali solution of base BOH the dissociation of HIn will be increased.

$$HInd \leftrightarrow \boxed{H^+} + In^- \text{ (Dissociation increased)}$$

$$BOH \leftrightarrow \boxed{OH^-} + B^+$$

Water (H_2O)

The hydrogen ions are removed by OH^- ions by formation of water molecules and equilibrium is shifted towards the right side and concentration of In^- ions will become more than HIn which give dissociated indicator colour.

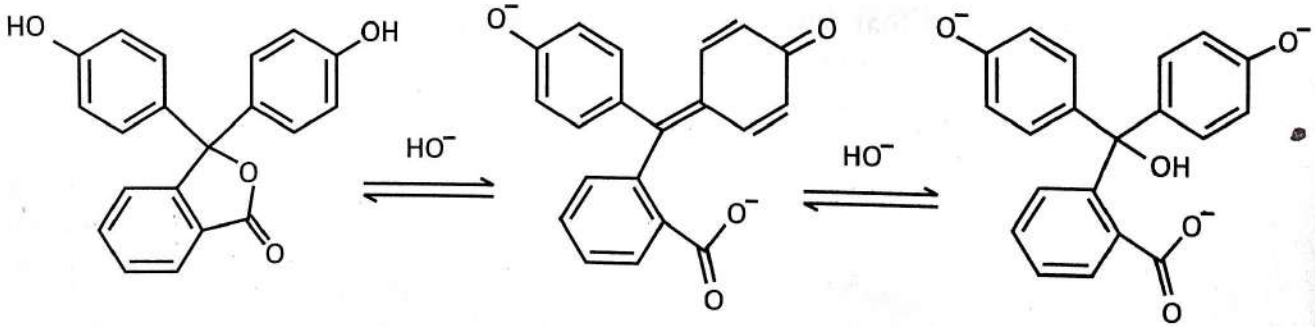
Similarly the indicator which is weak organic base poorly dissociated in alkali solution but its dissociation increased in acidic solution.

Phenolphthalein is weak acid and in undissociated form i.e. HPh it is colourless while in dissociated form i.e. Ph^- its give pink colour.

Methyl orange is a weak base and in undissociated form i.e. MeOH it gives orange colour while in dissociated form i.e. Me^+ its give red colour.

2. Quinonoid theory:- Quinonoid theory suggest that the colour change of indicator is due to the structural changes of indicator. In acidic solution indicator exist in different structural form and in basic solution it exist in different structural form. These structural forms have different colours, therefore in acidic solution indicator give different colour and in basic solution different.

For example:- Phenolphthalien is in beenzenoid form in acidic solution and is colourless but in alkaline solution it is converted into quinonoid form which give pink colour. In the presence of alkali the lactone ring of A opens and by loss of water resonating ion B is formed which is pink in colour and after that if it is treated with concentrated alcoholic alkali it again become colourless due to formation of C.



[A] Colourless [B] Pink [C] Colourless

CLASSIFICATION OF ACID BASE TITRATIONS

Acid base titrations are neutralizing titrations and the process in these titrations can be understood by studying the change in the hydrogen ion concentration during titrations. The pH near the endpoint suggest the choice of indicator for that particular titration. On the basis of strength of acid and base used, acid base titrations are majorly classified into five types:-

1. Titration of strong acid with strong base

2. Titration of weak acid with strong base
3. Titration of weak base with strong acid
4. Titration of weak base with weak acid
5. Titration of polybasic acid with strong base

1. Titration of strong acid with strong base:- Hydrochloric acid is a strong acid while sodium hydroxide is a strong base and chemical reaction between HCl and NaOH can be represented as follows:-

$$HCl + NaOH \rightarrow NaCl + H_2O$$
$$H^+ + OH^- \rightarrow H_2O$$

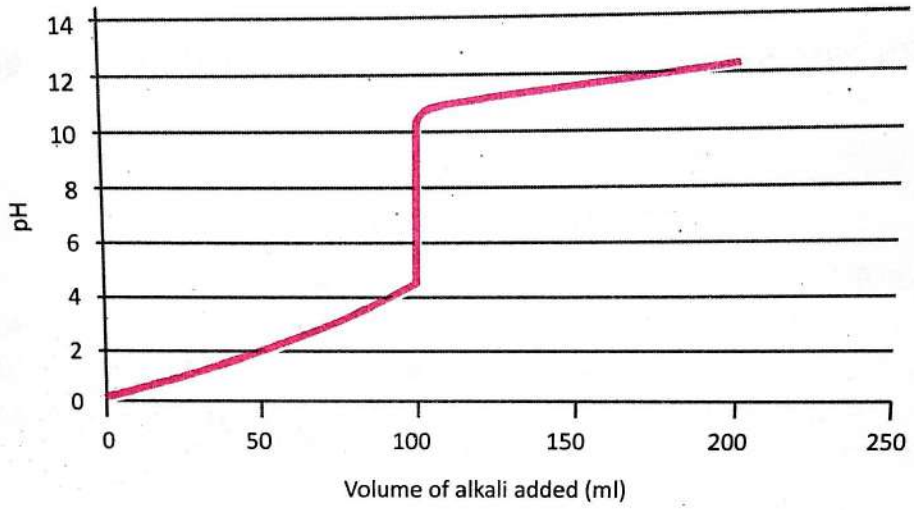
If we take 100ml of 0.1 M HCl and 0.1 N NaOH is added gradually in it. As the titration goes on H^+ ions from HCl are combined with OH^- ions from NaOH and H^+ ions continously decreased. When the 100ml of NaOH is added in the solution all the H^+ ions are neutralized by OH^- ions. At that point solution is nor acidic nor basic it is neutral having pH 7 because NaCl salt which is formed during reaction doesn't hydrolyzed and cannot disturb pH.

From above discussion it is concluded that the equivalence point in the titrationn is at pH 7. But for the proper selection of indicator pH at the endpoint is needed for that we have to study change in pH during titration.

In the table below, change in pH of 100ml 0.1 M HCl during titration with 0.1 M NaOH given.

Volume of NaOH added	pH changes in 0.1 M solution
0	1.0
50	1.5
75	1.8
98	3.0
99	3.3
99.8	4.0
99.9	4.3
100	7.0
100.1	9.7
100.2	10.0
101	10.4
110	10.7
150	12.3
200	12.5

In above table we can see that the at the equivaence point the pH change is very sharp i.e. 4.3 at 99.9 to 9.7 at 100.1. Therefore for 0.1 M solutions the inflection range is from pH 4.3 to 9.7. Any indicator have ph range between this inflection range can be used for this titration. Phenolphthalein indicator has pH range 8.2 to 10.0 therefore phenolphthalein is the indicator of choice for this titration. Neutralization curve obtainded for this titration is as follows:-



Similarly 0.01 M solution has inflection range from pH 5.5 to 8.5 and phenol red will be the suitable indicator while 1 M solution has inflection range of pH 3 to 10.5 for that phenolphthalein will be suitable.

2. Titration of weak acid with strong base:- Acetic acid is a weak acid and sodium hydroxide is a strong base. Titration is performed similarly as performed for strong acid and strong base. The chemical reaction between acetic acid and sodium hydroxide can be described as follows:-

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

But in case of acetic acid there are some differences that are:-

1. Due to being a weak acid it dissociates poorly therefore give smaller concentration of ions but initial pH is higher.

2. When strong base is added to the weak acid it form salt which give common ion effect which supress the dissociation of weak acid and decrease hydrogen ion concentration which results increase in pH.

$$CH_3COOH \leftrightarrow H^+ + \boxed{CH_3COO^-} \quad \text{(poorly dissociated)}$$

$$CH_3COONa \leftrightarrow Na^+ + \boxed{CH_3COO^-} \quad \text{(strongly dissociated)}$$

Common ion

3. Due to hydrolysis of salt formed on the completion of reaction pH of the solution is more than 7.

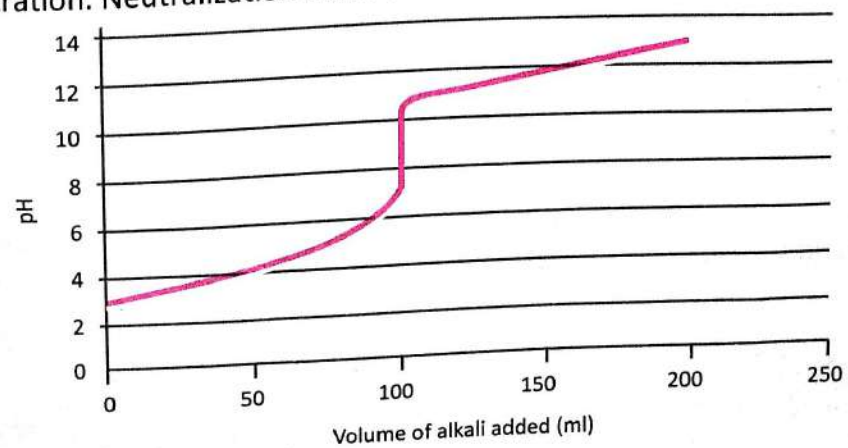
$$CH_3COONa + H_2O \rightarrow CH_3COOH + Na^+ + OH^-$$

Titration of 0.1 M acetic acid with 0.1 M NaOH is performed similarly as performed in strong acid with strong base. Only difference is the initial pH is higher, rate of increase of pH is higher and pH at equivalence point is also higher due to salt formation.

In the table below, change in pH of 100ml 0.1 M CH_3COOH during titration with 0.1 M NaOH given.

Volume of NaOH added	pH changes in 0.1 M solution
0	2.9
50	4.7
90	5.7
99	6.7
99.5	7.0
99.8	7.4
99.9	7.7
100	8.7
100.2	10.0
100.4	10.4
101	10.7
110	11.7
150	12.3
200	12.5

In above table we can see that the at the equivaence point the pH change is very sharp i.e. 7.7 at 99.9 to 10.0 at 100.2. Therefore for 0.1 M solutions the inflection range is from pH 7.7 to 10.0. Any indicator have p range between this inflection range can be used for this titration. Phenolphthalein indicator has pH range 8.2 to 10.0 therefore phenolphthalein is the indicator of choice for this titration. Neutralization curve obtainded for this titration is as follows:-



3. Titration of weak base with strong acid:- Aqueous ammonia solution is a weak base while hydrochloric acid is a strong acid. The chemical reaction between them can be represented as follows:-

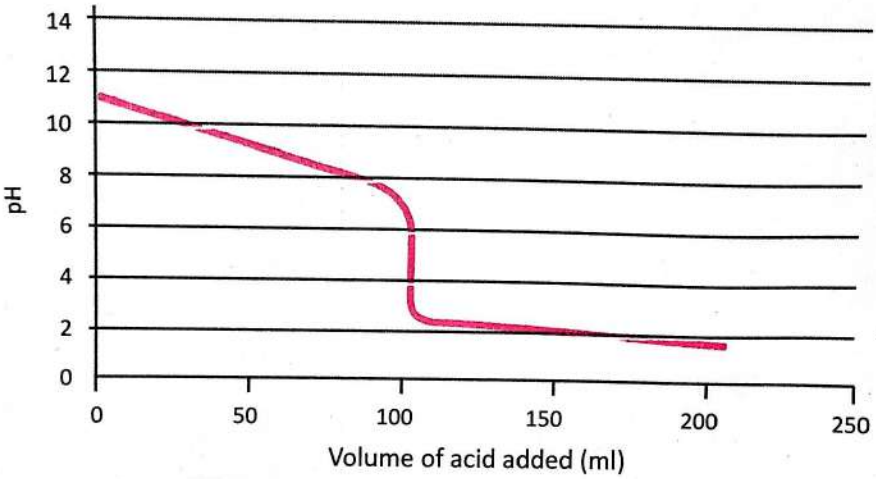
$$NH_4OH + HCl \rightarrow NH_4Cl + H_2O$$

When stong acid is added in the solution of weak base the salt is formed, which is further hydrolysed as follows:-

$$NH_4 + H_2O \rightarrow NH_4OH + H^+$$

In this titration due to hydrolysis of salt and formation of H^+ ions the pH of solution at equivalence point is less that 7.

If 100ml of 0.1 M NH_4OH is titrated against 0.1 M HCl the inflection range is from pH 3 to 6.5. Methyl red has pH range 4.8 to 6.0 therefore, it is a indicator of choice for this titration. Neutralization curve obtainded for this titration is as follows:-



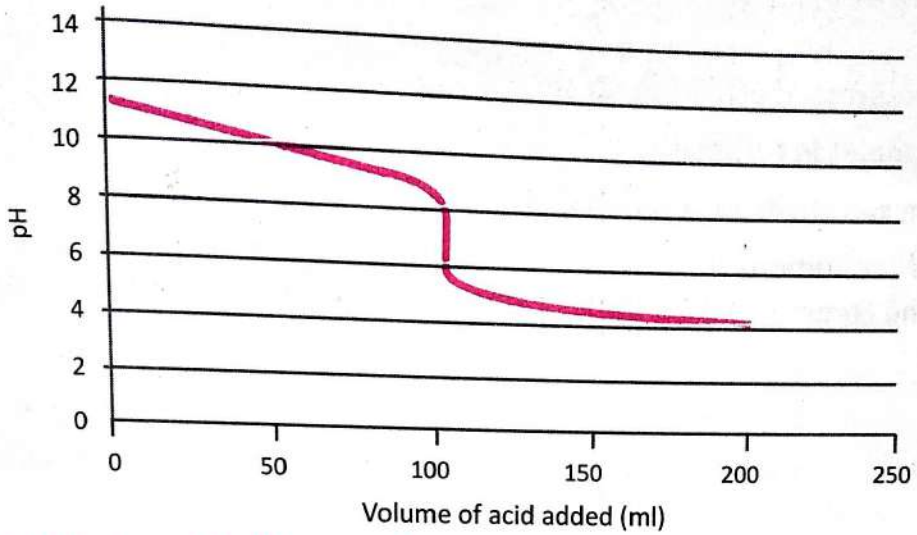
4. Titration of weak base with weak acid:- Acetic acid is weak acid and ammonium hydroxide is a weak base. The chemical reaction between them duribg titration is as follows:-

$$CH_3COOH + NH_4OH \rightarrow CH_3COONH_4 + H_2O$$

The salt formed during reaction is further hydrolysed as follows:-

$$CH_3COONH_4 + H_2O \rightarrow CH_3COOH + NH_4OH$$

If 100ml of 0.1 M ammonium hydroxide solution is titrated with 0.1 M acetic acid solution. The inflection range is between pH 6 to 8. Therefore it is very difficult to detect the end point by indicator method and accurate results are very dificult to obtain. Such sharp end point cannot be detected by simple indicators. Sometimes mixed indicator is used which have sharp colour change at limited pH range. For above titration, neutral red - methylene blue mixed indicator may be used. Neutralization curve obtainded for this titration is as follows:-



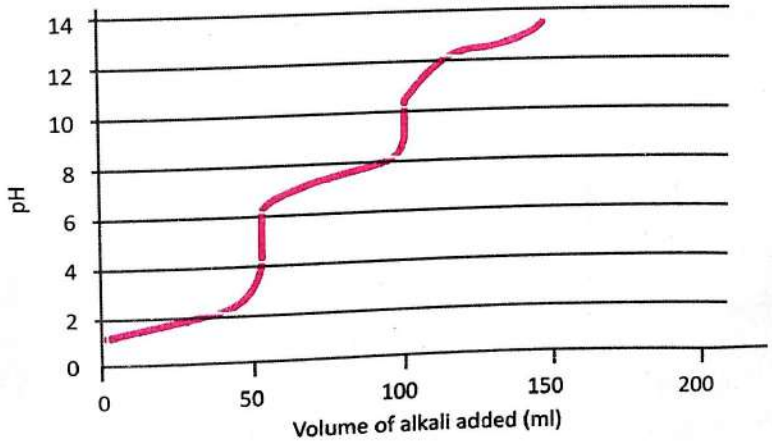
5. Titration of polybasic acid with strong base:- Polybasic acid is and acid whose basicity is more than one or which contain more than one ionizable hydrogen. They are also callled polyproticc solvents. For example, Sulphurous acid and carbonic acid are dibasic while orthophosphoric acid is tribasic acid.

Polyprotic solvent dissociates in stepwise manner and has more than one dissociation constants and behave like mixture of acids. For example, Sulphurous acid is a diprotic acid and dissociated in two steps:-

$$H_2SO_3 \leftrightarrow H^+ + H_2SO_3$$

$$HSO_3^- \leftrightarrow H^+ + SO_3^{2-}$$

In this titration first endpint, is seen at pH 4.58 for which methyl organe indicator is suitable for detection while second end point is detected at pH 10.13 for which thymolphthalein is used. Neutralization curve obtainded for this titration is as follows:-



NEUTRALIZATION CURVES

Neutlization curve represents the neutralization reaction between acid and base in neutralization titration. It is plotted between the pH and volume of acid or base added. Neutalization curve gives following information:-

1. This curve is useful in studying the neutralization process by studying the change in hydrogen ion concentration during titration.

2. It represents the progress of acid base titration.

3. It indicates the endpoint in titration.

4. It also indicates the sensitivity of titration and chances of error.

5. On the basis of pH conditions near inclination point the selection of indicator for particular titration is made.Some commonly used acid base indicators are listed in table below:-

Indicator	Colour		pK_{in}	pH range
	Acid	Base		
Thymol Blue -1st change	Red	Yellow	1.5	1.2-2.8
Methyl orange	Red	Yellow	3.7	3.2-4.4
Bromocresol green	Yellow	Blue	4.7	3.8-5.4
Methyl red	Yellow	Red	5.1	4.8-6.0
Bromothymol blue	Yellow	Blue	7.0	6.0-7.6
Phenol red	Yellow	Red	7.9	6.8-8.4
Thymol blue – 2nd change	Yellow	Blue	8.9	8.0-9.6
Phenolphthalein	Colorless	Pink	9.4	8.2-10.0
Congo red	Blue	Red	-	3.0-5.0

Neutralization curves for different acid base titrations are already described in classification of acid base titrations.

MULTIPLE CHOICE QUESTIONS

Q.1 According to Arrhenius theory base is a substance which give rise _____ when dissolved in water.

a. Hydroxyl ion
b. Hydronium ion
c. Hydrogen ion
d. None of these

Q.2 According Bronsted theory _____ is a substance that can accept protons.

a. Acid
b. Buffer Solution
c. Base
d. Both a and b

Q.3 Which theory is able to explain acid-base bahaviour in non aqueous solvents?

a. Arrhenius theory
b. Common ion effect
c. Bronsted theory
d. None of these

Q.4 _____ are basic in nature and form solvated protons by reacting with acids.

a. Protogenic solvents
b. Protophilic solvents
c. Amphiprotic solvents
d. Aprotic solvents

Q.5 Amphiprotic solvents are both _____ and _____ character.

a. Aprotic, Protophilic
b. Protophilic, Protogenic
c. Protogenic, Aprotic
d. None of these

FILL IN THE BLANKS

1. According to ..... rate of a chemical reaction is proportional to the active masses of the reactive substances.
2. Lesser the pKa ..... is the acid.
3. Hydrolysis can be defined as interaction between the ion of a ..... And ..... .
4. An acid is a substance which can ..... protons.
5. ..... is defined as the negative logarithm of hydroxyl ion concentration.

VERY SHORT ANSWER QUESTIONS

Q.1 Define the following:

a. Acid b. Base c. pH d. Hydrolysis

Q.2 What is the Arrhenius concept?

Q.3 Define amphiprotic and protogenic solvent.

Q.4 What is the Bronsted Lowery Concept?

LONG ANSWER QUESTIONS

Q.1 Explain in detail about the acid base titrations.

ANSWERS

MULTIPLE CHOICE QUESTIONS

1. c 2. c 3. c 4. b 5.b

FILL IN THE BLANKS

1. Low of Mass action 2. Stronger 3. Salt, water 4. Donate 5. pOH.

4 NON AQUEOUS TITRATIONS

INTRODUCTION

Non aqueous titrations are the titrations which are carried out in non aqueous solvents i.e. solvents other than water. Non aqueous titrations are method of choice when reactants or products are insoluble in water, react with water or are too weak acids or bases that cannot be titrated in water due to their poor infliction in pH at end point in water. Commonly used solvents in non aqueous titrations are acetone, glacial acetic acid, formic acid, ethylene diamine, acetic anhydride and chloroform etc.

CONCEPT OF NON AQUEOUS TITRATIONS

Non aqueous titrations are mainly based upon the Bronsted - lowry theory which suggest that an acid is a substance which donates proton while base is a substance which accept proton. This theory is equally applied to non aqueous titrations as in aqueous titrations.

Bronsted - lowry theory states that an acid dissociates in solution to give a proton and form conjugated base and a base combine with the proton from dissociated acid to produce a conjugate acid. An acid donate's proton only when there a base is present to accept this proton or vice-versa.

In reaction below, B^- is the conjugate base of acid HB and proton is only difference between acid and its conjugate base. Any base can combine with this proton to give a conjugate base.

$$\underset{\text{Acid}}{HB} \leftrightarrow \underset{\text{Proton}}{H^+} + \underset{\text{Conjugate base}}{B^-} \quad \text{.....1}$$

Therefore, base B combines with proton and produced conjugate acid of base B.

$$\underset{\text{Base}}{B} + \underset{\text{Proton}}{H^+} \leftrightarrow \underset{\text{Conjugate acid}}{HB^+} \quad \text{.....2}$$

Advantages and disadvantages of non aqueous titrations are listed here under:-

Advantages:-

1. Weak acids and base give poor end points in aqueous titrations but in non aqueous titrations they give good end point.
2. The substances which are poorly soluble in water but soluble in non aqueous organic solvents can be determined by non aqueous titrations.
3. Mixture of two or more acids can be analysed. The individual acid can give separate end point in different solvents.

Disadvantages:-

1. Temperature, moisture and carbon dioxide should be controlled.
2. Solvents used in non aqueous titrations are expensive.
3. Volatile solvents such as Ammonia can pollute solvent.
4. Indicators need to be prepared in non aqueous medium.
5. Some solvents are hazardous if mishandled such as ammonia which if inhaled too much can prove to be fatal.
6. It is not an environment friendly method.

NON AQUEOUS SOLVENTS

Solvent play an important role in non aqueous titration because the solvent supports the dissociation of weak acid or base and alter the behavior of analyte. Non aqueous solvents majorly classified into four types:-

1. Amphiprotic solvents:- These are the solvents which are able to donate as well as accept protons i.e. they posses both protophilic and protogenic properties. Examples of such solvents are water, weak organic acids and alcohols. Let's take an example of acetic acid. Acetic acid act as an acid by dissociation to give protons.

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

While in the presence of a strong acid like perchloric acid it acts as base and accept protons.

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

2. Aprotic solvents:- These are the solvents which are chemically inert and doesn't donate or accept protons therefore they don't have any acidic or basic nature. These type of solvents have low dielectric constant for example toluene,chloroform,benzene and carbontetrachloride.

3. Protophilic solvents:- These are the solvents which have high affinity for protons and are basic in nature. They produce solvated protons by abstracting protons from acids.

$$HB + S \leftrightarrow SH^+ + B^-$$

Acid Solvent Solvated proton Conjugates base

Some examples of protopholic solvents are liquid ammonia, ketones and amines etc.

4. Protogenic solvents:- These are the solvents which readily donate protons and are acidic in nature. Sulphuric acid and hydrogen fluoride are the examples of protogenic solvents.

EFFECTS OF SOLVENTS

In non aqueous titrations, two types of effects of solvents are seen which are:-

1. Leveling effect
2. Differentiating effect

1. Leveling effect:- Weak acids and bases are normally used in the presence of strong protophilic (pyridine, liquid ammonia) and strong protogenic solvents (HF, H_2SO_4) because their strengths are enhanced by these solvents. Weak acid act like strong acid in the presence of strong protophillic solvents as well as weak base act as strong base in the presence of strong protogenic solvents. This effect is called leveling effect and solvents are called leveling solvents.

2. Differentiating effect:- In less basic non aqueous solvent like glacial acetic acid, the dissociation of different acids varies i.e. dissociation of perchloric acid is more as compared to hydrochloric acid. Therefore, in glacial acetic acid perchloric acid act as a strong acid as compared to hydrochloric acid. This effect of differentiating between the strengths of acids is called differentiating effect and the solvents like glacial acetic acid etc, which show this effect are called differentiating solvents.

ALKALIMETRY AND ACIDIMETRY

The terms "alkalimetry" refers to the determination of strength of basic substances by titrating them with a standard acid solution and "acidimetry" refers to the determination of strength of acidic substances by titrating them with a standard base solution. In non aqueous titrations generally weakly acidic and basic substances are determined therefore in non aqueous titrations alkalimetry is defined as titrations of weak bases and acidimetry is defined as titrations of weak acids. These titrations are described here under.

Titration of weak bases:-

Titration of weak bases is done by using mainly perchloric acid as a standard acid. Acetic acid is generally used as the solvent for dissolving weak bases. Weak base dissolved in non aqueous solvent is titrated with standard perchloric acid solution. Reactions involved in the titration can be explained as follows.

When acetic acid is present alone, it behaves as a weak acid as it is poorly dissociated and has very little tendency to donate protons.

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

But on the addition of perchloric acid (which is a strong acid) to acetic acid, Onium ions are formed which have higher tendency to donate protons.

$$HClO_4 \leftrightarrow H^+ + ClO_4^-$$

$$CH_3COOH + H^+ \leftrightarrow CH_3COOH_2^+ \text{ (Onium Ion)}$$

Furthermore, on addition of pyridine (which is a weak base) to acetic acid, following reaction occurs:

$$C_5H_5N + CH_3COOH \leftrightarrow C_5H_5NH^+ + CH_3COO^-$$

Acetate ions produced have higher tendency to accept protons. Thus, accurate end point is generated on titrating a weak base in acetic acid using perchloric acid as the titrant.

Set of reactions taking place are:-

$$HClO_4 + CH_3COOH \leftrightarrow CH_3COOH_2^+ + ClO4^- \quad .....(1)$$

$$C_5H_5N + CH_3COOH \leftrightarrow C_5H_5NH^+ + CH_3COO^- \quad .....(2)$$

$$CH_3COOH_2^+ \text{ (from 1)} + CH_3COO^- \text{ (from 2)} \leftrightarrow 2CH_3COOH$$

Final reaction comes out to be.

$$HClO_4 + C_5H_5N \leftrightarrow C_5H_5NH^+ + ClO_4^-$$

From these reactions, it can be concluded that tendency of acid to donate proton is increased while tendency of base to accept a proton is increased leading to accurate and sharp end point.

Titration of weak acids:-

Titration of weak acids such as barbiturates, benzoic acid etc can be done using bases like alkali methoxides (sodium methoxide, potassium methoxide, lithium methoxide) or tetrabutylammonium hydroxide etc. Non aqueous solvents used in titration are ethylenediamine, Dimethyl formamide (DMF) etc. Reactions taking place during titration of benzoic acid in dimethyl formamide with sodium methoxide is as follows.

On dissolving benzoic acid in Dimethyl formamide (DMF), following reaction takes place.

$$C_6H_5COOH + H\text{-}CON(CH_3)_2 \leftrightarrow HCON + H(CH_3)_2 + C_6H_5COO^- \quad .....1$$

Ionization of sodium methoxide takes place as follows.

$$CH_3ONa \leftrightarrow CH_3O^- + Na^+ \quad .....2$$

From reaction 1 and 2 above,

$$HCON^+H(CH_3)_2 + CH_3O^- \rightarrow HCON(CH_3)_2 + CH_3OH$$

Final reaction comes out to be.

$$C_6H_5COOH + CH_3ONa \rightarrow C_6H_5COONa + CH_3OH$$

ESTIMATION OF SODIUM BENZOATE

Sodium benzoate is a white, crystalline or granular powder or flakes. It is hygroscopic in nature and mainly used as pharmaceutical aid (preservative).

PRINCIPLE:- Sodium benzoate is a base and is dissolved in glacial acetic acid. During the titration with strong acid, acetic acid behave like a base and accurate end point is determined. End point is detected by using 1-naphtholbenzein solution as an indicator.

PROCEDURE:-

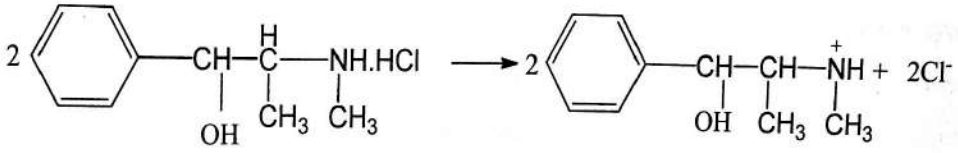
1. Weigh accurately about 0.25 g of sodium benzoate and transfer it in a conical flask.
2. Add 20 ml anhydrous glacial acetic acid and dissolve with the help of sonicator. Warm to 50°C if needed.
3. Add 2 drops of 1-naphtholbenzein indicator solution.
4. Then fill the burette with standardized solution of perchloric acid.

5. Start titration with the perchloric acid solution until reach the endpoint.
6. Record the reading of burette.
7. Repeat the titration three times to get precise readings.
8. Take mean of them and calculate percentage purity of sodium benzoate.
9. Repeat the titration similarly according to above procedure without sodium benzoate for blank determination.
10. Equivalent factor of sodium benzoate for 0.1 M perchloric acid solution is 0.01441.

ESTIMATION OF EPHEDRINE HYDROCHLORIDE

Ephedrine hydrochloride is a sympathomimetic and bronchodilator and is now used for mild bronchial asthma as well as for hypotension during spinal anesthesia.

PRINCIPLE:- Chloride anion present in ephedrine hydrochloride is a weak proton acceptor. This chloride ion is replaced with acetate ion with the addition of mercuric acetate. Acetate ions have higher tendency to accept proton which gives accurate end point when titrated against the acid like perchloric acid. Known amount of ephedrine hydrochloride is titrated with perchloric acid in glacial acetic acid and end point is detected by using methyl orange solution as an indicator. Reaction involved in this titration is as follows.



Ephedrine HCl — Protonated ephedrine — Chloride ion

$(CH_3COO)_2Hg + 2Cl^- \longrightarrow HgCl_2 + 2CH_3COO^-$

Mercuric acetate — Mercury (1) chloride (undissociated) — Acetate ion

$2CH_3COOH_2^+ + 2CH_3COOH^- \rightleftharpoons 4CH_3COOH$

Onium ion — Acetate ion — Acetic acid

PROCEDURE:-

1. Weigh accurately about 0.17 g of ephedrine hydrochloride and transfer it in a conical flask.
2. Dissolve in 10 ml of mercuric acetate solution by warming gently and add 50 ml of acetone, mix well.
3. Add 2 drops of methyl orange solution as indicator.
4. Then fill the burette with standardized solution of perchloric acid.
5. Start titration with the perchloric acid solution until reach the endpoint. Record the reading of burette.

6. Repeat the titration three times to get precise readings. Take mean of them and calculate percentage purity of ephedrine hydrochloride.
7. Repeat the titration similarly according to above procedure without ephedrine hydrochloride for blank determination.
8. Equivalent factor of ephedrine hydrochloride for 0.1 M perchloric acid solution is 0.02017.

REVIEW QUESTIONS

MULTIPLE CHOICE QUESTIONS

Q.1 Non aqueous titrations are based on:

a. Arrhenius theory
b. Lewis theory
c. Bronsted-Lowry theory
d. None of These

Q.2 Weakly acidic and weakly basic substances analysed by which titration method?

a. Aqueous titration
b. Non aqueous titration
c. Redox titration
d. Complexometric titration

Q.3 Given the following are indicators for non-aqueous titration except:

a. β-Naphtholbenzoin
b. Oracet blue B
c. Crystal violet
d. Complexometric titration

FILL IN THE BLANKS

1. Titration of .....Weak base..... is done by using perchloric acid.
2. Acetic acid, water and alcohol are the examples of .....Amphiprotic Solvents.....

SHORT ANSWER QUESTIONS

Q.1 Explain the followings:

a. Protophilic Solvents b. Protogenic Solvents
c. Amphiprotic Solvents d. Aprotic Solvents

Q.2 Give the list of some indicators used in non aqueous titration.

LONG ANSWER QUESTIONS

Q.1 Explain the scope and limitation of non aqueous titration.

ANSWERS

MULTIPLE CHOICE QUESTIONS

1.c 2.b 3.a

FILL IN THE BLANKS

1.Weak base 2. Amphiprotic solvents.

5 PRECIPITATION TITRATIONS

INTRODUCTION

Precipitation titrations are the titrations that involves the formation of precipitate. However the used of precipitation titrations is limited as compared to other titrimetric methods due to lack of suitable indicators and slow rate of reaction in dilute solutions. Silver nitrate is most important and mainly used precipitating agent and titrations which use silver nitrate as a precipitating agent is called argentimetric titrations. Precipitation titration is a method of choice when suitable indicator is available, there is no co-precipitation, analyte and reagent show stiochiometric relationship and as well as rate of reaction is fast for the analyte under examination.

CONCEPT OF PRECIPITATION TITRATIONS

Precipitation titrations are mainly based on the principle of solubility product. Solubility product can be explained by following example.

Consider that the solution of a slightly soluble salt i.e. BA is in equilibrium with its solid phase BA and represented as follows.

$$\underset{\text{(solid)}}{BA} \leftrightarrow \underset{\text{(solution)}}{B^+ + A^-}$$

By applying the law of mass action we get.

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

In the presence of undissolved solid BA concentration of BA in solution remains constant. Therefore,

$$K \times \text{constant} = [B^+][A^-]$$

$$= S_{BA}$$

Here S_{BA} is the solubility product of salt BA which remains constant at constant temperature. Some times S_{BA} also represented as K_{BA}.

At equivalence point in the precipitation titrations, the concentration of ions is given by the square root of solubility product. i.e. $\sqrt{S_{BA}}$. The sharpness of titration curve in precipitation titrations is depends upon the concentrations of solutions used as well as solubility product of precipitate. lesser the solubility product more accurate the titration will be.

For example:- Silver nitrate is most important and mainly used precipitating agent in precipitation titrations. When 100ml of 0.1M Sodium Chloride is titrated with 0.1M silver nitrate, various changes in ionic concentration takes place is described as follows.

$$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$$

Solubility product of AgCl at room temperature is 1.2×10^{-10}

At the start, concentration of chloride ions $[Cl^-]$ is 0.1mol L^{-1} or $pCl^- = 1$.

When 50ml of 0.1M silver nitrate (AgNO3) have been added, 50 ml of 0.1M sodium chloride (NaCl) remain in a total volume of 150ml. At that point concentration of chloride ions will be.

$[Cl^-] = 50 \times 0.1 / 150 = 3.33 \times 10^{-2}$ or $pCl^- = 1.48$ 1

When 90 ml of silver nitrate solution have been added, then concentration of choride ion will be.

$[Cl^-] = 10 \times 0.1/190 = 5.3 \times 10^{-3}$ or $pCl^- = 2.28$ 2

Now

$$a_{Ag^+} + a_{Cl^-} \approx [Ag^+][Cl^-] = 1.2 \times 10^{-10} K_{sol(AgCl)} \quad ....3$$

$$pAg^+ + pCl^- = 9.92 = pAgCl \quad .....4$$

but from equation (1), $pCl^- = 1.48$. Put this in equation (4)

$$pAg^+ + 1.48 = 9.92$$

$$pAg^+ = 9.92 - 1.48 = 8.44 \quad .....5$$

Based on the above calculations, various concentrations of chloride and silver ions can be calculated before reaching the equivalence point.

At the equivalence point i.e. at the end point:

$$Ag^+ = Cl^- = K^{1/2}{}_{sol(AgCl)}$$

$$pAg^+ = pCl^- = \tfrac{1}{2}\, pAgCl = 9.92/2 = 4.96$$

At the end point, a saturated solution of silver chloride is present with no excess of silver or chloride ions are present.

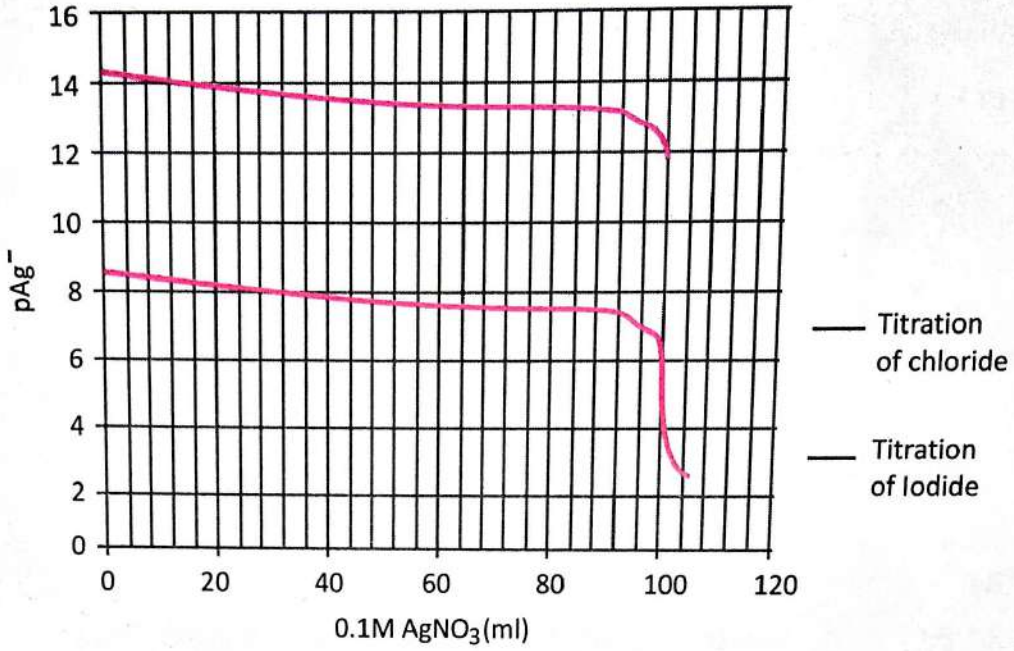
With 100.1ml of silver nitrate solution, $[Ag^+] = 0.1 \times 0.1/200.1 = 5 \times 10^{-5}$,

$$So\ pAg^+ = 4.30;\ pCl^- = pAgCl^- - pAg^+ = 9.92 - 4.30 = 5.62$$

The values calculated in this way up to the addition of 110 ml of 0.1M silver nitrate are tabulated in the Table 2.1. Similar values for the titration of 100 ml of 0.1M potassium iodide with 0.1M silver nitrate are also tabulated table below. ($K_{sol(AgI)} = 1.7 \times 10^{-16}$)

Volume of 0.1M $AgNO_3$ (ml)	Titration of chloride		Titration of Iodide	
	pCl^-	pAg^+	pI^-	pAg^+
0	1.0	-	1.0	-
50	1.5	8.4	1.5	14.3
90	2.3	7.6	2.3	13.5
95	2.6	7.3	2.6	13.2
98	3.0	6.9	3.0	12.8
99	3.3	6.6	3.3	12.5
99.5	3.7	6.2	3.7	12.1
99.8	4.0	5.9	4.0	11.8
99.9	4.3	5.6	4.3	11.5
100.0	5.0	5.0	7.9	7.9
100.1	5.6	4.3	11.5	4.3
100.2	5.9	4.0	11.8	4.0
100.5	6.3	3.6	12.2	3.6
101	6.6	3.3	12.5	3.3
102	6.9	3.0	12.8	3.0
105	7.3	2.6	13.2	2.6
110	7.6	2.3	13.5	2.4

The silver ion exponents closer to the equivalence point show that there is a marked change in the silver ion concentration and the change is more prominent for silver iodide than for silver chloride, since the solubility product of the silver chloride is about 106 larger than the solubility of the silver iodide. This is shown more clearly by the titration curve below which represents the change of pAg+ in the range between 10% before and 10% after the stoichiometric point in the titration of 0.1M chloride and 0.1M iodide with 0.1M silver nitrate. An almost identical curve s obtained by potentiometric titration using silver electrode; the pAg^+ values may be calculated from the e.m.f figures as in the calculation of pH.



MOHR'S METHOD

In mohars method, halides can be determined by titrating with $AgNO_3$ using K_2CrO_4 as an indicator and formation of colored precipitate takes place.

Silver nitrate is titrated directly against sodium chloride and form white precipitate silver chloride with sodium nitrate.

$AgNO_3$	+	NaCl	→	AgCl ↓	+	$NaNO_3$
Silver nitrate		Sodium chloride		Silver chloride (white ppt)		Sodium nitrate

When all the chlorides of sodium chloride is consumed. It reacts with potassium chromate and end point can be detected with appearance of brick red colour due to formation silver chromate along with potassium nitrate.

$AgNO_3$	+	K_2CrO_4	→	Ag_2CrO_4 ↓	+	$2KNO_3$
Silver nitrate		Potassium chromate		Silver chromate (Brick red colour)		Potassium nitrate

In the precipitation titration, precipitation of indicator must be take place near the equivalence point. When $AgNO_3$ solution is added to the solution containing Cl^- ions as well as CrO_4^{-2}. Chloride ions react first and when all the chloride ions are precipitated then the reaction of CrO_4^{-2} ions take place and Ag_2CrO_4 is produced. Equilibrium in this method is represented as follows.

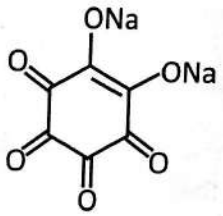
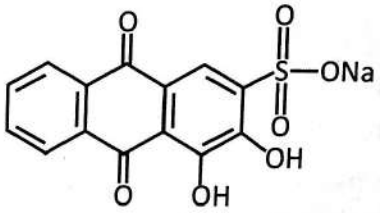
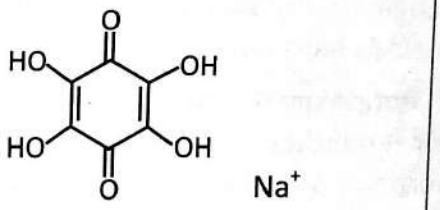
Ag^+	+	Cl^-	=	AgCl (white)	$K_{sp} = 1.0 \times 10^{-10}$
$2Ag^+$	+	CrO_4^{2-} (yellow)	=	Ag_2CrO_4	$K_{sp} = 1.7 \times 10^{-12}$

Under Optimum Conditions, Mohr's method is accurate and applicable at low Cl^- concentration. Mohr's Method is also used in water analysis.

While choosing colour indicator, following precaution must be taken:

1. Solubility of Colour indicating precipitate must be more than the main precipitate formed during the titration.
2. In addition to this, it should not be too soluble as this will lead to need of more reagents.

Indicators used in Mohr's method are listed in table below:-

Indicator Name	Structure
Sodium Rhodizonate	
Sodium Alizarine sulphonate	
Sodium Salt of Tetrahydroxyquinone	

VOLHARD'S METHOD

In this, Silver salt is titrated with NH_4SCN using ferric alum as indicator. During the titration AgSCN is formed while at the end point, excess NH_4SCN reacts with Fe(III) to form deep red $[FeSCN]^{2+}$.

A precipitate of silver thiocyanate (K_{sp} = 7.1 × 10^{-13}) is produced on addition of thiocyanate solution.

Reactions involved are:

$$Ag^+ + SCN^- \leftrightarrow AgSCN$$

When even a slightest excess of thiocyanate is present, a reddish brown coloration is produced due to the formation of a complex ion. This shows that the reaction is complete and end point is reached.

$$Fe^{3+} + SCN \leftrightarrow [FeSCN]^{2+}$$

Standard silver nitrate solution is added in excess and the excess is back titrated with standard thiocyanate solution. Determination of chlorides, bromides and iodides can be done in acid solution. When chloride estimation is done, following two equilibria are obtained during the titration of excess of silver ions:

$$Ag^{+} + Cl^{-} \leftrightarrow AgCl$$
$$Ag^{+} + SCN^{-} \leftrightarrow AgSCN$$

The two sparingly soluble salts will be in equilibrium with the solution, so

$$\frac{[Cl^{-}]}{[SCN^{-}]} = \frac{K_{sol(AgCl)}}{K_{sol(AgSCN}} = \frac{1.2 \times 10^{-10}}{7.1 \times 10^{-13}} = 169$$

After the excess of silver has reacted, silver chloride may react with thiocyanate, as silver thiocyanate is the less soluble salt, until the ration of ($[Cl^{-}]/[SCN^{-}]$ in the solution is 169:

$$AgCl + SCN^{-} \leftrightarrow AgSCN + Cl^{-}$$

This produces significant titration error as this reaction takes place before the reaction occurs with the iron (III) ions in the solution. So, it is very important to prevent the reaction between thiocyanate and the silver chloride. This can be done in following ways:-

1. Before back titrating, filter off the silver chloride. As the precipitates will be contaminated with adsorbed silver ions at this stage, so the suspension must be boiled for a few minutes to coagulate the silver chloride before filtering. This removes most of adsorbed silver ions from its surface before filtration. Then the cold filtrate is titrated.

2. Potassium nitrate is added as a coagulant after adding silver nitrate. Then suspension is boiled for 3 minutes, cooled and titrated immediately. This leads to desorption of silver ions and Read sorption on cooling is prevented by the presence of potassium nitrate.

3. Silver chloride particles are coated using an immiscible liquid such as nitrobenzene to protect silver chloride particles from interaction with the thiocyanate.

MODIFIED VOLHARD'S METHOD

Volhard's method is mainly used for determination of chlorides and it is subjected to manu modifications time to time. In volhard'c method there is a need of filtration before back titration for the removal of precipitated silver chloride and it has another disadvantage that volhard's method give fading end point when silver chloride is not removed because silver chloride is more soluble than silver thiocyanate. Caldwell J.R. and Moyer V.H. found that nitrobenzene forms an insoluble layer over the precipitate as the result of this silver chloride does not interfere in thiocyanate titration. Addition of nitrobrnzene improves the end point.

Method:- 50 ml of 0.206 g silver chloride free from interfering ions is acidified with 8 to 10 drops of concentrated nitric acid. Then add 1ml of nitrobenzene for each 0.05g of chloride. Add

standard silver chloride solution to an excess of 1 to 5 ml. Shake well for 30 seconds. Then add 1 ml ferric alum indicator and titrate with standard potassium thiocyanate solution.

FAJAN'S METHOD

Fajan's method is based on the use of Adsorption indicators. Adsorption indicators are adsorbed by the precipitates and during the process of adsorption change occurs in the indicator which leads to a substance of different colour. Hence they are termed as adsorption indicators.

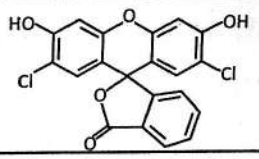
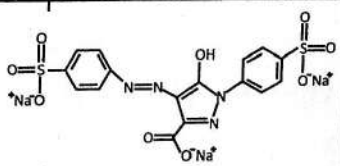
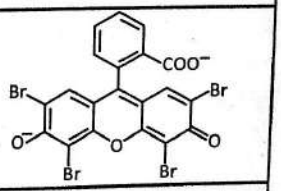
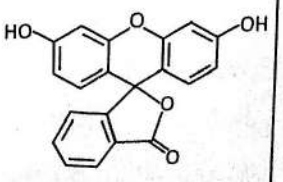
They are of two types:-

Acid dyes (for example Eosin, fluorosin) Used in Na salts.

Basic dyes (Rhodamine series as halides)

Method:- 0.1N NaCl or KCl is prepared as standard solution. Silver nitrate solution is used as titrant. Standard NaCl solution is put in the conical flask along with few drops of dichlorofluorescein indicator and 0.1 g of dextrin. Dextrin is added to prevent coagulation of colloidal silver chloride. Silver nitrate is added till the colour of the solution changes to definite pink colour. The color is reversible and back titration is possible with a standard NaCl Solution.

Indicators used in Fajan's method are listed in table below:-

Name of Indicator	Uses	Experimental Conditions	Colour Change at end point	Structure
Dichlorofluorescein	Cl-.Br-,with Ag+	pH range 4.4 to 7	Yellow green →red	
Tartrazine	Ag+ with I- or SCN-; I- + Cl-; excess Ag+,back titration with I	Sharp colour change in I- + Cl- , back titration	Colourless →green	
Fluorescein	Cl-.Br-,I- with Ag+	Neutral or weakly basic solution	Yellow green→pink	
Tetrabromo fluorescein(eosin)	Br-,I- with Ag+	Ethanoic acid solution	Pink? red violet	

ESTIMATION OF SODIUM CHLORIDE (MOHR'S METHOD)

PRINCIPLE:- Silver nitrate is titrated directly against sodium chloride and form white precipitate silver chloride with sodium nitrate.

$$\underset{\text{Silver nitrate}}{AgNO_3} + \underset{\text{Sodium chloride}}{NaCl} \longrightarrow \underset{\text{Silver chloride (white ppt)}}{AgCl\downarrow} + \underset{\text{Sodium nitrate}}{NaNO_3}$$

When all the chlorides of sodium chloride is consumed. It reacts with potassium chromate and end point can be detected with appearance of brick red colour due to formation silver chromate along with potassium nitrate.

$$\underset{\text{Silver nitrate}}{AgNO_3} + \underset{\text{Potassium chromate}}{K_2CrO_4} \longrightarrow \underset{\text{Silver chromate (Brick red colour)}}{Ag_2CrO_4\downarrow} + \underset{\text{Potassium nitrate}}{2KNO_3}$$

PROCEURE:-

1. Take 10 ml of sodium chloride (sample) solution in a conical flask.
2. Add 2 to 3 drops of potassium chromate solution as an indicator.
3. Then fill the burette with standardized silver nitrate solution.
4. Start titration with the silver nitrate solution until reach the endpoint.
5. Record the reading of burette.
6. Repeat the titration three times to get precise readings.
7. Take mean of them and calculate the percentage purity of sodium chloride.
8. Equivalent factor of sodium chloride for 1 ml of 0.1 M silver nitrate is 0.005845.

MULTIPLE CHOICE QUESTIONS

Q.1 Which method is based on precipitation of adsorption indicators?

a. Fajan's method b. Mohr's metho
c. Volhard's method d. None of These

Q.2 Which method is used in water analysis?

a. Fajan's method b. Mohr's method
c. Volhard's method d. None of These

Q.3 Adsorption indicators work best when:

a. They do not precipitate out silver ion when the indicators are at low concentration

b. They bind to the precipitate only when excess silver ion is present to produce colour

c. They do not precipitate out silver ion when the indicators are at low concentration

d. Both a and b

FILL IN THE BLANKS

1. Halides can be determined by titrating with AgNO3 using Na_2CrO_4 as an indicator.
2. Argentometric titrations involve addition of silver nitrate to form the precipitates of an insoluble silver salt.

SHORT ANSWER QUESTIONS

Q.1 Explain the followings:

a. Precipitation titration

b. Argentometric titration

c. Solubility product

Q.2 Give the limitation of argentometric titrations.

LONG ANSWER QUESTIONS

Q.1 Describe in details the influence of:

a. Acid

b. Temperature

c. Solvent

Q.2 Explain in detailed about the following precipitation reactions, namely:

a. Volhard's method

b. Mohr's method

c. Gay-Lussac's method

d. Fajan's method.

ANSWERS

MULTIPLE CHOICE QUESTIONS

1. a 2.b 3.d

FILL IN THE BLANKS

1. Na_2CrO_4 2. Argentometric titrations.

6 COMPLEXOMETRIC TITRATIONS

INTRODUCTION

Complexometric titration involves titration between metal ions and complexing agent or chelating agent (Ligand). This titration is based on the analytical mechanism of a complexation reaction. In this method, an ion is changed into a complex ion and the equivalence point is determined with the help of metal indicators or electrometrically. An EDTA (disodium edetate) is a popular complexing agent or chilon. The chilons react with metal ions to form a special type of complex known as chelate.

CONCEPT OF COMPLEXATION AND CHELATION

According to the International Union of Pure and Applied Chemistry (IUPAC), ***"chelation involves the formation or presence of two or more separate coordinate bonds between a polydentate (multiple bonded) ligand and a single central atom".*** These ligands are organic compounds called chelating agents, chelants, chelators or sequestering agents.

Chelates are also called electron donating ion or molecule which can form one or more covalent or co-ordinate bonds with metal ions. The complex are formed by the reaction of a metal ion with an anion or a neutral molecule or a positive ion very rarely. The complex formed differs in properties from that of metal ion.

The groups attached to the central cation or a metal is called a ligand. Complexing agent forming a single bond is called unidentate and called as a co-ordination compound. If complexing agent forms more than one bond with the polyvalent ion, then is said to be polydentate ligand and called as chelating ligand.

If complex formed between complexing agent and metal is soluble in water, it is called as sequestering agent.

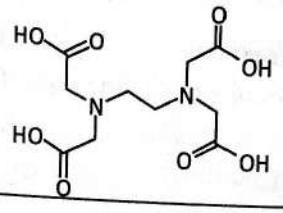
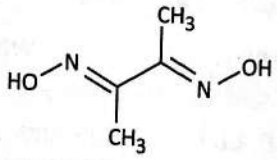
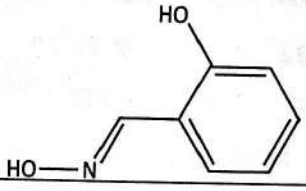
Complexing agents are of different types:

1. Neutral molecules: Neutral molecules having lone pair of electron also act as complexing agent. Example: Ammonia forms cuprammonium complex with copper $[Cu(NH_3)_4]^{2+}$
2. Groups whose proton can be easily replaced such as –COOH, phenolic, and enolic OH
3. Sequestring agents having groups like COOH, SO_3H, NH_2 and OH.

Example of chelating agents:- Dimethylglyoxime and salicylaldoxime

Example of sequestering agents:- Ethylene Diamine Tetra Acetic Acid (EDTA)

Structures of some complexing agents are listed in table below:-

Name of complexing agent	Structure
EDTA (Ethylenediamine tetra acetic acid	
Dimethylglyoxime	
Salicylaldoxime	

CLASSIFICATION OF COMPLEXOMETRIC TITRATIONS

Complexometric titrations can be classified as follows:-

1. Direct Titration: In this type of titrations, the sample solution of metal ion, in the presence of a suitable buffer, is titrated against standard disodium edetate solution. Metal indicators such as Mordant red 7 are used in these titrations which show change in colour at the end point. Precipitation of metal hydroxide is prevented by adding some auxillary complexing agent. At the equivalence point the concentration of metal ion decreases abruptly. A blank titration is also carried out using the blank solution without adding analyte. Blank titration is one in which all the components of the main titration are added but analyte is not added. The volume of edetate consumed in the blank titration is subtracted from the original estimation.

Examples of substances estimated by direct titrations:

Magnesium salts such as magnesium carbonate, bismuth salts such as bismuth nitrate, calcium salts such as calcium chloride, zinc salts such as zinc oxide etc.

2. Back Titration: Sometimes direct titration is not possible because of various reasons such as:-

1. Insolubility of substance e.g. lead sulphate, calcium oxalate.
2. Stability of complex being very low.
3. Precipitation of metal hydroxide in alkaline solution of buffer.
4. Due to slow reactivity with the sodium edetate.

For above problems back titration is a method of choice. In this titration, a known excess of disodium edetate along with buffer solution and indicator solution is added. Heating of the solution is done which promotes complex formation. Then it is cooled and excess edetate is back titrated using magnesium sulphate or zinc sulphate.

Example of substances which are back titrated: aluminium hydroxide gel, dried aluminium hydroxide gel, calcium phosphate, alum.

3. Replacement Titrations: when both back titration and direct titration is not possible because of end point not being sharp enough. Then the replacement titration is a method of choice. In this, determination of metal ion is done by displacing magnesium or zinc ions from EDTA complex with an equivalent amount of metal ion and then liberated magnesium or zinc ions are titrated against edetate. Example:

Calcium salt is determined in this way. In this, add standard volume of Magnesium-EDTA solution to calcium salt in the presence of buffer. Calcium displaces magnesium ion and forms a stable complex with EDTA as Calcium-EDTA complex. The displaced and liberated magnesium ions are then titrated with standard EDTA solution using Mordant black as indicator.

$$Ca2^{+} + \text{Mg-EDTA} \rightarrow \text{Ca-EDTA} + Mg^{2+}$$

$$Mg^{2+} + EDTA^{2-} \rightarrow \text{Mg-EDTA}$$

Cadmium, Lead and mercury can also be determined by this titration.

4. Alkalimetric titrations of metals: Metal-EDTA complex formation reaction explains that protons are liberated from disodium edetate leading to formation of acid.

$$M^{+} + H_4Y \rightarrow MY + 4H^{+}$$

The acid that is formed can be titrated against a standard alkali but in **an unbuffered solution.** End point detection can be done by using acid base visual indicator or potentiometric method of detecting end point.

Neutralisation of the solution of metal has to be done before carrying out this titration.

METAL ION INDICATORS

A number of metal ion indicators are used in complexometric titrations. Metal ion indicatorcan itself act as chelating agent. But their metal complexes have different colour from the reagents themselves. They are called metallochromic indicators. Based on the concentration of metal ions, these indicators change their colour which indicate the end point of the titration. These are also called **pM indicators**

pM is the negative logarithm of metal ion concentration and can be represented as:

$$pM = -\log [M]$$

the value of pM can be derived from stability constant equation as follows:

$$K = [MX]/[M][X]$$

$$\text{Then , } [M] = [MX]/[X]\ K$$

Take log on both sides, then

$$\text{Log } [M] = \text{Log } ([MX]/[X]) - \text{Log } K$$

$$pM = \text{Log } ([X]/[MX]) - pK$$

When [X] = [MX] which means that there is equal activity of metal ion and complex,

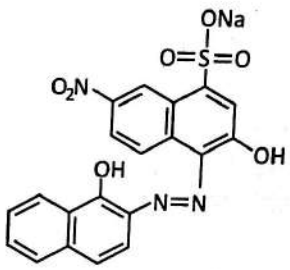
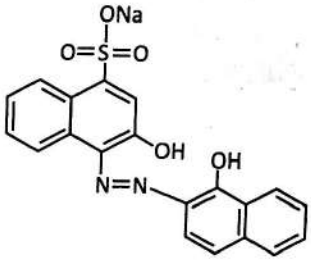
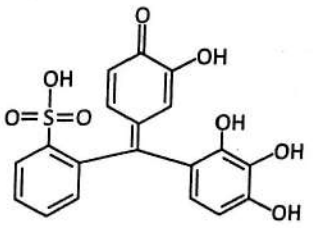
So pM = -pK

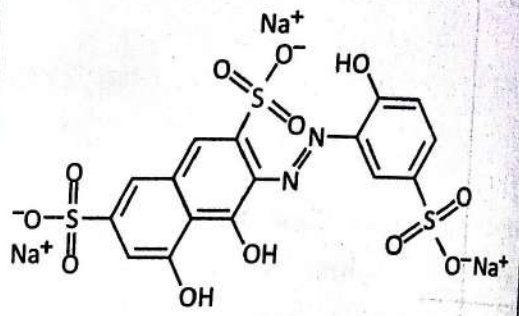
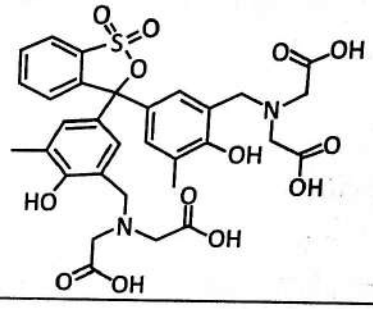
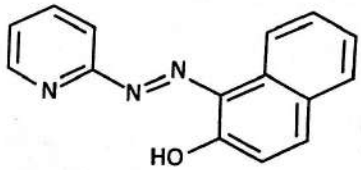
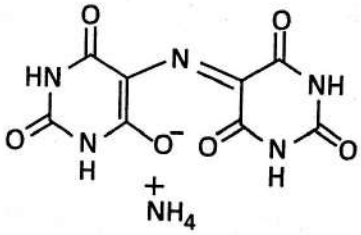
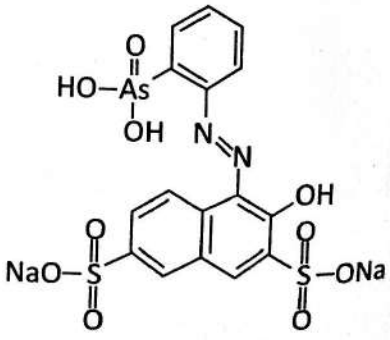
or pM = pK'

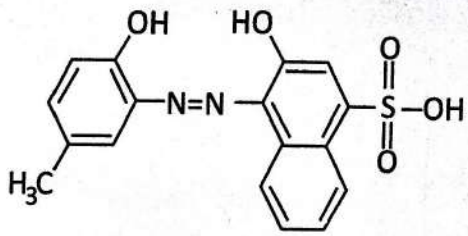
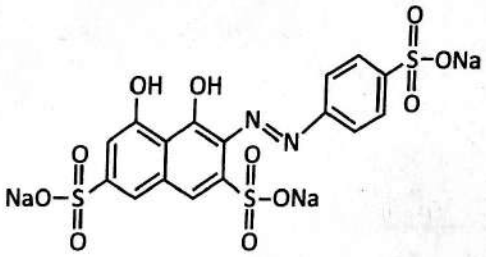
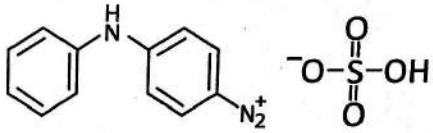
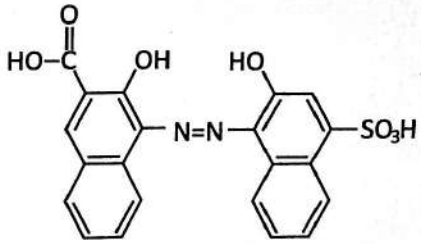
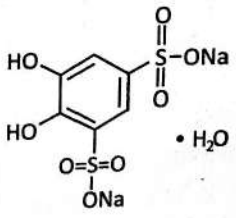
where K' = -K

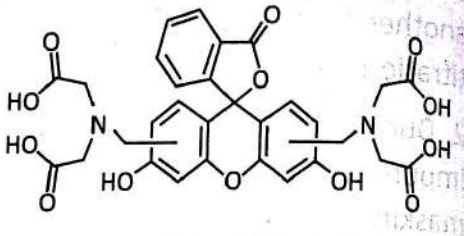
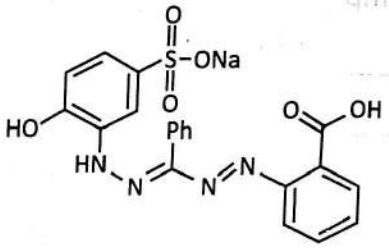
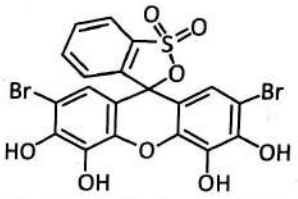
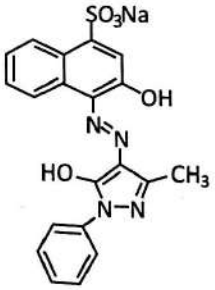
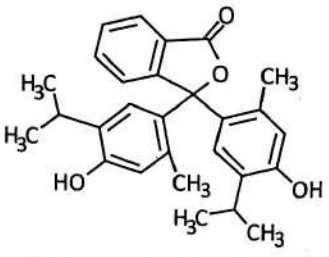
The choice of indicator depends upon its stability. The indicator should be half complexed and half free at pM value. **So pM value can also be defined as value when 50% of the metallochromic indicator is complexed and 50% is in free form.**

Table : Metallochromic indicators

S.NO.	Name of Metallochromic indicator	Structure
1	Eriochrome black T	
2	Eriocchrome blue black B	
3	Pyrocatechol violet	

4	Acid chrome blue	
5	Xylenol orange	
6	1-(2-Pyridylazo)-2-naphthol	
7	Murexide	
8	Thorin	

9	Calmagite	
10	SPADNS (Sulfanilic acid azochromotrop)	
11	Variamine Blue	
12	Patton reeder's dye (Calconcarboxylic acid)	
13	Tiron	

14	Calcein	
15	Zincon	
16	Bromopyrogallol red	
17	Eriochrome red	
18	Thymolpthelin	

MASKING AND DEMASKING AGENTS

Masking may be defined as a process in which a substance is so altered that it does not take part in the reaction without any physical separation of the same substance. On the contrary, **demasking** is the process in which masked substance reverts back to its ability to take part in the reaction.

Need of Masking and Demasking agents:-

1. A masking agent can be used to carry out determination of a metal ion in the presence of another metal ion without the latter intervening in the reaction. Masking can be used for the titration of a substance in a mixture.

2. During the titration of a metal ion using EDTA, EDTA may form complexes with some of the impurities also. So this will give wrong reading. Thus, these impurities can also be masked using masking agent.

Examples of Masking Agents:

Table : Masking agents with their use

Name of Masking agent	Metals that can be masked
Triethanolamine	Aluminium, Iron
Thioglycerol	Copper
Potassium Cyanide and Sodium cyanide	Heavy metals
Ammonium Fluoride	Iron,Aluminium

Examples of Demasking Agent:-

Formaldehyde-acetic acid solution is a demasking agent that is used to damask cyanide complexes of zinc and cadmium.

$$[Zn(CN)_4]^{-} + 4H^{+} + 4HCHO \rightarrow Zn^{++} + 4HO.CH_2\text{-}CN$$

This can be done by 3 methods:-

1. Addition of precipitants:- Precipitating agents can be used to precipitate some of the interfering ions. These ions are precipitated and then separated and estimated individually.

   For example: oxalate used in the precipitation of interfering ions such as lead or calcium, ferrocyanide used in the precipitation of interfering ions zinc and copper.

2. Addition of complexing agents:- Some complexing agents form complexes with the interfering ions which are more stable complexes than EDTA complexes. So these ions do not interfere in the titration of main ion.

   For example:- Ascorbic acid and ferrocyanide used as complexing agent to complex ferric ion , Tiron complexing agent used to complex Aluminium or titanium ion,Triethanolamine complexing agent used to complex Aluminium and iron .etc.

3. pH control: pH changes can be used to eliminate interference in the titration by any impurity. For example: EDTA complexes are unstable below pH 7 but Tin (Sn^{4+}), Iron (Fe^{3+}), Cobalt (Co^{3+}) and Thorium (Th^{4+}) complexes are stable between pH 3 to 7.

ESTIMATION OF MAGNESIUM SULPHATE

PRINCIPLE:- Magnesium sulphate is titrated directly against disodium edetate in the presence of strong ammonia-ammonium chloride solution. End point is detected by mordant black II mixture as an indicator. Reaction involved in this titration is as follows.

Mg^{2+}	+	EDTA	⟶	Mg - EDTA	+	$2H^{+}$
Magnesium ion		Disodium edetate		Magnesium - disodium edetate complex		

PROCEDURE:-

1. Weigh accurately about 0.3 g of magnesium sulphate in a conical flask and dissolve in 50 ml of distilled water.
2. Add 10 ml of strong ammonia-ammonium chloride solution.
3. Add 2 drops of mordant black II mixture as an indicator.
4. Then fill the burette with standardized disodium edetate solution.
5. Start titration with the disodium edetate until reach the endpoint.
6. The approach of the endpoint is suggested by the change of pink colour to blue.
7. Record the reading of burette. Repeat the titration three times to get precise readings.
8. Take mean of them and calculate the percentage purity of magnesium sulphate.
9. Equivalent factor of magnesium sulphate for 1 ml of 0.05 M disodium edetate is 0.00602.

ESTIMATION OF CALCIUM GLUCONATE

PRINCIPLE:- This is a replacement titration. Magnesium forms complex with mordant black II mixture indicator which shows first colour.

Mg^{2+}	+	In^{-}	⟶	Mg - In
Magnesium ion		Indicator		Magnesium- Indicator complex (coloured1)

Magnesium-indicator complex is much more stable than calcium-indicator complex therefore calcium has not any effect on magnesium-indicator complex. On titration against disodium edetate complex of calcium and disodium edetate is formed.

Ca^{2+}	+	EDTA	⟶	Ca - EDTA
Calcium ion		Disodium edetate		Calcium - disodium edetate complex

When calcium is totally consumed, next drop of disodium edetate breaks the magnesium-indicator complex and make complex with magnesium by liberating free indicator. End point is detected by observing second colour at that time.

Mg - In	+	EDTA	⟶	Mg - EDTA	+	In^{-}
Magnesium- Indicator complex (coloured1)		Disodium edetate		Magnesium - disodium edetate complex		Free indicator (coloured 2)

PROCEDURE:-

1. Weigh accurately about 0.5 g of calcium gluconate in a conical flask and dissolve in 50 ml of warm water.
2. Allow to cool.
3. Add 5 ml of 0.05 M magnesium sulphate.
4. Add 10 ml of strong ammonia-ammonium chloride solution.
5. Add 2 drops of mordant black II mixture as an indicator.
6. Then fill the burette with standardized disodium edetate solution.
7. Start titration with the disodium edetate until reach the endpoint.
8. Record the reading of burette. Repeat the titration three times to get precise readings.
9. Take mean of them and calculate the percentage purity of calcium gluconate.
10. Repeat the titration again using same procedure without calcium gluconate for blank reading.
11. Equivalent factor of calcium gluconate for 1 ml of 0.05 M disodium edetate is 0.02242.

MULTIPLE CHOICE QUESTIONS

Q.1 Which one is the masking agent for complexometric titration with EDTA?

a. CN-1 b. Buffer c. Indicator d. All of these

Q.2 Which masking agent is used for masking the aluminium and iron?

a. Thioglycerol b. Aluminium fluoride

c. Potassium cyanide d. Triethanolamine

FILL IN THE BLANKS

1. ..... having one pair of electron also act as complexing agent.
2. The number of small groups which can be attached to the central atom in a complex is called ..... and it is denoted by ..... .
3. Stability complex is based on ..... .

SHORT ANSWER QUESTIONS

Q.1. Define the followings:

a. Ligand b. Complexometric titration c. Chelation

Q.2 Give the list of indicators used in complexometric titration.

LONG ANSWER QUESTIONS

Q.1 Discuss the neutralization curve for strong acid v/s strong base titration and show how pH changes during the titration.

Q.2 Discuss the various types of titration curves obtained in acid –base titration.

Q.3 Explain in detail about the various types of complexometric titration.

Q.4. Explain in detail about the metal ion indicator with appropriate examples?

Q.5 Write a short note on followings:

a. Masking agent b. Demasking agent

ANSWERS

MULTIPLE CHOICE QUESTIONS

1.a 2.d

FILL IN THE BLANKS

1. Neutral molecules 2. Werner's coordination number 3. Low of mass action, K.

7 GRAVIMETRY

INTRODUCTION

Gravimetric methods are quantitative methods that are based on determining the mass of a pure compound to which the analyte is chemically related.

Or

Gravimetric analysis is the quantitative isolation of a substance by precipitation and the Analytical of the precipitate.

CLASSIFICATION OF GRAVIMETRIC METHODS

1. Precipitation Gravimetry
2. Particulate Gravimetry
3. Volatilization Gravimetry
4. Electrogravimetry

This is a classical method which have no need of any calibration while it is used for the calibration of instrumental methods.

PRINCIPLE AND STEPS INVOLVED IN GRAVIMETRIC ANALYSIS

Chosen precipitation method must precipitate the element or ion in a form which has very low solubility to prevent any loss of precipitate when it is separated from the mother liquor by filtration and weighed.

Sometimes the constituent being determined is different from the precipitate. For example, in the determination of magnesium, it is precipitated in the form of ammonium magnesium phosphate ($Mg(NH_4)PO_4.6H_2O$) but then it is converted into magnesium pyrophosphate ($Mg_2P_2O_7$) by igniting in a crucible at 1000-1100°C.

Following factors govern success of the method chosen for precipitation:-

1. The precipitate produced must be insoluble in the mother liquid to prevent any loss when it is filtered and weighed. Practically, the quantity of precipitate remaining in the mother liquid should be less than 0.1mg which is the lower limit that can be weighed buy an analytical balance.
2. Precipitate must have a physical nature in such a way that it can be easily separated from the solution by filtration.
3. Precipitate must be inert to the washing liquid. It should be able to be washed free of soluble impurities.
4. Particle size of the precipitates must remain unaffected by the use of washing liquid.
5. The precipitate must be capable of being converted into a pure substance of definite chemical composition. This can be achieved by ignition or by simple chemical operation such as evaporation.

The process of **precipitation** takes place in 3 steps:-

1. Supersaturation:- The amount of substance that can be dissolved in a known weight of the solvent at a given temperature in a given solvent is called **solubility of a substance.** Solubility is decreased on increasing the particle size of the solute. The solution that contains greater concentration of solute than that corresponding to equilibrium solubility at a given temperature is called **supersaturated solution.** When a reagent is added to an analyte solution forming a sparingly soluble substance, it exceeds the solubility product of sparingly soluble compound which leads to solution becoming supersaturated. Particle size and filterability of the precipitate is dependent on extent of supersaturation of the solution.

2. Nucleation:- When a more stable phase is formed from the metastable phase of supersaturation, it is called nucleation. In this, primary nuclei of submicroscopic dimensions is formed by the aggregation of collection of small ions or molecules.

3. Precipitate Particle Growth:- Further growth of particles of precipitate continues after the nucleation. In this, small ions or molecules come together to form larger precipitate particles.

Relative rate of particle growth and nucleation rate governs the physical nature of precipitated particles. Particle growth can be affected by following ways:-

1. When nucleation rate is more than particle growth rate, more number of nuclei formed and leads to formation of smaller particles. Thus, a colloidal precipitate will be produced with particle size in the range of 10-7 – 10-5 cm. Colloidal precipitates do not settle down and are not filterable.

2. When particle growth rate is more than the nucleation rate, precipitates having larger particle size with particle diameter above 10-3cm are formed. These precipitates settle down easily and can be easily filtered off.

Digestion of precipitates:- On allowing the precipitate to stand in presence of liquid from which it is originally precipitated, large crystals grow at the cost of small ones. This process is called Digestion or Ostwalds ripening. In this process, small particles get dissolved and reprecipitated on the surface of larger crystals. Furthermore, individual particles come together to agglomerate and share a common counter ion layer. Thus these individual particles combine together to form large crystals.

Higher temperatures are usually used to speed up the process of digestion, whereas room temperature can also be used in some cases.

Digestion has following of advantages:

1. Dissolving and reprecipitation of smaller crystals to form larger crystals leads to decrease in surface area of crystals. Thus decreasing coprecipitation and facilitating filtration

2. Rapidly formed precipitates are irregular and have more surface area. Digestion converts the irregular precipitates with more surface area into regular, dense, crystalline particles having lesser surface area. This decreases adsorption co-precipitation.

Washing of precipitates:- Gravimetric precipitates need to be washed to remove any impurities that may have been precipitated along with the main precipitate. Washing liquid should be inert to the main precipitate. Washing liquid must be volatile enough to be evaporated at the drying temperature. Mostly used washing liquids are dilute aqueous solutions of electrolytes containing a common ion with the precipitate so as to minimize the solubility of precipitate in washing liquid and to prevent peptization i.e. dispersion of the precipitate back to colloidal state which poses difficulty in filtration. Ammonium salts are mostly favoured as they are volatile at most drying temperatures.

Example of washing liquid: Dilute ammonium oxalate solution is used to wash calcium oxalate precipitate. Another example is dilute ammonium nitrate used to wash iron hydroxide precipitate. Acidified Hydrogen sulphide is used to wash the precipitate, when the precipitate is susceptible to air oxidation such as in case of copper sulphide.

Filtration of precipitates:- The process of separating the precipitate from the parent liquid is called filtration. The primary aim is to get the precipitate and the filtering medium quantitatively free from the solution. Various systems used for filtration are:

1) Filter paper

2) Porous fitted plates made of resistance glass, e.g. Pyrex (sintered glass filtering crucibles), of silica (Vitreosil filtering crucibles), or made of porcelain (porcelain filtering crucibles). The choice of filter is governed by the nature of precipitate and the cost.

Drying/ignition and wighing of precipitates:- Drying is the term used when temperature is below 250°C and ignition above 250°C and below 1200°C.

Adsorbed water, occluded water, sorbed water and water of hydration may be present in the precipitates. Based on the knowledge of chemical properties of the substances, ignition temperatures are selected. Heating should be uniform and continued till constant weight is obtained. The weight of filter paper ash should also be accounted. Thermogravimetric curve can be used to ascertain the suitable drying temperature.

Drying is possible for precipitates filtered on filter paper, Gooch crucible, sintered glass or porcelain crucibles. Ignition is done by placing the crucible in muffle furnace or by using appropriate burner.

After drying the crucible and precipitate are placed in a desiccator for 30 minutes and weighed. The heating cooling and Analytical operation is repeated until two successive weights do not differ by a limited value.

PURITY OF PRECIPITATE

Several types of impurites are generally incllude in the precipitation mainly during its formation. Impurities or contaminants that can affect the purity of precipitate can be prevented by using various precautions. Purity of precipitate can be interfered mainy by two processes:-

1. Coprecipitation
2. Post precipitation

COPRECIPITATION

In this, soluble impurities also get included in the precipitate during the process of precipitation and it leads to increase in the mass of precipitate.

Different types of coprecipitation are:-

1. Adsorption:- Adsorption is dependent on surface area of particles of the precipitate. In this kind of coprecipitation, formation of colloidal particles always takes place at the initial stages and lead to growth of particle into larger sized coarse particles progressively. As particle size of colloidal particles is very small, so they have large surface area which facilitates adsorption of different types of ions/impurities in the primary layer. These ionic impurities of primary layer along with the counter ion layer precipitate along with the main precipitate. Crystalline precipitates with large sized crystals have lower incidence of surface adsorption. Washing of the colloidal particles have to be done to remove adsorbed impurities.

2. Mixed crystal contamination:- In this type of coprecipitation, substitution in the precipitate lattice of main precipitate by the impurity ions of similar crystallinity takes place. For example: Mixed crystal contamination in the precipitation of barium as barium sulphate in the presence of lead ions. Isomorphic substitution of K^+ for NH_4^+ in $MgNH_4PO_4$ also leads to coprecipitation. Mixed crystal contamination type of coprecipitation can take place in both colloidal and crystalline precipitates.

Remedy to prevent mixed crystal contamination:- Mixed crystal contamination can be prevented by separating the analyte from the contaminating ions before the precipitation process.

3. Occlusion:- In this, formation of precipitate takes place when foreign ions in the counter ion layer get trapped within the rapidly growing crystal.

Remedy to prevent occlusion:- occlusion can be prevented by keeping the rate of precipitation process as low as possible and degree of supersaturation also low. Digestion of precipitates also prevents occlusion.

4. Mechanical entrapment of non-isomorphic substances:- when a number of crystals growing together come close to each other, a portion of solution gets entrapped in the pockets between the crystals.

Remedy to prevent Mechanical entrapment on non-isomorphic substances:- Mechanical entrapment of non-isomorphic substances can be prevented by keeping the rate of precipitation process as low as possible and degree of supersaturation also low. Digestion of precipitates also prevents this coprecipitation.

POST PRECIPITATION

In this, an impurity having low solubility gets deposited on the surface of analyte (main) precipitate during the formation of analyte precipitate. Impurity has same properties as that of the analyte precipitate. For example: during the precipitation of calcium oxalate, magnesium oxalate impurity gets deposited on it. Though calcium oxalate precipitates out alone acceptably in the presence of magnesium ions, but if precipitates are kept for long time in contact with the solution containing magnesium ions, than magnesium oxalate deposits on the calcium oxalate precipitate.

Remedy to prevent post precipitation:- Filter off calcium oxalate precipitates within the first hour of precipitation.

ESTIMATION OF BARIUM SULPHATE

PRINCIPLE:- Precipitates of barium sulphate are crystalline in nature and losses due to solubility are negligible.

Precipitant used: 2N H_2SO_4 or 5% K_2SO_4.

Usually $BaCl_2.2H_2O$ solution is preferred to $Ba(NO_3)_2$ for the precipitation of Ba as $BaSO_4$. Digestion of precipitates is need to increase the particle size of the particles of the precipitates and to prevent to coprecipitation of anions NO_3^-, ClO_2^- and bivalent,trivalent cations particularly Fe(III). The precipitate of BaSO4 in the presence of carbon from filter paper is reduced to BaS at 600æ%C. Then, precipitate is removed from the filter paper as much as possible and the burnt ash is treated with conc. HCl and conc. H_2SO_4 in turn to convert BaS into $BaSO_4$

Ignition:- $BaSO_{4\,(s)} + 4C\text{(filter paper)}\,(s) \rightarrow BaS_{(s)} + 4CO_{(g)}$

$BaS + 2HCl\ (conc.) \rightarrow BaCl_2 + H_2S$

$BaCl_2 + H_2SO_4\ (conc.) \rightarrow BaSO_4 + 2HCl$

PROCEDURE:-

1. Take 25 ml of barium chloride in a beaker.
2. Add 80 ml water and 5ml of 1N HCl.
3. Heat to 80-90°C and dropwise add 2N H_2SO_4 solution.
4. Thick precipitate of $BaSO_4$ is formed.
5. Continue adding 2N H_2SO_4 and precipitate is allowed to settle down.
6. Then test for complete precipitation is done by adding few drops of 2N H_2SO_4 in the supernatant liquid.
7. The precipitate is digested for about 30-40 minutes on a low flame.
8. Then whatman filter paper 42 is used to filter the precipitates.
9. Precipitates are then washed with hot water and test for absence of Cl^- and SO_4^{2-} ions in last washings is done.
10. Now whole of the precipitate is transferred to the paper.
11. Dry the precipitates and keep them safely.
12. Filter paper is incinerated and ash is collected in a previously weighed crucible.
13. Add one drop of conc. HCl and evaporate it.
14. Then add one drop of conc. H_2SO_4 and heat till the fuming ceases.
15. Then the crucible is heated strongly for about 15 mins so that contents of the crucible become white.
16. Now the precipitates of $BaSO_4$ are transferred to the crucible and heated again.
17. Then crucible is cooled and weighed. This process is repeated until a constant weight is obtained.

Gravimetric factors:

$$BaSO_4 \equiv Ba\,SO_4^{2-} \equiv BaCl_2.2H_2O \equiv CuSO_4.5H_2O \equiv Na_2SO_4$$

$$233.42 \equiv 137.36 \equiv 96.06 \equiv 244.3 \equiv 249.70 \equiv 142.06$$

REVIEW QUESTIONS

MULTIPLE CHOICE QUESTIONS

Q.1 Given the following are properties of good precipitate except:

a. Easily filtered and washed free of contaminants.
b. Significant loss of the analyte occurs during filtration and washing.
c. Unreactive with constituents of the atmosphere
d. Both a and b

Q.2 ..... analyte is separated from a solution of the sample as a precipitate and is converted to a compound of known composition.

a. Volatilization gravimetry
b. Precipitation gravimetry
c. Electrogravimetry
d. Precipitation Point

FILL IN THE BLANKS

1. Precipitation gravimetry, the ..... is converted to a sparingly soluble precipitate.
2. The amount of substance that can be dissolved in a known weight of the solvent at a given temperature in a given solvent is called .....

VERY SHORT ANSWER QUESTIONS

Q.1 Define the following

a. Coprecipitation b. Post precipitation c. Superstturation

Q.2 What is organic precipitants:

LONG ANSWER QUESTIONS

Q.1 What is Colloidal State? Enumerate the properties of colloidal particles.
Q.2 Give the difference between lyophobic colloid and lyophilic colloid.
Q.3 What do you mean by coprecipitation? Explain the types of coprecipitation.
Q.4 Define digestion or ostwalds ripening and give its significance in gravimetric analysis.
Q.5 Give the applications of gravimetric techniques in the quantitative determination of:
a. Calcium ion – as Calcium Oxalate
b. Magnesium ion – as Magnesium Pyrophosphate
c. Aluminium Ion – as Aluminium Oxide

ANSWERS

MULTIPLE CHOICE QUESTIONS

1. b 2. b.

7A DIAZOTIZATION TITRATIONS

Compounds that possess primary aromatic amino groups can be estimated quantitatively by using diazotisation titrations. Sodium nitrite solution is required to convert them into diazonium salt in the presence of cold acid (HCL), therefore they are also known as sodium nitrite titrations. However, drugs that contain acetyl, succinyl, phthalyl and nitro groups are converted to amino groups by hydrolysis and reduction, and then they are estimated.

Principle

Aromatic amino group is reacted with sodium nitrite in cold acid solution to form diazonium salts.

$$C_6H_5NH_2 + NaNO_2 + HCl \longrightarrow C_6H_5N_2Cl + NaCl + 2H_2O$$

The addition of sodium nitrite to hydrochloric acid causes formation of nitrous acid. Nitrous acid diazotises the aromatic amino group. At the end point, excess nitrous acid is formed and observed by formation of deep blue colour with starch iodide paper.

$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$

Starch iodide paper is prepared by immersing a filter paper in starch mucilage and potassium iodide solution.Colour change of indicator paper is due to following chemical reaction.

$$KI + HCl \longrightarrow KCl + HI$$

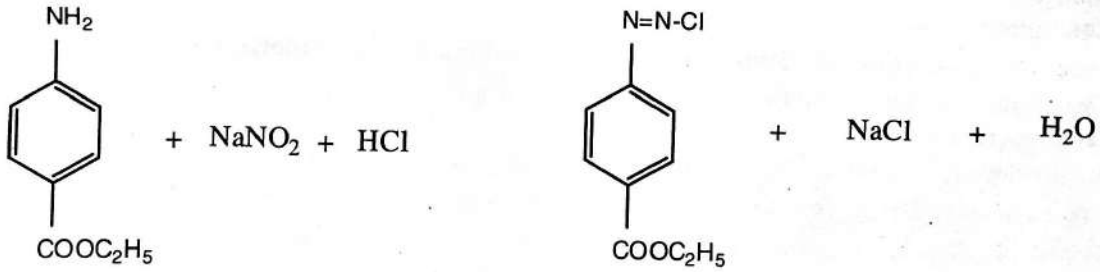
$$2HI + 2HNO_2 \longrightarrow I_2 + 2NO + 2H_2O$$

Iodine formed reacts with mucilage to give blue colour.

External indicator like starch iodide paper sometimes make difficult to locate end point. In such cases amperometric titrations can be utilized. In amperometric method, a pair of platinum electrodes is immersed in the titration liquid. Polarisation of electrode occurs when a small voltage (30-50 mV) is applied across the electrodes and no current flows galvanometer included in the circuit. At the end point, liberation of excess nitrous acid depolarizes the electrode and current starts flowing through the galvanometer and known as dead stop end point.

Note: Electrodes must be clean; otherwise end point may be delayed.

Benzocaine is a local anaesthetic and can be determined by using diazotization titrations.



Preparation and standardisation of 0.1M Sodium nitrite solution:

Dissolve 7.5 g of sodium nitrite in sufficient water to produce 1000ml. Take 0.5 g of previously dried sulphanilamide in 100 ml beaker. Add 50ml of water and 20ml of hydrochloric acid. Stir to dissolve and cool at 15° C. Then contents in beaker are titrated against 0.1M sodium nitrite solution.

Note: Each ml of 0.1M sodium nitrite solution Ξ 0.01722 g of sulphanilamide.

Assay procedure of diazotisation titrations

Dissolve specified amount of drug in 50ml water and 20ml HCl. Stir to dissolve and cool at 15° C. Mixture is titrated against 0.1M sodium nitrite solution. End point can be determined by using external indicator i.e. starch iodine paper or by using amperometric dead stop end point technique by using platinum electrodes.

Types of Diazotisation titrations

There are three types of techniques which are employed in diazotisation titrations.

1. **Direct titration:** In case of direct titration, One mole of drug is treated with three moles of concentrated HCl. Temperature is lowered to 4° C by using ice or ice cold solution externally to the reaction mixture. Titration is carried out by using 0.1M sodium nitrite. End point can be detected by external indicator or by amperometricdead stop end point technique.
2. **Reverse method:** This method is employed when resulting diazonium salt is insoluble like napthylaminesulphonic acid. Zwitter ions are formed in such cases, which are difficult to solubilise. In those conditions, amine solution is first treated with sodium nitrite and resulting solution is run into HCl solution.
3. **Special method:** In case of aminophenols, direct method cannot be used because on treatment with sodium nitrite they form quinones, which are highly unstable. Therefore, titration is not possible to carry out. In such conditions, reaction is carried out in the presence of copper sulphate which forms a stable diazo oxide and diazo coupling reaction then easily carried out.

Applications of Diazotization titrations

A. Analysis of drugs carried out by direct titration method.
   1. Dapsone
   2. Benzocain
   3. Primaquine phosphate and its tablets
   4. Procainamide HCl and its injection
   5. Procaine HCl
   6. Sodium amino salicylate, tablets and granules
   7. Suramin
   8. All sulpha drugs that contains free aromatic amino group i.e. Sulphapyridine, Sulphacetamide sodium, Sulphdioxine, Sulphadimethoxine, Sulphadiazine, Sulphaguanidine, Sulphadimidine, Sulphaphenazole, Sulphamethizole, Sulphalene, Sulphamethoxazole and Sulphamethoxypyridazine.

B. Analysis of drugs carried out by conversion of amino group by chemical reaction.
   a. **By reduction:**Drugs containing nitro group can be reduced to aromatic amino group by using reducing agent. This primary aromatic amino group can be diazotised by using nitrite solution. Example: Metronidazole, Secnidazole and Chloramphenicol.
   b. **By hydrolysis:** Drugs containing derivatives of amino groups like acetyl, phthalyl or succinyl cab be hydrolysed to get free amino group and then titrated with nitrite solution. Example: Paracetamol (Acetyl derivative), Phthalylsulphathiazole (Pthalyl derivative) and Succinylsulphathiazole (Succinyl derivative).

MULTIPLE CHOICE QUESTIONS

Q.1Compounds possess ..... can be estimated quantitatively by using diazotisation titrations.

a. Primary aromatic amino groups b. Secondary aromatic amino groups
c. Tertiary aromatic amino groups d. Primary chlorogroups

Q.2 Aromatic amino group is reacted with .....in cold acid solution to form diazonium salts.

a. Sodium peroxide b. Sodium nitrite
c. Silver nitrite d. Sodiumhydroxide

Q.3.....method is employed when resulting diazonium salt is insoluble like napthylaminesulphonic acid.

a. Reverse method b. Direct method
c. Indirect method d. Special method

Q.4 At the end point in diazotization titration, excess .....is formed and observed by formation of deep blue colour with starch iodide paper.

a. Hydrochloric acid b.Sulphuric acid
c. Phosphoric acid d. Nitrous acid

FILL IN THE BLANKS

1. ..... can be analysed by direct titration method.
2. Temperature is lowered to ..... by using ice or ice cold solution externally to the reaction mixture in diazotization titrations.
3. This primary aromatic amino group can be diazotised by using .....solution.
4. Starch iodide paper is prepared by immersing a filter paper in starch mucilage and .....solution.

VERY SHORT ANSWER QUESTIONS

Q.1 What are diazotisation titrations?
Q.2 Which methods are employed in end point determination in diazotisation titrations?
Q.3 What is the principle involved in diazotization titrations?

LONG ANSWER QUESTIONS

Q.1 Explain principle, assay procedure and types of diazotization titrations?
Q.2 Give detail about the applications of diazotization titrations.

ANSWERS

MULTIPLE CHOICE QUESTIONS

1. a 2. b 3. a 4. d

FILL IN THE BLANKS

1. Dapsone 2. 4° C 3.Nitrite 4.Potassium iodide

8 REDOX TITRATIONS

INTRODUCTION

Redox titrations involve gain or loss of electrons. Oxidation involves loss of electrons and reduction involves gain of electrons. Both of these occur simultaneously in a redox system. There are several oxidising and reducing agents. For example: cerric ammonium sulphate is an oxidizing agent and titanous chloride is a reducing agent.

Generally, a redox titration can be expressed as:

$$\text{Oxidized form} + ne^- \leftrightarrow \text{Reduced form}$$

The redox potential of such redox system can be measured by using the redox solution as one half cell and reference electrode as the other half cell. When normal hydrogen electrode is used as reference electrode, the potential of the system is the redox potential. The redox potential is the potential at which there is equal concentration of the oxidized form and reduced form. This redox potential differs for every pair of oxidized or reduced form. E.g.

Ferric/ Ferrous - +0.77V, $Cr_2O^{2-}_7/Cr^{3+}$ - 1.36V.

For selection of redox indicators for the titrations, a knowledge of redox potential is required.

CONCEPTS OF OXIDATION AND REDUCTION

Redox titration involves the change in valency or oxidation states of reactants. Oxidation and reduction are takes place simultaneously in redox titration reaction. One substance is oxidized and other is reduced at a time.

Oxidation can be defined in following terms:-

a. Addition of oxygen:-

$$SO_2 + O \longrightarrow SO_3$$

b. Removal of hydrogen:-

$$H_2S + O \longrightarrow H_2O + S$$

c. Loss of electrons:-

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

The substance which loses electrons and get itself oxidized is called reducing agent. Some common reducing agents are antimony trioxide, ferrous sulphate, sodium thiosulphate, stannous chloride, oxalic acid etc.

Reduction can be defined in following terms:-

a. Addition of hydrogen:-

$$C_2H_2 + 2H \longrightarrow C_2H_4$$

b. Removal of oxygen:-

$$CuO + 2H \longrightarrow Cu + H_2O$$

c. Gain of electrons:-

$$Cl_2 + 2e^- \longrightarrow 2\,Cl^-$$

The substance which gain electrons and get itself reduced is called oxidizing agent. Some common oxidizing agents are potassium permanganate, potassium dichromate, potassium bromate, potassium iodate etc.

A system containing an oxidant and its reduced form is called **redox system.** For example: A solution containing Fe^{3+} ions (oxidant) and Fe^{2+} ions (reduced form of Fe^{3+}ions). If an inert electrode such as a platinum electrode, is dipped into such a solution, it acquires a certain potential called **redox potential** which is given by following equation:-

$$E_{redox}=E^{\circ}_{redox} + RT/nF \log_e a_{ox}/a_{red}$$

here,

E_{redox} = redox potential of the system

E°_{redox} = standard redox potential of the system

R = gas constant

T = Absolute temperature

n = number of electrons gained by a molecule of the oxidant in gettingconverted into the reductant

F = Faraday (96, 500 coulombs)

a_{ox} = activity of the oxidant

a_{red} = activity of the reductant

For dilute solution activity is replaced by concentration of the oxidant and reductant:

$$E_{redox}= E^{\circ}_{redox} + RT/nF \log_e [Ox] / [Red]$$

REDOX REACTIONS

Redox Reaction is a process involving the transfer of electrons from one element or ion to another resulting in the change of the valency of reacting atoms or ions.

When a change in the valency of reacting elements or ions takes place in the chemical processes, it is called redox reactions. The number of electrons which are taken up by an atom

or given up by an atom during reaction with other elements is known from the valency of an element. Depending on the compound in which element is available, the valency of some elements varies e.g. iron can be bivalent or trivalent (in $FeCl_2$, $FeCl_3$ respectively), the manganese can have valencies from 2 to 7 (MnO, MnO_2, Mn_2O_3, Mn_2O_7). To conclude, atoms or ions of different elements can give different number of electrons depending upton the reaction. When an atom looses electrons , it gets oxidized, and leads to increase in th positive valency or decrease in the negative valency of an element.

When an atom gains electrons, it undergoes reduction and leads to increase in the negative valency of an element and decrease in the positive valency of an element. Example: conversion of $FeCl_3$ to $FeCl_2$

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

In above reaction, iron gains one electron resulting in the decrease in the positive valency of the iron from +3 to +2.

Oxidising agents are those which themselves get reduced while they help in the oxidation of the other substance. Oxidizing agents get reduced and leads to decrease in their positive valency. Example: halogens, $KMnO_4$

Reducing agents are those which themselves get oxidized while they help in the reduction of the other substance. Reducing agents get oxidized and leads to increase in their positive valency. Example: $FeCl_2$, H_2S.

HALF REACTIONS

In acid-base titrations, an acid is a proton donor and a base is a proton acceptor. The acid-base properties of a conjugate pair are not possible in absence of a second conjugate pair. Transfer of a proton takes place from one conjugate pair to another in acid-base reactions. Similarly, in redox reactions, two half reactions must be involved , each half reaction includes a redox conjugate pair and the net result of redox reaction will be transfer of one or more electrons from one pair to the other.

Half reaction of a redox reaction can be written as:

$$\text{Reducing agent} \leftrightarrow \text{oxidizing agent} + n$$

Where,

n = number of electrons

Two half reactions take place simultaneously,one to accept electrons and one to liberate electrons. Example:

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

$$2I^- \leftrightarrow I_2 + 2e^-$$

$$H_2 \leftrightarrow 2H^+ + 2e^-$$

Redox indicators

Indication of end point of titration is based upon either visual method or instrumental technique. These are:

1. Self indicator:

The reagent which itself shows change in color due to redox reaction is called self indicator and redox reactions that employing that reagents do not need any indicator for end point detection. For example: Potassium permanganate shows end point by imparting pink colour to the solution while iodine shows brown colour.

2. External indicator:

In external indicator, few drops of the titration solution is removed periodically from the flask and placed on a white tile after which it is mixed with indicator showing colour change depicting the end point. In this indicator chances of error is much. This method is utilised rarely due to end point error. For example: Ferrous ions gives deep prussian blue colour with potassium ferricyanide.

3. Internal indicator:

In internal indicator, few drops of indicator are added to the titrand which shows the end point by changing its colour. These are compounds which have characteristic colours in the oxidised and reduced state. Their oxidation and reduction is reversible. For example: Ortho-phenanthroline ferrous ion has red colour in the reduced form. When few drops of this indicator are added to $K_2Cr_2O_7$ solution, its reduced form will be oxidised by $K_2Cr_2O_7$ and the solution will become blue which is the colour of the oxidised form:

$$[Fe(C_{12}H_8N_2)_3]^{2+} - e^- \rightarrow [Fe(C_{12}H_8N_2)_3]^{3+}$$

reduced form (red) oxidised form (blue)

If to this solution an excess of $FeSO_4$ solution is added, this oxidised indicator is reduced so the solution again become red. This reaction of oxidation and reduction is reversible:

$$In_{ox} + ne \leftrightarrow In_{red}$$

Here, In_{ox} and In_{red}, are oxidised and reduced forms of the indicator.

4. Instrumental techniques:

With the help of potentiometer and conductometer, the end point of titration is determined.

In potentiometry, a platinum electrode is used as indicator electrode and saturated calomel electrode as reference electrode. An e.m.f scale is used for getting the accurate end point. While in conductometry, a pH scale is used .

TYPES OF REDOX TITRATIONS

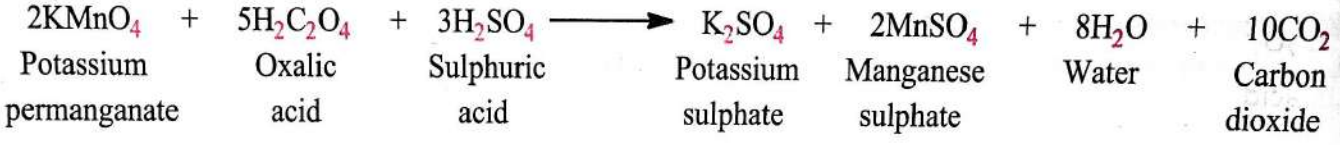
Redox titrations are mainly classified in six major types on the basis of oxidant or reductant used and they are.

1. Permangnametry

2. Dichrometry
3. Cerimetry
4. Iodimetry and iodometry
5. Bromatometry
6. Titrations with potassium iodate

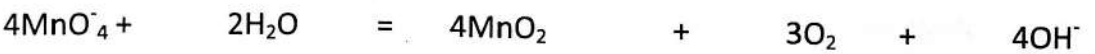
1. Permangnametry:- Potassium permanganate is a very powerful oxidising agent and is widely employed in various redox titrations. It is also used as a self indicator due to its intense colour. The titration which employs potassium permanganate as an oxidising agent is called permanganametry.

Principle:- Potassium permanganate is used in redox titrations by standardizing it with a primary standard like oxalic acid therefore it in not a primary standard. Potassium permanganate acts as an strong oxidizing agent in acidic medium that oxidizes oxalic acid into carbon dioxide. Known strength of oxalic acid is titrated directly with potassium permanganate. End point can be detected with appearance of permanent pink colour, potassium permanganate acts as self indicator. Reaction involved in this titration is as follows.



Standardization of potassium permanganate (0.1 N):- Take 20 ml of prepared oxalic acid solution (0.1 N) in a conical flask. Add 5 ml of sulphuric acid (1 M). Warm the mixture to about 70°C. Then fill the burette with potassium permanganate solution. Start titration with the potassium permanganate solution until reach the endpoint. Record the reading of burette. Repeat the titration three times to get precise readings. Take mean of them and calculate normality of potassium permanganate solution.

Limitation:- The major problem in permangnametry is that, it is difficult to get potassium permanganate in pure form and completely free from manganese dioxide. Ordinary distilled water contain some organic impurities that are reducing substances and formed manganese dioxide. Manganese dioxide catalyses the decomposition of potassium permanganate as follows.



and permanganate is unstable in the presence of manganese (II) ions.

Remedy:- Potassium permanganate solution when prepared it is heated on a water bath for 1 hour, allowed to stand for 2 days and filter it through a funnel containing plug of glass wool. It stored in dark coloured bottle to protect from sunlight.

Applications:- Various applications of permangnametry are listed here under.

1. It is used for the assay of hydrogen peroxide.

2. Permanganmetry is readily used for the determination of nitrates and perchlorates.
3. Assay of ferrous sulphate and ferrous ammonium sulphate can be performed by permangnametry.
4. Etamsylate is a haemostatic which can be determined by permangnametry.
5. Malic acid determination in chertty jiuce can be done by permangnametry.
6. Determination of calcium as calcium oxalate can be done by permangnametry.

2. Dichrometry:- The titration involving potassoum dichromate as an oxidising agent is known as dichrometry. Potassium dichromate is however less powerful oxidizing agent as compare to potassium permanganate having redox potential 1.33 V. But it has some advantages i.e. it is readily available in pure form, thermaly stable, has idefinite shelf life and is less expensive. Therefore is used as a primary standard.

Principle:- Potassium dichromate reduced rapidly at ordinary temperature in acidic medium to form a green chromium (III) salt.

In the determination of iron in iron ore, ore is dissolved in hydrochloric acid where iron (III) is reduced to iron (II) and solution is then titrated with standard dichromate solution.

$$Cr_2O_7^{2+} + 6Fe^{2+} + 14H^+ \leftrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

In acidic solution the reduction of potassium dichromate is as follows.

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

Applications:- Various applications of dichrometry are listed here under.

1. Determination of iron in iron ore can be done by using dichrometry.
2. Dichrometry is aldo used in determiation of chromium in chromium (III) salt.
3. Chemical oxygen demand can be determined by dichrometry.

3. Cerimetry:- The titration involving cerric ammonium sulphate as an oxidising agent is known as cerimetry. Cerric ammonium sulphate is a powerful oxidising agent in acidic medium.

Principle:- Cerric salt solution has bright yellow colour but on reduction the cerous salt is formed which is colourless. Therefore it is easy to detect end point in strong solutions but in dilute solutions indicator is necesssary. Following change take place on reaction of salt in acid solution.

$$Cr^{4+} + e \leftrightarrow Ce^{3+}$$

Cerimetry has various advantages over permanganametry and dichrometry which are:-

a. Solutions remain stable over prolong periods and there is no need to protect from light.
b. Cerimetry is capable of determination of reducing agents in high concentration of HCl.
c. On reduction of Cr^{4+} only Ce^{3+} is produced while on permangnametry MnO_4^- can be reduced to any one of its several oxidation states.

Appliactions:- Various applications of cerimetry are listed here under.

1. Ferrous fumarate can be assayed by using cerimetry.

2. Determination of acetomenaphthone can be made by cerimetry.
3. Copper and molybdate are also determined by cerimetry,
4. Various pharmaceutical substances and dosage froms are determined by using cerimetry some of them are listed here under:-
   a. Ferrous gluconate (tablets)
   b. Ferrous fumarate (tablets)
   c. Ferrous succinate (tablets)
   d. Ferrous sulphate dried
   e. Ferrous sulphate (tablets)
   f. Menadione
   g. Paracetamol
   h. Tocopheryl acetate
   i. Acetomenapthone(tablets)
   j. Ascorbic acid (tablets)
   k. Chlorpromazine (tablets)
   l. Iron - dextran (injection)
   m. Iron - sorbitol (injection)

4. Iodimetry and Iodometry:- Iodimetry and iodometry both are the redox titrations which are based upon the determination of iodine i.e. directly in iodimetry and indirectly in iodometry.

Principle:- Iodine is a weak oxidant and it is used for the redox titrations of easily oxidized substances. Iodine is reduced by the reductants like stannous chloride, sodium thiosulphate and arsenious oxide. In iodimetry known volume of standard iodine solution is titrated directly with the reductant which is to be determined using starch as an indicator. End point is detected by change of blue colour to colourless. In all iodimetric titrations iodine is reduced to from iodide ion.

$$I_2 + 2e \rightarrow 2I^-$$

Reduction of iodine by some reductants is as follows:-.

1. $Sn^{2+} + I_2 \rightarrow Sn^{4+} + 2I^-$
2. $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$
3. $H_3AsO_3 + I_2 \rightarrow H_3AsO_4 + 2H^+ + 2I^-$

On the other hand, the redox titrations in which iodine is liberated in analyte solution through oxidation of iodide and liberated iodine is titrated with strong reductant is called indirect iodine titration or iodometry.

Consider that we have strong oxidant solution like $CuSO_4$ solution. To this we added excess KI solution in the presence of acid. Iodide ions get oxidised to form iodine.

$$2I^- + 2e \rightarrow I_2$$

The elctrons liberated by iodide ions are accepted by oxidant and get reduced.

$$2Cu^{2+} + 2e \rightarrow 2Cu^{+}$$

Iodide ions are present in excess therefore, amount of iodine ions liberated is equivalent to the concentration of reductant $CuSO_4$.

i.e. $2CuSO_4 \equiv 2Cu^{2+} \equiv I_2$

One iodine molecule is produced corresponding to two $CuSO_4$. Therefore, by determining quantity of liberated iodine we can determine the amount of Cu^{2+} ions and from that concentration of $CuSO_4$. The liberated iodine can be determined by titration with standard thiosulphate solution.

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 2NaI$$

Therefore,

$$2CuSO_4 \equiv I_2 \equiv 2Na_2S_2O_3$$

Applications:-

a. Various applications of iodimetry are listed here under.

1. Iodimetry is used for determination of reductants like stannous chloride, sulphurous acid, sodium thiosulphate and arsenious oxide.
2. Iodimetry is useful in determination of analgine and acetarsol.
3. Assay of Ascorbic acid, Sodium ascorbate and sodium thiosulphate can be performed by iodimetry.

b. Various applications of iodometry are listed here under.

1. Determination of $KMnO_4$.
2. Determination of KIO_3
3. Determination of $K_2Cr_2O_7$.
4. Determination of copper sulphate.
5. Determination of hydrogen peroxide.
6. Determination of chlorine in hypochlorites.
7. Determination of Ferric ammonium citrate.
8. Iodometry is also used in determination of thyroxine in thyroid gland.
9. Assay of diiodohydroxyquinoline, mannitol and phenindione can be performed by iodometry.

5. Bromatometry:- Potassium bromate is a oxidising agent which is mainly used for the determination of inorganic reducers. Redox titration which employed potassium bromate as an oxidising agent is called bromatometry.

Principe:- Potassium bromate is a strong oxidising agent in acidic medium and smoothly reduc to bromide.

$$BrO^-_3 + 6H^+ + 6e \leftrightarrow Br^- + 3H_2O$$

At the end of the titration along with water free bromine appears which produce yellow colou

$$BrO^- + 5Br^- + 6H^+ \leftrightarrow 3Br_2 + 3H_2O$$

Bromatometry can be done by direct or indirect titration methods. Some example of dire titrations carried out in the presence of HCl with bromate solution are:-

$$BrO^-_3 + NH_2OH \rightarrow Br^- + NO_3^- + H^+ + H_2O$$

$$2BrO^-_3 + 3N_2H_4 \rightarrow 2Br^- + 3N_2 + 6H_2O$$

$$BrO^-_3 + 3H_3AsO_3 \rightarrow Br^- + 3H_3AsO_4$$

In indirect methods, Excess bromine is added to the analyte solution under examination. Then excess of bromine is determined iodometrically i.e. by adding excess KI and liberated iodine is determined by sodium thiosulphate solution.

Applications:- Various applications of bromatometry are listed here under.

1. Various metals like aluminium, iron, copper, zinc, cadmium, cobalt, nickel etc can be detremined by using oxine i.e. 8-hydroxyquinoline and bromatometry
2. Phenols are also determined by bromatometry.
3. Hydroxyl amine is also determined by bromatometry using indirect titration method.

6. Titrations with potassium iodate:- Potassium iodate is a poweful oxidising agent and used for various redox titrations.

Principle:- Potassium iodate is a powerful oxidant and reacts with reducing agents like iodide or aesenic (III) oxide under moderately acidic conditions and reaction stops on reduction of iodate to iodine.

For iodide.

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

For arsenic (III) oxide.

$$2IO_3^- + 5H_3AsO_3 + 2H^+ \leftrightarrow I_2 + 5H_3AsO_4 + H_2O$$

The above reaction produce known amount of iodine which is determined by titrating with sodium thiosulphate.

For example the principle involved in standardization of sodium thiosulphate by potassium iodate is that when known strength of potassium iodate is reacted with excess potassium iodide in acidic condition iodine is liberated. Liberated iodine is titrated directly with sodium thiosulphate. End point can be detected with disappearance of permanent blue colour due to conversion of iodine into sodium iodide. Reaction involved in this titration is as follows.

KIO_3 (Potassium iodate) + $5KI$ (Potassium iodide) + $3H_2SO_4$ (Sulphuric acid) → $3K_2SO_4$ (Potassium sulphate) + $3I_2$ (Iodine) + $3H_2O$ (Water)

I_2 (Iodine) + $2Na_2S_2O_3$ (Sodium thiosulphate) → $Na_2S_4O_6$ (Sodium tetrathionate) + $2NaI$ (Sodium iodide)

Applications:- Various applications of potassium iodate titrations are listed here under.

1. Determination of arsenic in arsenic (III) compounds.
2. Assay of hydrazine sulphate.
3. Determination of copper compounds and thallium (I) salts.

MULTIPLE CHOICE QUESTIONS

Q.1 The reagent which undergoes reduction is an ..... agent and the reagent which undergoes oxidation ..... is a reducing agent.

a. Oxidizing, Reducing
b. Reducing, Oxidizing
c. Complexing, Reducing
d. None of these

Q.2 Given the following are the example of reducing agent except:

a. Alkali earth metal
b. Formic acid
c. Peroxy disulfuric acid
d. Sulfite compounds

Q.3 Given the following are the example of oxidizing agent except:

a. Hydrogen peroxide
b. Sulfuric acid
c. Nitric acid
d. Formic acid

FILL IN THE BLANKS

1. ..... is a process involving the transfer of electrons from one element or ion to another.
2. Oxidation involves ..... of electrons and reduction involves ..... of electrons.
3. Cerric ammonium sulphate is an ..... and titanous chloride is a reducing agent.

SHORT ANSWER QUESTIONS

Q.1 Define the followings:

a. Oxidation b. Reduction

c. Redox Indicator

Q.2 Give some examples of oxidizing and reducing agents.

LONG ANSWER QUESTIONS

Q.1 Explain the theory of redox titrations.

Q.2 Write a note on following

a. Theory of Redox reactions

b. Concept of oxidation and reduction.

ANSWERS

MULTIPLE CHOICE QUESTIONS

1.a 2.d 3.c

FILL IN THE BLANKS

1. Redox reaction 2. Loss, gain 3. Oxidizing agent, reducing agent.

9 CONDUCTOMETRY

INTRODUCTION

Conductometric titration is an electro-analytical method of analysis which is very useful when no suitable colour indicators are available for the detection of end point or when the indicator methods are not suitable for analysis. Conductometric titration is based on measurement of conductance of ions in a solution. The conductance is due to the migration of ions. Conduction involves migration of positively charged ions (H^+, Na^+, K^+, NH_4^+ etc) towards cathode and negatively charged ions (OH^-, Cl^-, I^-, Br^-, CO_3^-, SO_4^- etc) towards anode. The movement of ions occurs in such a way that the solution remain neutral throughout. So in Conductometric titration end point of a particular titration is detected by measuring the conductance of solution which is due to mobility of an ion depends upon many factors like charge, size, mass and degree of salvation of an ion.

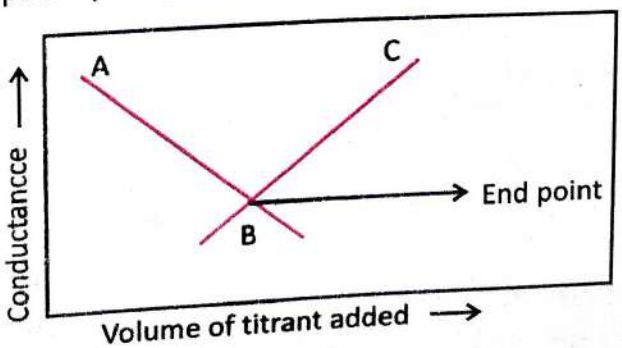
CONCEPT OF CONDUCTOMETRIC TITRATIONS

Each cation and anion has different degree of ionic mobility (conductance). When a solution of one electrolyte is added (titrant) to a solution of another electrolyte the overall conductance will depend upon whether a reaction occur between them or not. If no chemical reaction occurs then overall conductance of a solution will increases and each ion contribute to conductance of solution.

When a chemical reaction occurs replacement or substitution of ions takes place which decides that conductance will either increase or decrease. Conductometric titration is based on the principle of substitution of one ions of particular conductance by the ions of different conductance.

$$A^+ B^- + C^+ D^- \rightarrow A^+ D^- + C^+ B^-$$

In Conductometric titration, titrant is added in small amount and after each addition of titrant, conductivity of the solution is measured. Then graph is plotted between amount of titrant added and conductance of solution. The graph consists of two straight lines intersecting at a point known as equivalent point (end point).



INSTRUMENTATION

There are two main components for measurement of conductance of an electrolytic solution. These are

1) Conductivity cell
2) Conductometer

CONDUCTIVITY CELL

The solution whose conductance is to be measured is taken in a cell known as conductivity cell. These are generally made up of high quality glass (Pyrex), Quartz and sometimes fitted with platinum electrodes. The electrodes usually consist of platinum plates sealed into glass tubes. Electrodes of the conductivity cell are connected to circuit by means of mercury placed in the tubes. There are different forms of conductivity cells. Some common types are as follows:-

a)Conductivity cell having wide mouth bottle with cork having holes for passing two platinum wires. It is generally useful for low conductance measurement.

b) Conductivity cell consists of electrodes which are fixed in the lid which is having opening for the stirrer and the burette. Electrodes are firmly fixed and the faces of electrodes plates are vertical and parallel. It is helpful for measuring the conductance of precipitation types of reactions.

c) Conductivity cell having a wide bore glass tube, the tip of which has two platinum plates. Glass tube contains two fixed copper wires, the terminals of which are taken out for connection. Platinum plates are coated with platinum black to reduce polarization effect. For determining the cell constant, cell is placed in a standard solution of known specific conductance at 25°C or 18°C and resistance is measured. KCl solution (0.02 or 0.01) is used as standard solution for determination of cell constant.

Determination of cell constant by using 0.02 KCl at 25°C.

$$\text{Cell constant} = \frac{2765}{\text{conductivity of 0.02 KCl at 25°C in } \mu\text{mhos}}$$

Determination of cell constant by using 0.01 KCl at 18°C.

$$\text{Cell constant} = \frac{1221}{\text{conductivity of 0.01 KCl at 18°C in } \mu\text{mhos}}$$

2765 is the specific conductivity of 0.02 KCl at 25°C and 1221 is the specific conductivity of 0.01 KCl at 18°C.

CONDUCTOMETER

The apparatus used for conductance measurement is a form of wheat stone bridge also known as Conductivity Bridge. It is made by using wheat stone bridge circuit having four arms. Cell is

placed in one arm and resistance constitutes the second arm. The other two arms are in the form of calibrated slide wire resistor. The detector used may be a galvanometer, or calibrated digital display. An alternating current of frequency 50-60 Hz is used in the circuit. A calibrate switch is there to calibrate the desired value of conductance. In order to determine the conductance, the conductivity cell is dipped into the solution and the terminals are connected to the conductivity bridge. The selector switch is set to the proper conductance range and reading is recorded from galvanometer.

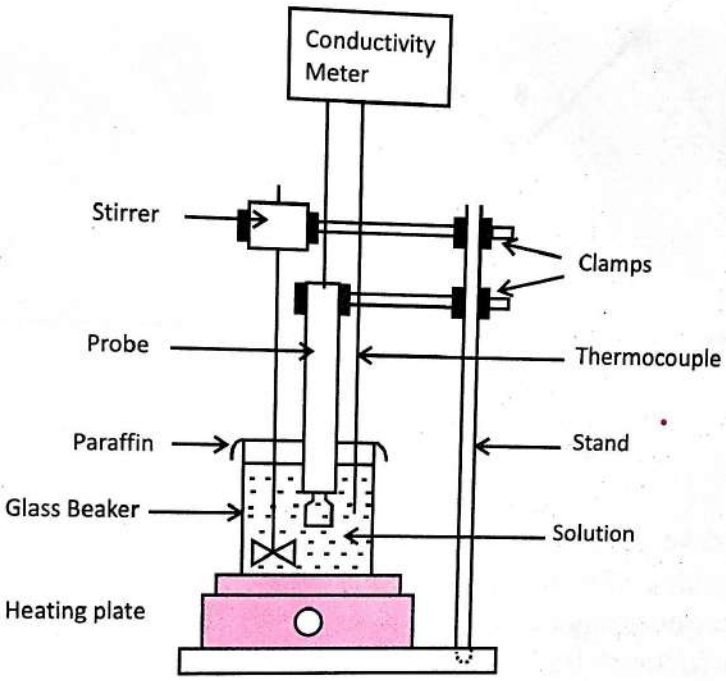


Figure 9.1: Conductometer

CONDUCTOMETRIC TITRATIONS

Various types of titrations can be perfomed using conductometry. Major titration which can be performed with conductometry can be classified as under:-

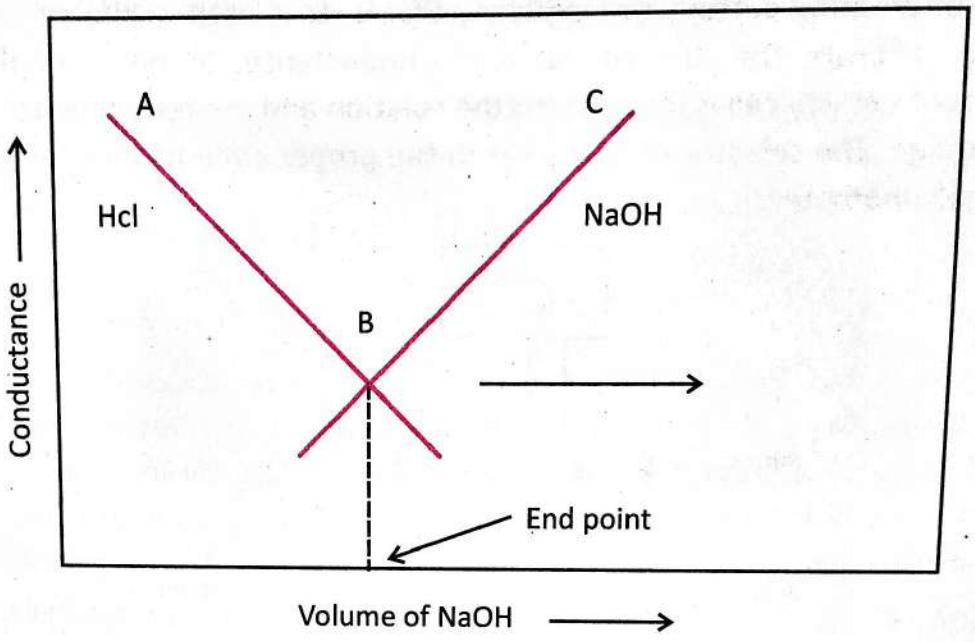
(A) Acid base titrations

It can be classified into following types:-

1) Titration of strong acid with strong base:-

HCl is a strong acid and NaOH is a strong base. The strength of HCl can be determined by titrating it directly with standard NaOH solution. When electrode is immersed in a beaker containing HCl sample solution its conductivity is high which is called initial conductivity. This is because strong acid completely dissociates into H^+ ions. When NaOH is added, OH^- of NaOH reacts with H^+ of HCl and produce water. Which results in decrease of conductivity on every addition. At the end-point all the H^+ of HCl reacts with OH^- of NaOH resulting water. After that point, further addition of NaOH increase conductance due to OH^- which results in 'V' shaped graph is obtained.

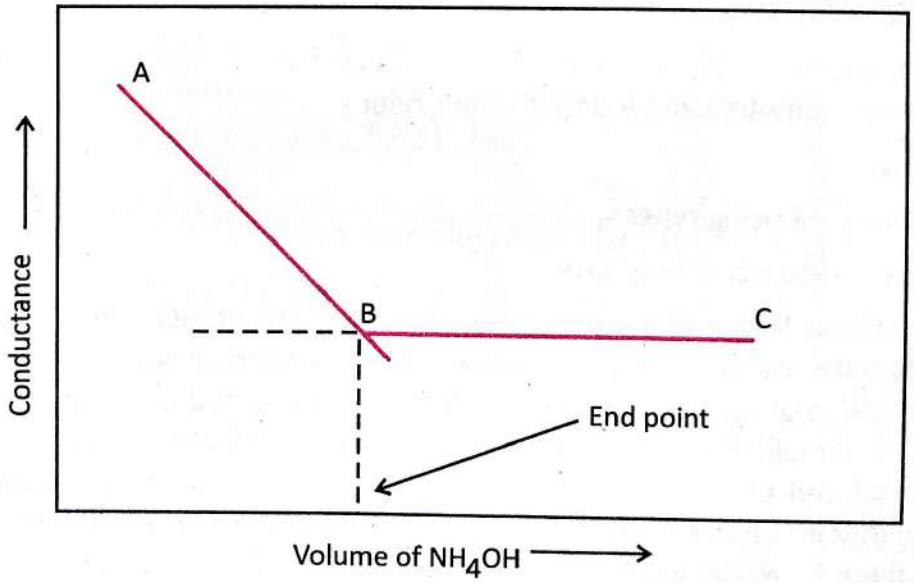
$$(H^+ + Cl^-) + (Na^+ + OH^-) \rightarrow (Na^+ + Cl^-) + H_2O$$



2) Titration of strong acid with weak base:-

HCl is a strong acid and NH_4OH is a weak base. Initially conductivity of solution is high due to HCl. When NH_4OH is added, OH^- of NH_4OH reacts with H^+ of HCl and produce water. Which results in decrease of conductivity on every addition. After end point , further addition of NH_4OH cause no change in conductance because NH_4OH poorly dissociates into OH^-.

$$HCl + NH_4^+OH^- \rightarrow NH_4^+Cl^- + H_2O$$

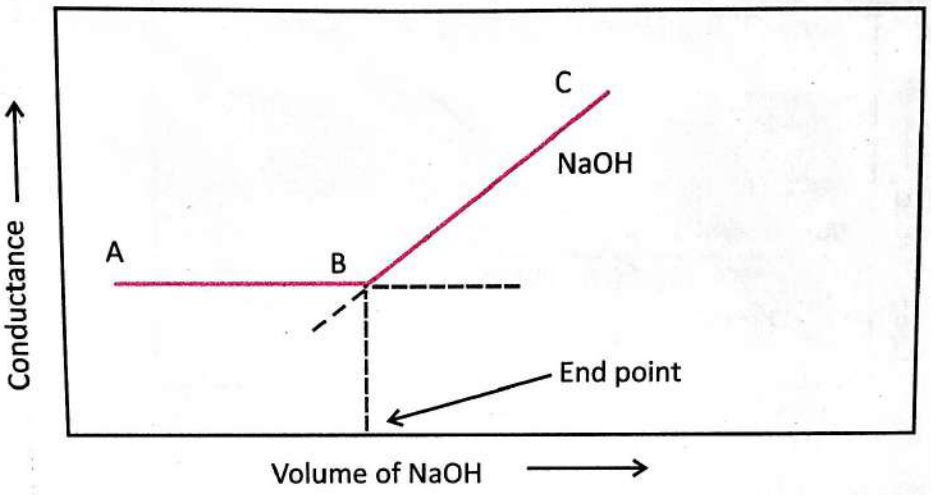


3) Titration of weak acid with strong base

Acetic acid is a weak acid and NaOH is a strong base. Initially the conductivity of solution is low because acetic acid doesn't dissociate into H^+ ions. On addition of NaOH, CH_3COONa formed and

conductivity slightly increased till the end point. After end point, further addition of NaOH cause sharp increase in conductivity due to OH^- ions.

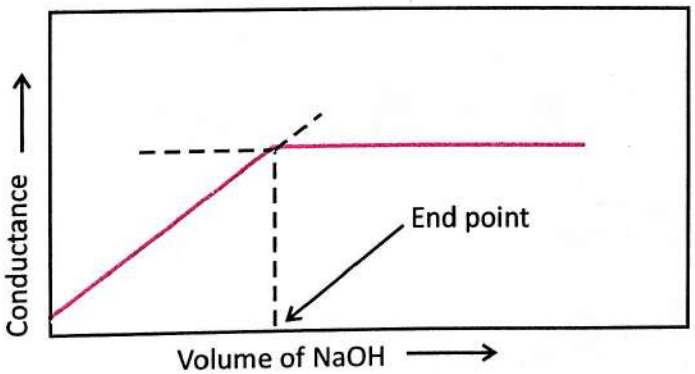
$$CH_3COOH + Na^+OH^- \rightarrow CH_3COO^-Na^+ + H_2O$$



4) Weak acid with weak base

Acetic acid is a weak acid and NH_4OH is a weak base. Initially conductivity is low because acetic acid doesn't dissociate into H^+ ions. On addition of NH_4OH, ammonium acetate salt is formed which has good conductivity and conductivity increased on every addition of NH_4OH till end point. After end point, further addition of NH_4OH cause no change in conductance and plateau is obtained.

$$CH_3COOH + NH_4OH \rightarrow CH_3COO^-NH_4^+ + H_2O$$



(B) Displacement titrations:-

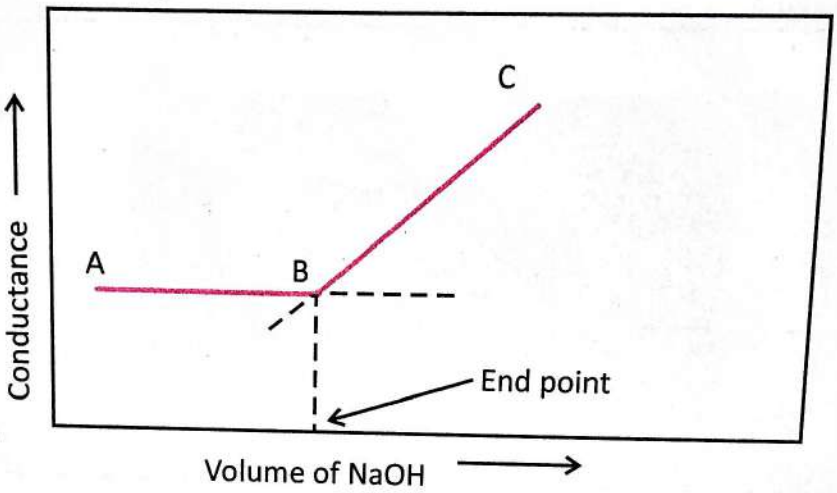
Displacement titrations involves displacement of one ion by another. Displacement titrations are of following types:-

1) Titration of salt of strong acid and weak base v/s strong base:-

Ammonium chloride is a salt of strong acid and weak base while sodium hydroxide is a strong base. Initially there is plateau because only displacement of ammonium and chloride ions with

sodium and chloride ions takes place till the end point. After end point, further addition of NaOH cause sharp increase in conductivity.

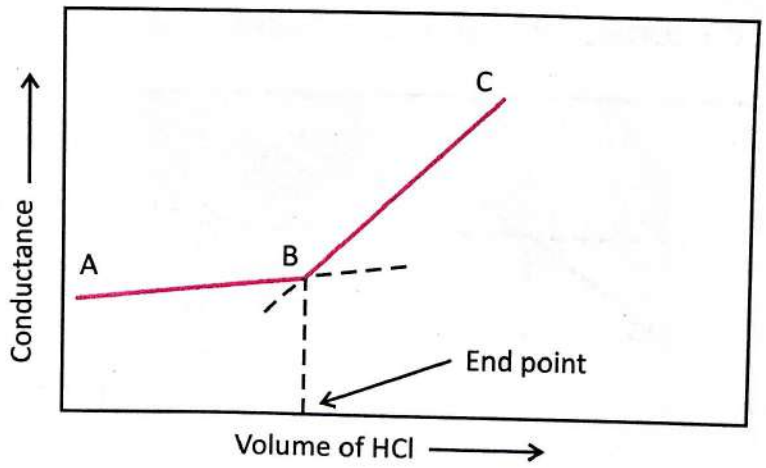
$$NH_4Cl + NaOH \rightarrow NH_4OH + NaCl$$



2) Titration of salt of strong base and weak acid v/s strong acid:-

Sodium acetate is a salt of strong base and weak acid while hydrochloric acid is a strong acid. Initially there is displacement of acetate ions by chloride ions and conductivity increased gradually till the end point. After end point, the further addition of HCl cause sharp increase in conductivity.

$$CH_3COONa + HCl \rightarrow CH_3COOH + NaCl$$



The displacement titrations are mainly useful in determination of alkaloids because alkaloids are weak bases and insoluble in water.

(C) Precipitation titration:-

The precipitation titration does not involve H^+ and OH^- ions therefore cannot be carried out much effectively as the acid base titration. In precipitation titration one pair of ions gets

substituted for another. If a cation is to be precipitated, a titrant whose cation has less mobility is selected for e.g. titration of silver nitrate with KCl.

$$KCl + AgNO_3 \rightarrow KNO_3 + AgCl$$

Initially with addition of $AgNO_3$ there is no change in conductance because Cl^- ions are replaced by nitrate ions and both have same ionic conductance but after end point excess of $AgNO_3$ results in sharp increase in conductance.

(D) Redox titration:-

In redox titrations, there is decrease in conductivity due to decrease in hydrogen ion concentration at the end point. Initial conductivity is kept at low level because it is difficult to detect small change in conductivity due to change in H^+ ion concentration. Redox titrations mainly performed in acidic medium. Titration of ferrous ions with dichromate ions is an example of redox titration using conductometry.

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

(E) Non-aqueous titrations:-

Non-aqueous titrations of weak acid and weak bases can be performed by conductometry. Example of non-aqueous titrations performed by conductometry are:-

1) Titration of tertramethyl ammonium hydroxide in methanol-benzene with weak organic acids in methanol or pyridine.

2} Titration of perchloric acid in dioxan-formic acid with weak bases.

APPLICATIONS

1) Determination of ionic product of water

The product of ionic concentration of H^+ and OH^- in gm moles per liter is constant at a constant temperature which is known as ionic product of water. The ionic product of water can be calculated by knowing the specific and equivalent conductance at infinite dilution i.e.

$$\lambda_o = K_o/C \times 1000$$

Here K_o = Specific conductance at infinite dilution

C = Concentration (gm eq./liter)

2) Determination of solubility of sparingly soluble salts

Substances like AgCl, $BaSO_4$ etc. are regarded as sparingly soluble in water and their solubility cannot be determined easily by other chemical methods. Conductometric titration helps in determining the solubility of these sparingly soluble salts.

The saturated solution of these salts may be regarded as completely ionized. As small amount of salt present in the solution gets completely dissociated so value of

$$\lambda_v = \lambda_\infty \text{ (equivalent conductance at infinite dilution)}$$

so $$\lambda_v = \lambda_\infty = K_v \times V$$

V = volume containing one gm equivalent of solute.

According to **Kohlrausch's law**

$$\lambda_\infty = \lambda_\infty(\text{cation}) = \lambda_\infty(\text{anion})$$

By knowing the value of λ_∞ and K_v (specific conductance) the volume can be determined and from this solubility (S) can be calculated.

$$S = 1000/V \times E$$

$$S = 1000 \times E \times K_v / \lambda_\infty \qquad \text{Because } V = \lambda_\infty/K_v$$

3) Determination of basicity of an organic acid

According to Ostwald, basicity of an acid can be given by-

$$B = \lambda_{1024} - \lambda_{32} / 10.8$$

Where λ_{1024} and λ_{32} = equivalent conductivities of sodium salt of acid at dilution of 1024 litrs and 32 litrs/gm. equivalent respectively.

4) Kinetic studies

Rate of a reaction can be calculated with help of conductometric titrations. It is based on measurement of conductivity before, during and at end of chemical reaction.

5) Determination of degree of dissociation of weak electrolytes

Determination of degree of dissociation of weak electrolytes can be calculated from equivalent conductance at infinite dilution i.e.

$a = \Lambda_v/\Lambda_o$

Λ_v = Equivalent conductance at dilution V.

Λ_v = Equivalent conductance at infinite dilution.

6) Determination of concentration

A series of dilutions with known concentration of electrolyte is prepared and their conductivities are then measured. A graph is plotted b/w conductivities of each solution and concentration of the electrolyte. Then the conductivity of unknown solution is determined and its concentration is calculated by using calibration curve.

7) Purity of water

Pure water has specific conductivity value 5×10^{-8} ohm^{-1} cm^{-1} and if specific conductivity of test water is less or more than this value it means water quality is defected.

MULTIPLE CHOICE QUESTIONS

Q1. SI unit of conductance is

a. mho
b. siemens
c. volt
d. None of these

Q.2 Current used for meaurement of conductance is

a. A.C.
b. D.C.
c. Any one of these
d. None of these

Q.3 Equivalent conductance is .....related with concentration.

a. Inversely
b. Directly
c. Not
c. Logarithmicaly

Q.4 Solubility of sparingly soluble salts can be determined by

a. Polarography
b. Potentiometry
c. Conductometry
d. IR spectroscopy

FILL IN THE BLANKS

1. Conductometry is an ..... method of analysis.
2. Specific conductivity of pure water is.....
3. Sodium acetate is a salt of.....
4. Ammonium chloride is a salt of.....

VERY SHORT ANSWER QUESTIONS

Q.1 Define ohm's law.
Q.2 Define specific resistance.
Q.3 Define specific conductivity.
Q.4 Define equivalence conductivity

LONG ANSWER QUESTIONS

Q.1 Give detail about conductometric titrations, its principle and instrumentation.

Q.2 What are the factors affecting conductance and give the applications of conductometric titrations.

Q.3 Give detail about the titrations performed by conductometry.

Q.4 Give detailed applications of conductometry.

ANSWERS

MULTIPLE CHOICE QUESTIONS

1. b 2. a 3. a 4. c

FILL IN THE BLANKS

1. Electroanalytical 2. 5×10^{-8} ohm^{-1} cm^{-1} 3. strong base and weak acid
4. salt of strong acid and weak base

10 POTENTIOMETRY

INTRODUCTION

In potentiometric titration reference and indicator electrodes are immersed in the solution of particular analyte (titrand) and the potential on indicator electrode is measured with relation to reference electrode. Titrant is added in the analyte solution (titrand) and change in potential is noted down. At the end point there is sharp change in potential on indicator electrode. Graph is plotted between the indicator electrode potential and volume of titrant added. This method is used for determination of sharp end point.

CONCEPT OF POTENTIOMETRY

Potentiometric titration is an electrochemical analytical method of analysis which is based upon the measurement of change in the electrode potential of a solution using two electrodes i.e. reference electrode and indicator electrode. Reference electrode has its own standard potential and remains unchanged when dipped in the solution while indicator electrode responds to the change in EMF (electromotive force) of a solution. EMF of an elecrolyte cell can be calculated as follows:-

$$E_{cell} = E_{reference} + E_{indicator} + E_{junction}$$

$E_{juction}$ remains constant and $E_{reference}$ is the potential on refernce electrode which is independent of composition of solution. Therefore, potential on indicator electrode gives the information about the nature and composition of the solution and it depends upon the nature, concentration and temperature of ions of analyte.

There is linear relationship exist between the potential and pH of a solution at given temperature therefore sometimes pH instead of potential is determined.

$$E = K - 0.0591pH$$

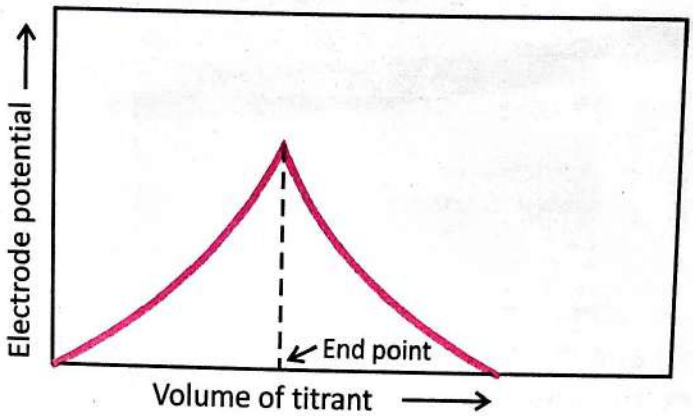
or

$$\Delta E/\Delta\ pH = -0.0591$$

Where,

E = electrode potential

k = constant potential (asymmetric potential)



NERNST EQUATION

When à metal A is immersed in the solution that contains its own ion A^{n+} an electrode potential is established whose value is given by the nernst equation.

$$E = E^{\circ} + \left(\frac{RT}{nF}\right) \text{In } a_{A^{n+}}$$

Where,

E = electrode potential

E° = standard electrode potential for metal A

$a_{A^{n+}}$ = metal ion activity in the solution

n = valency of ions

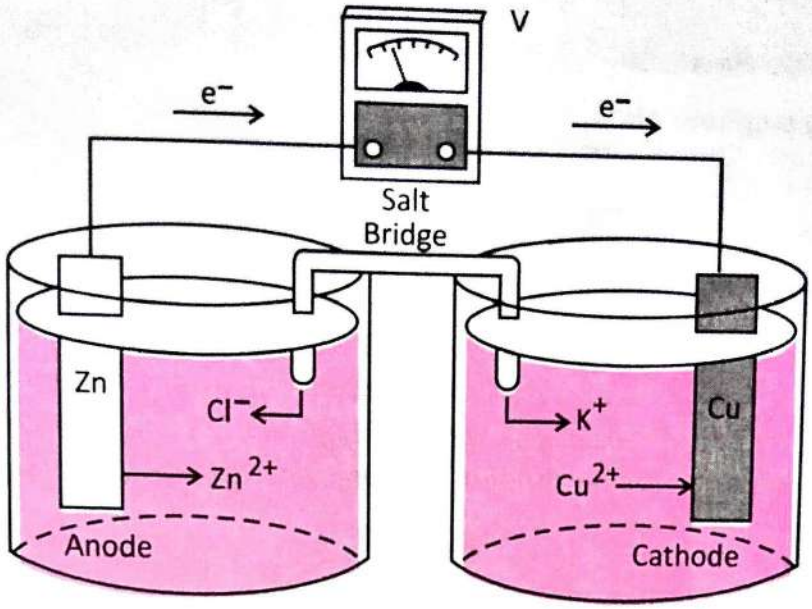
R and T = both are constants

T = temperature.

ELECTROCHEMICAL CELL

An electrochemical cell is consist two electrolyte solutions which are connected to each other by electrodes and a salt bridge. Each solution with electrode acts as a half cell therefore we can say that an electrochemical cell is consist of two half cells which are connected to each other to form an electrical circcuit.

Let's take an example of en electrochemical cell consist of two half cells and these half cells consist of two metallic electrodes Zinc and copper electrode immersed in zinc sulphate ($ZnSO_4$) and copper sulphate ($CuSO_4$) solution. These two half cells are connected to each other through a voltmeter and a salt bridge which is consist of a tube filled with saturated salt solution like KCl, NaCl etc. Through the salt bridge movement of ions between the solutions takes place. Ends of the salt bridge tube are fitted with porous frits which prevent mixing of solutions but uniform movement of ions is allowed through them.



In $CuSO_4$ solution, Copper electrode acts as a cathode and positivelly charged copper ions move toward it and negatively charged sulphate ions away from it. While in $ZnSO_4$ solution, zinc electrode acts as a anode and positivelly charged zinc ions move away from it and negatively charged sulphate ions move towards it. Through the salt bridge positive ions move to the left side and negative ions to right side. On electrodes following reactions take place.

On zinc electrode,

$$Zn \rightarrow Zn^{2+} + 2e^-$$

On copper electrode,

$$Cu^{2+} + 2e^- \rightarrow Cu\downarrow$$

ELECTRODES USED IN POTENTIOMETRY

For determination of potential of a given solution, two electrodes are used. One electrode is reference electrode whose potential is known and is constant. Second electrode is indicator electrode which determines the potential of the solution under examination. Electrodes used in potentiometry are:-

A) Reference electrodes

B) Indicator electrodes

REFERENCE ELECTRODES

The potential of reference electrode is known and has constant value i.e. it is independent of analyte composition. Electrodes used as reference electrodes are of two types:-

a. Pimary electrodes.

1) Hydrogen electrode

b. Secondary electrodes.

2) Saturated calomel electrode

3) Silver-silver chloride electrode

4) Mercury-mercury sulphate etc.

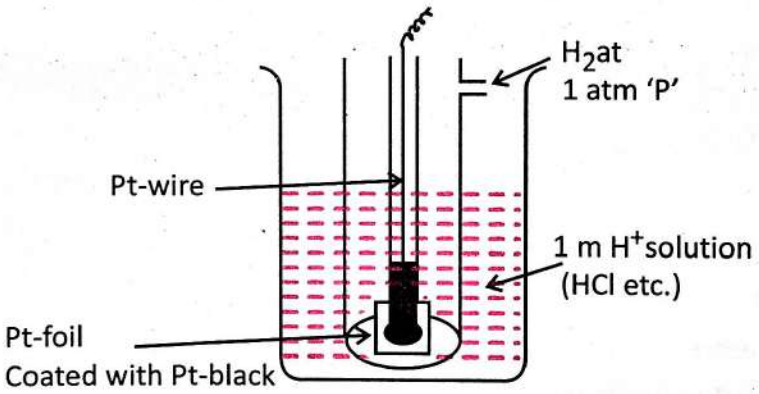
a. Pimary electrodes.

1) Hydrogen electrode

It can be used as both reference electrode as well as indicator electrode. It is used as a primary standard for the measurement of potential of other electrodes therefore also called primary reference electrode. Hydrogen electrode when dipped in the standard acid solution can be used as reference electrode while when dipped in analyte or test solution can be used as indicator electrode.

APPARATUS

It consists of a glass tube having holes at bottom. This tube consists of one more tube having platinum or copper wire with a platinum foil. Platinum foil is coated with platinum black. The hydrogen gas (99.8 % purity) is passed through this tube which can come out from hole at the bottom of the tube. The whole tube is dipped into solution of 1.8 M of HCl at 25°C. Some Hydrogen gas gets absorbed by the platinum black which allows the exchange of hydrogen from gaseous to ionic form. By this way, it acts as hydrogen electrode.



Working:-

The potential of this electrode is taken as zero at all temperatures. When hydrogen electrode is connected to other electrode (indicator) through the salt bridge, the potential of indicator electrode can be measured easily. For e.g. Zn electrode is connected to hydrogen electrode through KCl salt bridge.

$$Pt, H_2 / H^+ // Zn^{++} / Zn$$

The cell reaction is

$$H_2 + Zn^{+2} \rightarrow 2H^+ + Zn$$

Half cell reaction is

$$Zn^{+2} + 2e^- \rightarrow Zn$$

In this way we can determine potential of any electrode.

If hydrogen electrode is connected to another hydrogen elctrode by KCl salt bridge, EMF of the cell can be measured as:-

$$Pt, H_2 / H^+ // H^+ / H_2, Pt$$

$$E = E^o - 0.0591/n \times \log [1/H^+]$$

E^o = Zero as it is standard potential and n = 1

$$E = -0.0591/1 \times \log [1/H^+]$$

$$E = -0.0591\ pH$$

$$pH = -E / 0.0591$$

Advantages:-

1) It gives reproducible results.
2) It has no salt error.
3) It can be used over entire pH range.
4) It is used as a fundamental electrode.
5) It can be used as both indicator as well as reference electrode.

Disadvantages

1) It is not useful in solutions containing strong oxidizing or reducing agents.
2) It is not useful in solution having metal ions that are below Hydrogen in potential series.

B. Secondary electrodes.

These are the electrodes which are used instead of primary electrode to overcome the problems in primary electrode. The most commonly used secondary electrode are:-

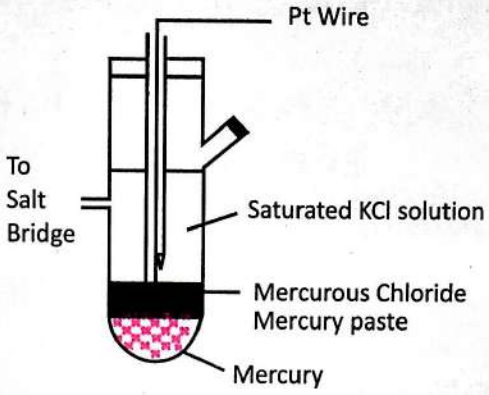
1) Calomel electrode:-

It is also known as Mercury–Mercurous chloride electrode.

Apparatus

It consists of glass tube having a side arm tube. Pure mercury is placed at the bottom of glass tube and is covered with a paste of calomel (mercury chloride) and KCl. The tube is filled with KCl solution through the side arm tube. A platinum wire is also placed at the centre of the glass tube which makes electrical connection with mercury. The potential of this calomel electrode depends upon the concentration of KCl solution used. Most commonly 0.1 N KCl, 1 N KCl or standard KCl and saturated KCl solutions are used. The potentials with respect to concentration of solution are listed in table below:-

Concentration of solution in electrode	Potential in mV at different temperature conditions	
	20° C	25°C
Saturated KCl	250	246
1 N KCl	286	285
0.1 N KCl	338	338



Calomel Electrode

Working

When calomel electrode is connected with another electrode (indicator), EMF of the indicator electrode can be calculated. Half cell of calomel can be written as:-

$$Hg / Hg_2Cl_2 \text{ (saturated) } KCl //$$

Calomel electrode can be connected to hydrogen electrode for measuring pH of a solution i.e.

$$Hg / Hg_2Cl_2 . KCl // H^+ / H_2 . Pt$$

$$pH = E_{observed} - E_{calomel} / 0.0591$$

Advantages

1) It can be used over wide pH range.

2) It can be used in various solvents.

Disadvantages

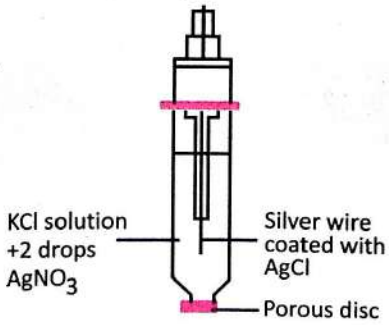
1) It is unstable at temperature above 80°C.

2) It is not suitable when chloride ions show incompatibility.

2) Silver-silver chloride electrode

Apparatus

It consists of a silver wire, coated electrically with silver chloride and is dipped in a solution of



KCl of known concentration. Generally 0.1 M KCl or saturated KCl solution is used. Potential of this half cell depends upon the concentration of potassium chloride as well as temperature.

Concentration of solution in electrode	Potential in mV at 25°C
Saturated KCl	200
1 N KCl	235.5
0.1 N KCl	288

Working

The standard potential of this electrode is obtained by combining it with hydrogen electrode. The EMF of the cell can be calculated i.e.

$$Ag / AgCl \text{ saturated } KCl // H_2 / H^+ Pt$$

This electrode is used similarly as calomel electrode. It can't be used where chloride ions interfere.

3) Mercury-Mercurous sulphate electrode

This electrode is useful where chloride ions have been found to interfere. This electrode is useful in solution containing sulphate ions. It consists of mercury in a solution containing sulphate ions and has been saturated with Mercurous sulphate. The standard potential of indicator electrode can be determined by combining it with this electrode. Standard potential of this electrode when measured against hydrogen elctrode is 0.680 volts. The half cell can be written as-

$$Hg / Hg_2SO_4 \text{ saturated } SO4^{-2} //$$

INDICATOR ELECTRODES

In order to determine the EMF of a given solution proper indicator electrode is required. This electrode measures potential when it is connected to a suitable reference electrode. So an electrode which is useful for measuring potential or pH of a solution is called as indicator electrode. Various types of indicator electrodes are –

1) Quinhydrone electrode

This electrode is mainly useful in measuring pH of a given solution. This electrode was introduced by E.Billman in 1921. Quinhydrone is a composed of quinine and hydroquinone and in solution form it gives equal molecules of these two substances. Quinhydrone electrode consists of a platinum wire dipped into a saturated solution of quinhydrone. In solution form quinhydrone gets dissociated into equal quantities of quinone and hydroquinones.

$$\underset{\text{Quinhydron (Q)}}{C_6H_4O_2 \cdot C_6H_4[OH]_2} \leftrightarrow \underset{\text{Quinone}}{C_6H_4O_2} + \underset{\text{Hydroquinone } (QH_2)}{C_6H_4[OH]_2}$$

There occurs reversible oxidation reduction of quinone, hydroquinone i.e.

$$C_6H_4O_2 + 2H^+ + 2e^- \leftrightarrow C_6H_4[OH]_2$$

The potential of an inert electrode is given by

$$E_{(H+,Q,QH_2)} = E^{\circ}_{(H+,Q,QH_2)} - \frac{0.0591}{n} + \log \frac{[QH_2]}{[(Q)H^+]^2}$$

$$= E^{\circ}_{(H+,Q,QH_2)} + \log$$

$$= E^{\circ}_{(H+,Q,QH_2)} + \log H^+$$

Where E° is 0.699 so

$$E^{\circ}_{(H+,Q,QH_2)} = 0.699 - 0.0591pH$$

For measuring the pH of a particular solution this electrode is dipped into the solution and is connected with any good reference electrode like calomel electrode. So equation becomes –

$$Hg, Hg_2Cl_2 . KCl // H^+ Q . QH_2 / Pt$$

The EMF of cell is given by

$$E_{cell} = E_{quinhydrone} - E_{calomel}$$

$$E_{calomel} = 0.242$$

$$E_{quinhydrone} = 0.699 - 0.0591pH$$

So the above equation becomes

$$E_{cell} = [0.699 - 0.0591pH] - 0.242$$

Or

$$0.0591pH = 0.699 - 0.242 - E_{cell}$$

$$pH = 0.699 - 0.242 - E_{cell} / 0.0591$$

By measuring EMF of the cell i.e. E_{cell} we can easily calculate pH of the solution.

The electrode consists of a platinum wire into solution containing excess of quinhydrone. Platinum wire is generally cleaned with chromic acid and water. For preparing the quinhydrone, dissolve 60 gm of ferric alum in 100 ml of water and pour this solution into a warm solution of 5 gm of hydroquinone in 60 ml of water.

Advantages

1) It is free from salt errors.

2) It is highly simple and gives rapid response.

3) It attains equilibrium very quickly.

4) It is not affected by presence of dissolved oxygen.

5) It is less sensitive than the hydrogen electrode to the presence of oxidizing agents.

Disadvantages

1) It can not be used in the solution whose pH is above 8.

2) It is not suitable for long time.

3) The solution must be free from oxidizing and reducing agents.

4) The solution under examination gets contaminated.

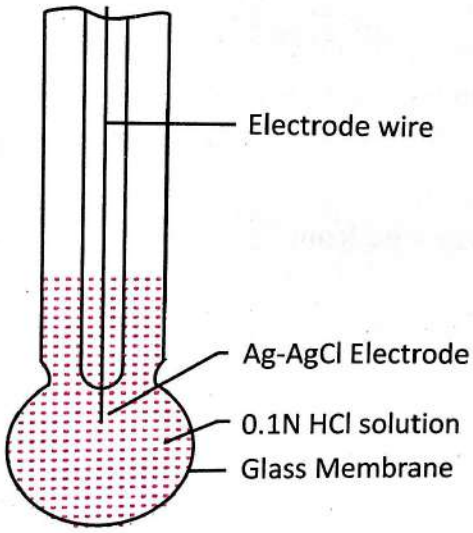
5) It readily gets oxidized by air in alkaline medium.

2) Glass electrode

This electrode is useful in determining pH of a solution. It selectively responds to the change in concentration of hydrogen ions. It consists of very thin walled glass bulb made from glass membrane of high electrical conductivity. The bulb contains HCl of a particular concentration and Ag/AgCl wire to make electrical contact. The glass membrane is made from soft soda lime glass containing lithium silicate and barium ions added to it. The measurement of pH of solution is based on the fact that when a glass surface is placed in a solution then a potential is established between the glass and the solution. The value of this potential depends upon hydrogen ions concentration of the solution. From the above basis pH of the solution can be calculated as:-

$$E_G = E_{OG} - 0.0591pH$$

E_{OG} is a constant and depends upon the nature and composition of the glass



The surface of glass membrane must be hydrated all the time as the hydration of glass membrane involves ion exchange reaction between cation in glass lattice and proton from the solution i.e.

$$\underset{\text{solution}}{H^+} + \underset{\text{glass}}{Na^+[Cl]^-} \leftrightarrow \underset{\text{solution}}{Na^+} + \underset{\text{glass}}{H^+[Cl]^-}$$

Glass bulb acts like a semipermiable membrane for H+ ions. The H+ ions easily enter the glass lattice. Due to this presence of water in glass, it is essential for measuring pH of a solution, glass electrode is dipped into it and is connected with reference electrode like calomel electrode. The cell can be written as-

$$Pt, 0.1N\ HCl\ /\ glass\ /\ solution\ //\ KCl\ (sat.),\ Hg_2Cl_2\ /\ Hg$$

pH can be calculated from

$$E_G = E_{OG} - 0.0591pH$$

Advantages

1) It is not affected by oxidizing and reducing agents, colloids and salts, dissolved gases etc in the solution.
2) It can be used over entire pH range.
3) It is simple to operate.
4) It can be used in viscous, colored solution and suspensions.
5) It has no salt error.
6) Modern glass electrodes are very strong to withstand high pressure.

Disadvantages

1) It is fragile, so should be handled carefully.
2) Minute scratches make glass electrodes useless.
3) It is not useful in highly alkaline solution as there occurs partial exchange of other cations than H^+ ions.
4) It must be hydrated all the time.

3) Antimony Electrode

This electrode is useful in determining pH of a solution. It consists of antimony rod coated with antimony trioxide i.e. antimony rod is covered with its oxide. The electrode reaction is –

$$Sb_2O_3 + 6H^+ + 6e^- \leftrightarrow 2Sb + 3H_2O$$

The potential and pH can be calculated from

$$E = E° - 0.0591pH$$

The antimony electrode can be prepared by casting a stick of antimony in air. A wire is attached at one end of the antimony rod and other is placed into the solution whose pH is to be determined. EMF can be calculated by combining it with a suitable reference electrode.

Advantages

1) It is useful in viscous and turbid solutions.
2) It can be used over wide pH range i.e. 3-8.
3) It is not affected by the presence of oxidizing agents.
4) It is sturdy and not easily broken.
5) It attains equilibrium rapidly and has low electrical resistance.

Disadvantages

1) It suffers from a salt error.
2) Complexing agents if present in the solution causes interference.
3) It is not useful below pH 3 as the oxide gets dissolved.
4) It cannot be used in the presence of strong oxidizing agents.
5) Every time calibration is required.

ION SELECTIVE ELECTRODES

Many ions like hydronium ions, do not take part in a half cell that includes a metal. So, a large number of ion selective electrodes are used. These are membrane electrodes in which the membrane potential is selective for a given ion as the potential of glass electrode was selective towards H^+ ions. Ion selective electrodes are specific and permeable to certain selective ions. These electrodes are easy to use, available in different size and shape, give rapid response and are of low cost. These are generally combined with saturated calomel electrode (reference electrode) and helps in measuring the concentration of a particular ion.

Types

Ion selective electrodes are membrane electrodes and involve exchange of ions through its membrane. These are of three types-

1) Glass membrane electrode

It is similar to glass electrode which was used for measuring pH of solution. In this composition of glass membrane varied which makes hydrated glass permeable for various monovalent cations other than H^+ ions. There are generally three types of glass membrane electrode –

a) Cation sensitive electrode

In this type the glass membrane is permeable to monovalent cations only. The selective order is

$$H^+ > K^+ > Na^+ > NH^{4+} + > Li^+$$

b) Divalent cation sensitive electrode

This electrode is mainly used for the measurement of calcium and magnesium like divalent ion i.e. in determination of total hardness of water and for complexometric titrations using EDTA.

c) Sodium sensitive electrode

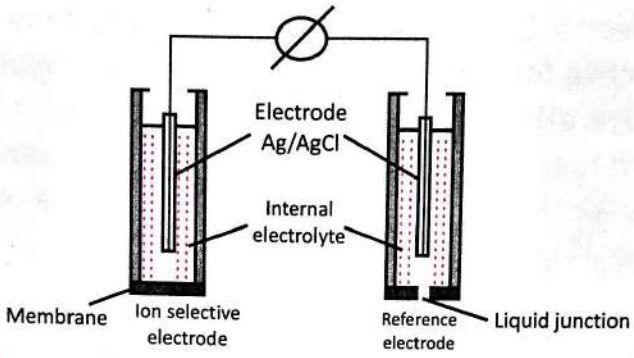
This electrode is selective to sodium ions. It is useful to measuring the activity of sodium ions in presence of other cations like K^+ ions. Glass membrane electrodes consist of a hard glass tube, at the end of which a thin glass membrane permeable to selective ion is present. Glass tube is filled with chloride salts of cation to which the electrode is most sensitive.

2) Liquid – Liquid electrodes

It is also known as liquid membrane electrode. In this, membrane is made up of a layer of water immiscible liquid type ion exchanger held in place by an inert porous membrane. This porous membrane makes contact with the test solution and ion exchanger. It does not allow mixing. Internally it is filled with the ions for which the ion exchanger is specific. It also contains Ag-AgCl reference electrode. For example:- In calcium selective electrode the ion exchanger is an organic phosphoric acid that binds calcium ions more strongly than other cations. For calcium ion determination, porous membrane containing the ion exchange liquid separates the solution under examination from reference solution. The equilibrium attained can be given as –

$$\underset{\text{(Organic)}}{RCa} \leftrightarrow \underset{\text{(Aqueous)}}{Ca^{+2}} + \underset{\text{(Organic)}}{R^{-2}}$$

Sometimes ion selective electrodes are used in combination with immobilized enzymes so that these electrodes become selective for specific enzyme substrate.



3) Solid state membrane electrodes

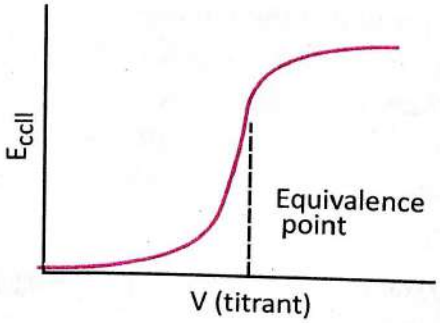
It is also known as crystal membrane electrodes. It consists of a solid membrane which separates the standard and solution under test. In solid state electrode the membrane is a single crystal dopped with another salt. It consists of a hard glass tube having opening at the bottom where a single crystal membrane is fitted. Tube is filled with internal filling solution and Ag-AgCl reference electrode. The crystal membrane is selective for a particular ion.

For example:- In fluoride electrode the membrane consists of a large single crystal of Lanthanum fluoride containing small amount of Europium. Lanthanum fluoride is highly insoluble and has large selectivity for fluoride ions than other ions. Large crystal membrane can be prepared by making a pellet of proper size and shape. Its mechanism is similar to that of glass electrode. There is presence of various anionic sites on crystal membrane which shows affinity towards certain cations. Similarly cationic sites show affinity towards certain anions.

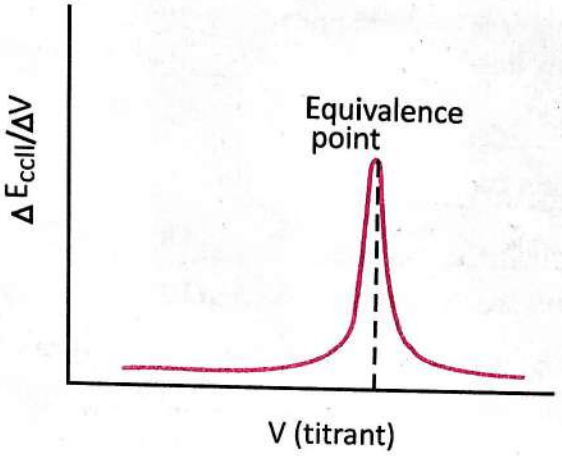
METHODS FOR DETERMINING END POINT BY POTENTIOMETRIC TITRATIONS

There are various methods to locate the end point. The main purpose is to know the end point at which the quantities of reacting species are present in equal amount. The equivalence point (end point) is generally found graphically. There are following methods for calculating end point:-

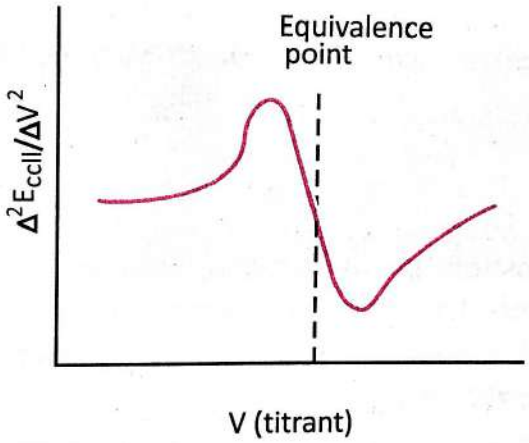
1) Normal titration curve:- Values of EMF (E) or pH are recorded after addition of each volume of titrant. Then a graph is plotted between volume of titrant added v/s values of pH or EMF. At equivalence point there is sharp increase in potential or there is maximum slop of curve. Generally S-shaped curve is obtained.



2) First derivative curve:- Difference of EMF or pH for the volume of titrant added ($\Delta E / \Delta V$) is plotted against titrant (V) added. A bell shaped graph is obtained and at end point there is maximum change in EMF or pH. The end point can be recorded by drawing perpendicular from peak of graph on volume excess.



3) Second derivative curve:- $\Delta^2 E / \Delta V^2$ against the volume of titrant added is plotted. The end point can be obtained as a zero point where the slope curve of $\Delta^2 E / \Delta V^2$ is maximum.



APPLICATIONS OF POTENTIOMETRY

With the use of potentiometry various types of titrations can be performed. Different titrations performed by using potentiometry with examples are described here under.

1) Acid-Base titration

This type of titration involves H^+ and OH^- ions. The indicator electrode used may be hydrogen, glass or antimony while calomel is used as a reference electrode. Dibasic, tribasic and polybasic acids can be titrated with alkali to full end point. The potential of any hydrogen electrode can be given by

$$E = E° - 0.0591pH$$

Examples of acid-base titrations using potentiometry are listed in the table below:-

In aqueous medium		
Sr. no.	Nature of titration	Example
1	Weak acid v/s weak base	CH_3COOH v/s NH_4OH
2	Weak acid v/s strong base	CH_3COOH v/s NaOH
3	Strong acid v/s weak base	HCl v/s NH_4OH
4	Strong acid v/s strong base	HCl v/s NaOH
5	Mixtures acids v/s bases	CH_3COOH + HCl v/s NaOH
6	Mixtures of bases v/s acids	NH_4OH + NaOH v/s HCl
7	Polybasic acids v/s bases	Citric acid v/s NaOH Tartaric acid v/s NaOH
In non-aqueous medium		
1	Weak acids v/s potassium or lithium methoxide	Barbituric acid v/s Lithium methoxide
2	Weak bases v/s perchloric acid	Metronidazole, Ephedrine hydrochloride vs 0.1 N $HClO_4$

2) Redox titration

Many redox titrations are possible by using potentiometer. In this platinum is used as an indicator and calomel or silver-silver chloride electrode is used as reference electrode. This titration involves the transfer of electron from oxidized substances to reduce substances. So potential of redox titration is given by

$$E = E^\circ + \frac{0.0591}{n} \log \left[\frac{ox}{red}\right]$$

Where,

E = electrode potential

E° = standard electrode potential

n = number of electrons involved in the reaction.

ox = concentration of oxidant

red = concentration of reductant

Examples of redox titrations are given in table below:-

Sr.no.	Examples
1	Ferrous ammonium sulphate in dilute H_2SO_4 v/s $KMnO_4$ or $K_2Cr_2O_7$
2	Ferrous sulphate in 6N H_2SO_4 v/s Cerric ammonium sulphate
3	Sodium arsenite v/s $KBrO_3$

3) Precipitation titration

Potentiometric titration is possible only for limited types of reaction involving precipitation i.e. in determination of ions or elements using precipitating agents. Calomel, Hydrogen or Silver-silver chloride electrode is used as reference electrode while Silver wire electrode is generally used as indicator electrode. Potential can be given by

$$E = E^\circ + \frac{0.0592}{n} \log [M^{n+}]$$

Where,

E = electrode potential

E° = standard electrode potential

M = concentration of ions

n = electronic state

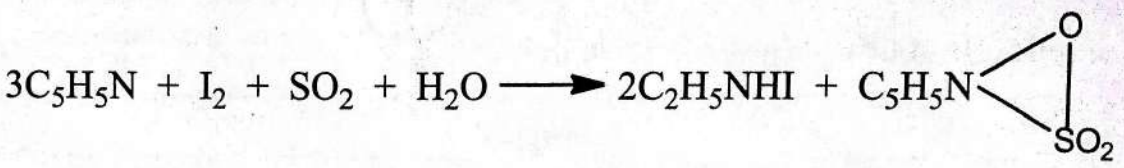
Precipitation titrations can be used for the determination of Silver, Lead, Copper, Mercury etc using precipitating agents to form insoluble salts.

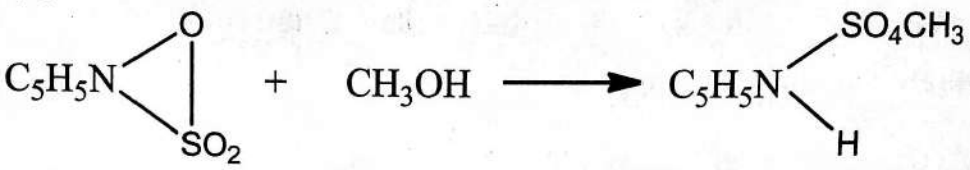
4) Complexometric titrations

When a metal ion forms a complex with ligand its potential can be determined by using proper indicator electrode. Various divalent , trivalent ions etc are titrated against EDTA and can be determined by potentiometric method. Silver or Mercury chloride electrodes are used as an indicator electrode while Calomel electrode is used as reference electrode.

5) Biamperometry (Dead stop end point technique)

Two platinum electrodes are dipped in a solution and between them small e.m.f is applied. An automatic burette is attached to it. There is no any current flow in the solution due to absence of polarising substances. Current only flows when both the electrodes are depolarised i.e. at the end point. Titrant is added through the automatic burette which automatically closed at the end point. At the end point there is sharp transition is seen between the one polarised electrode at beginning and depolarisation of both platinum electrodes i.e. at the end point. Determination of moisture content by Karl fischer reagent is an example of this technique. Reaction taken place in titration of water with Karl fischer reagent is given below:-





6) Assay of drugs

Various drugs are assayed by potentiometry and their detailed procedures are available in various official compendia. Some of the drugs which are assayed by potentiometry are:-

a. Carbidopa

b. Clonidine hydrochloride

c. Bendrofluazide

d. Cimetidine

e. Ethinyloestradiol

f. Flunitrazepam

g. Lomustine

MULTIPLE CHOICE QUESTIONS

Q.1 Potentiometry is an.....method of analysis

a. Sectroscopic
b. Analytical
c. Electroanalytical
d. None of these

Q2. There is a linear relationship exist between the pH and.....of solution

a. Colour
b. Turbidity
c. Potential
d. None of these

Q.3 Hydrogen electrode can be used as

a. Reference
b. Indicator
c. Both of above
d. None of these

Q.4 Antimony electrode is an

a. Indicator electrode
b. Secondary reference electrode
c. Reference electrode
d. None of these

FILL IN THE BLANKS

1. pH gives the degree of.....of a solution.
2. E_{cell} is the sum of .....
3. In hydrogen electrode hydrogen gas is passed having purity of .....
4. In potentiometry graph is plotted between the.....

VERY SHORT ANSWER QUESTIONS

Q.1 What do you mean by e.m.f. ?
Q.2 Define pH.
Q.3 Define electrode potential.
Q.4 What is nernst equation?

LONG ANSWER QUESTIONS

Q.1 Give detail about potentiometric titrations, its principle and instrumentation.

Q.2 Give detail about the electrodes used in potentiometry.

Q.3 Give detail about the titrations performed by potentiometry.

Q.4 Give detailed applications of potentiometry.

ANSWERS

MULTIPLE CHOICE QUESTIONS

1. c 2. c 3. c 4. a

FILL IN THE BLANKS

1. Acidity or alkalinity
2. $E_{reference} + E_{indicator} + E_{junction}$
3. 99.8 %
4. indicator electrode potential and volume of titrant added

11 POLAROGRAPHY

INTRODUCTION

Polarographic method was developed by Aczech Chemist Jaroslov Heyrovsky in 1922. Polarography is an electrochemical method of analysis and is a branch of voltametry in which varying negative potential(voltage) is applied across the non-polarisable and a polarisable electrode i.e. droping mercury electrode and current is recorded. The graph is plotted between the current and applied voltage to get current-voltage curve which is called polarogram. From polarogram diffusion current (I_d) and half wave potential ($E^{1/2}$) is calculated, diffusion current is proportional to the concentration of analyte.

PRINCIPLE

Polarography is based upon the principle that gradually increasing negative potential (voltage) is applied between two electrodes one of which is polarisable (dropping mercury electrode) and other is non-polarisable and current produced is recorded. A sigmoid shape current-voltage curve is obtained (Figure 11.1) from which half wave potential as well as diffusion current is calculated. Diffusion current is used for the determination of concentration of substance and half wave potential is characteristic for every element or functional group and used for qualitative purpose.

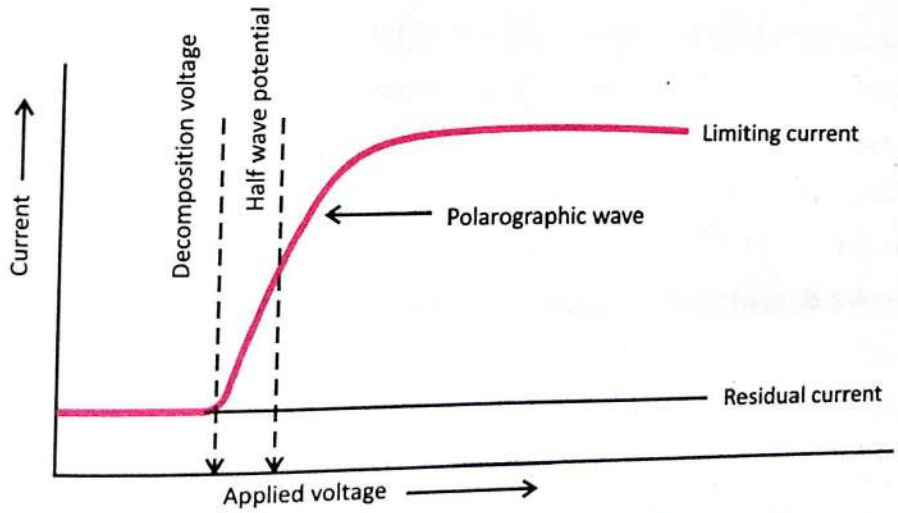


Figure 11.1: Current-voltage curve (polarogram)

For example, when voltage is applied to a solution containing lead ions in 1M KCl (supporting electrolyte) the positively charged lead ions will be attracted to DME by an electrical force and a diffusion force due to concentration gradient formed at the surface of the electrode. Current

starts flowing through the cell. The applied voltage is allowed to increase with time and the current produced is recorded. A graph is plotted between applied voltage and current produced.

ILKOVIC EQUATION

The diffusion current produced by dropping mercury electrode can be designated by Ilkovic equation which is as follows.

$$i_d = 607\ n\ D^{1/2}\ c\ m^{2/3}\ t^{1/6}$$

Where

i_d = diffusion current in microamperes

n = no. of electrons transferred

c = concentration in mmol/litres

D = diffusion coefficient in cm^2sec^{-1}

m = mass of mercury drop flowing per sec. in mg

t = drop time in sec

Half wave potential ($E_{1/2}$):-

Half wave potential is the potential at which the concentration of the oxidised and the reduced forms at electrode surface becomes equal i.e. 50% reduced and 50% oxidised forms are present. $E_{1/2}$ value is characteristic for every compound which is used for qualitative analysis. Relation between the potential applied, diffusion current and half wave potential can be describedd as follows:-

$$E_{app} = E_{1/2} + \frac{0.0592}{n} \log \frac{(i_d - i)}{i}$$

Where,

E_{app} = potential applied

$E_{1/2}$ = half wave potential

n = number of electrons involved

i_d = diffusion current

I = current at applied potential

Types of currents:-

Various types of currents which constitutes the polarographic wave are:-

1) Residual current

When the mercury drop grows up, the ions from supporting electrolyte gather around it i.e. they remain close to the mercury surface and forms an electrical double layer. This effect is just like charging up a condenser. When the drop falls off, a new drop is formed and a new condenser is charged again. This produces a continuous flow of electric current. Sometimes traces of impurities are present in the electrolyte, which produces small faradic current. Therefore, residual current is a sum of faradic and condenser current.

Residual current = Faradic current + Condenser current

2) Migration current

As the name indicates the migration current is due to migration of particles. The current is carried through the cell by all the ions present in the solution. The ions of the solution reaches to the surface of electrode by two means:-

a) By diffusion of the ions

b) Due to potential difference which exists between the electrode surface and the solution.

Current produced due to above two processes is known as migration current. Migration current can be eliminated by adding an indifferent electrolyte to the solution in high amounts so that its ions carry almost all the current. There is no need of migration current as we are concerned only with the diffusion current. Diffusion current is the only current which helps in determining the concentration of oxidant or reductant.

3) Diffusion current

This current is the basis of quantitative polarographic analysis. The difference between the residual current and the limiting current is known as diffusion current. It is denoted by i_d . This current is of great importance in polarography as this current is directly proportional to the concentration of the substance being reduced or oxidised. Diffusion current is given by ***Ilkovic equation—***

$$i_d = 607n\, D^{1/2} c\, m^{2/3} t^{1/6}$$

If we know the value of diffusion current from the polarographic wave or current voltage curve, we can easily calculate the concentration of the substance under analysis.

The Ilkovic equation tells that—

a) Diffusion current is directly proportional to the concentration of the electroactive substance.

b) Diffusion current is directly proportional to the product $m^{2/3}\, t^{1/6}$

This product is known as **capillary constant.** If we use different capillaries we get different results otherwise identical conditions should be maintained to get accurate results.

c) Diffusion current varies as the square root of its diffusion coefficient (D).

The diffusion coefficient D varies with the viscosity of the medium, with the size and charge of the diffusing species.

4) Kinetic current

Various molecules and ionic species do not undergo reaction at DME. These ionic species exhibit potentials of varying magnitude at a mercury electrode surface. These ions produces irreversible polarograhic waves. For example, O_2, CO_2, oxyanions like nitrates, sulphate, perchlorate etc. The current produced due to this non-electrode reaction is called the kinetic current. It depends upon the size of the mercury drop and is independent of the velocity of the flow of mercury from the capillary. This current is produced when the oxidized or the reduced form of the

electroactive substance is involved in a chemical reaction with other substances. It is a rate process so known as kinetic current.

5) Limiting current

After certain potential, the current reaches at a steady value i.e. no increment in current is seen by increasing voltage. At that point the rate of diffusion of ions become equal to the rate of reduction this condition is also called surface saturation or electrode is said to be concentration polarised. The value of current obtained is called limiting current.

All the above currents affect the current-voltage curve in one or the other way.

DROPPING MERCURY ELECTRODE

Dropping mercury electrode (DME) is a polarisable electrode and most widely used electrode too.

Construction

Dropping mercury electrode is consist of a fine capillary having a bore size ranged from 20 to 50 μ and 10 to 15 cm long which is connected to a mercury reservoir by a rubber tubing. The height of reservoir is adjusted to set the drop time as required i.e. 1 to 5 seconds. Drop time is the time required to form every fresh drop of mercury from capillary. Inside the tubing wire contact is made where mercury flows.

Working

Dropping mercury electrode is a polarisable elctrode and can act as both anode and cathode. Generally it is used as cathode but in some experiments it is used as anode by reversing polarity. The pool of mercury act as a counter electrode i.e. anode if DME is cathode or anode if DME is anode. The counter electrode which is a pool of mercury due to large surface area has low current density and is non-polarisable therefore has constant potential. To the analyte solution supporting electrolyte like KCl is added i.e. 50 to 100 times of the sample concentration). Pure nitrogen or hydrogen gas is bubbled through the solution to expel out the dissolved oxygen. If analyte solution is composed of cadmium than cadmium ions are discharged at cathode.

$$Cd^{2+} + 2e \rightarrow Cd$$

The gradually increasing voltage is applied to the polarographic cell and corresponding value of current is recorded. A graph is plotted between voltage applied and current to get a current voltage curve. The graph is the representation of polarisation of DME therefore is called polarogram and apparatus is known as polarograph. The diffusion current produced is directly proportional to the concentration of analyte therefore used as quantitative analysis while half wave potential is characteristic for every compound therfore used for qualitative analysis.

Advantages of DME

1) Surface area is reproducible with a given capillary.
2) Constant renewal of electrode surface eliminate poisoning effect.

3) Mercury forms amalgum with most of the metals.
4) Surface area of a drop can be calculated from the weight of drop.
5) Mercury have high hydrogen over voltage. Due to this reduction of alkali metal ions can be easily observed.

Limitations of DME

1) Surface area of each drop of mercury is never constant.
2) Mercury is very poisonous, so careful handling is required.
3) On changing the applied voltage there is change in surface tension and drop size.
4) It is limited in its voltage range in the positive direction.
5) DME gets easily oxidized and this limits the use of mercury as an anode. It is useful only for the analysis of reducible or very easily oxidisable substances.

ROTATING PLATINUM ELECTRODE

Dropping mercury electrode has a disadvantage that it can't be used at higher positive potentials due to oxidation of mercury. Therefore, platinum electrode is used to extend the range of polarography towards the positive potentials, But in stationary platinum electrode steady diffusion current is very slowly attained, to overcome this problem platinum electrode is rotated at constant speed which results in increase in sensitivity and rate of attainment of steady diffusion current.

Construction

Rotating platinum electrode (Figure 11.2) consist of a about 5mm platinum wire having 0.5mm diameter below standard mercury seal. The copper wire is passed through the 6mm glass tubing ranging from platinum mercury seal to the upper mercury seal by passing through the small hole blown in the stem of the stirrer. A wire from mercury seal is connected to the source that apply voltage. Tubing is rotated at a constant speed of 600 rpm.

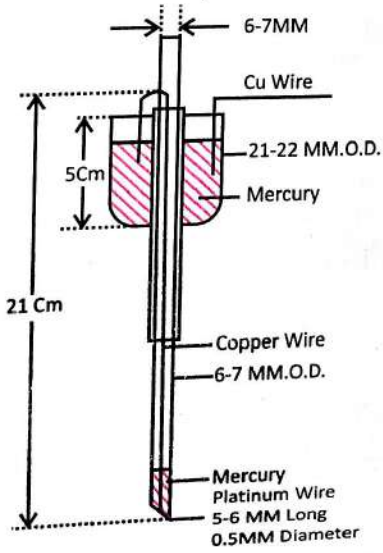


Figure 11.2: Rotating platinum electrode.

Working

Rotating platinum electrode is mainly used as an indicator electrode with reference electrode which is non polarisable electrode i.e. saturated calomel electrode in amperometry. To the analyte solution supporting electrolyte like KCl is added i.e. 50 to 100 times of the sample concentration. Pure nitrogen gas is bubbled through the solution to expel out the dissolved oxygen. Potential corresponding to the limiting current required for substance to be analysed is applied and titration is started. A graph is plotted between the volume of solution added v/s diffusion current and end point is detected.

SUPPORTING ELECTROLYTE

The purpose of using supporting electrolyte in polarography is to eliminate the effects of electrical migration on the reducible ions. The high concentration of supporting electrolyte ions eliminates the attractive or repulsive forces between the electrode and the analyte. The inert electrolyte ion does not get electrolysed at the given applied potential. Some of the examples are potassium chloride, potassium hydroxide, sodium chloride etc.

Supporting electrolyte is helpful in reducing migration current to about zero. Migration current is due to electrical attraction between the electrode and oppositely charged ions. Effect of this migration current can be eliminated by adding supporting electrolyte to the solution in a concentration so large that its ions carry almost all the current. For example, a solution containing potassium ions and cadmium ions carries current which is produced by each ion and further depends upon its relative concentration. It means 90% of the current transported to the cathode is by the potassium ions and only 10% by cadmium ions. When the concentration of potassium ions gets increased then the relative current carried by other cations gets reduced to zero and all the current passing through the cell will be transported only by the potassium ions.

APPLICATIONS

The two major applications of polarography are qualitative analysis and quantitative analysis.

1) Qualitative analysis

Qualitative identification of a given sample can be done from half wave potential of the current v/s voltage graph. The value of half wave potential is directly related to the standard potential for redox reaction under study. This method is useful for environmental analysis and for marine study. Qualitative analysis also helps in characterization of organic matter and various metal interactions.

2) Quantitative analysis

Polarography is useful in determining the concentration of drugs, metal ions etc. in the given sample. Concentration of a particular substance can be calculated from Ilkovic equation as:-

$$i_d = 607\ n\ D^{1/2}\ c\ m^{2/3}\ t^{1/6}$$

There are various methods by which quantitative estimation can be done.

a) Direct comparison method

In this the diffusion current of standard solution of an ion is compared with that of unknown sample and then by using Ilkovic equation the diffusion current quotient i.e. i_d/C is calculated.

b) Standard curve method

In this various concentrations of the standard solutions are prepared and their diffusion currents are calculated. Then a plot of diffusion current v/s concentration is plotted. Unknown sample solution is prepared, its diffusion current is measured and with the help of plot concentration of unknown solution can be calculated easily.

c) Internal standard method

This method is based on the fact that relative diffusion current does not depend upon the capillary properties. In this method a standard substance i.e. internal standard is added to each solution (sample and standard solution) and the ratio of i_{d1}/i_{d2} is calculated. This ratio is known as pilot ion ratio. The pilot ion ratio of the standard ions and the test ions are calculated and from this the concentration of unknown test solution can be determined.

d) Standard addition method

In this method polarogram of unknown solution of known volume is recorded and to this a known quantity of standard substance is added and second polarogram is recorded. The concentration of unknown solution can be determined from the increase in diffusion current.

3) Other applications

a) Determination of inorganic compounds

Polarography is useful in determination of cations and anions in the presence of other interfering ions. For example determination of bromated, iodate, nitrate etc. The polarogram of these substances gets affected by pH of the solution so buffers are used.

b) Determination of organic compounds

Polarography is helpful in determination of structure, quantitative identification of compounds and for the qualitative analysis of mixture of organic compounds. Estimation of sugars can also be carried out with the help of polarography. The composition of the given metal complex can be easily studied.

c) Estimation of dissolved oxygen

Amount of oxygen dissolved in aqueous solution or organic solvent can be calculated with the help of polarography. In this method oxygen waves are measured and the amount of dissolved oxygen can be calculated. Dissolved oxygen produces two reaction waves.

d) Pharmaceutical applications

Drugs like Acetazolamide, Chloremphenicol, Epinephrine etc can be analyzed by this method. Sulphonamides can be determined in the solution of tetraalkylammonium salts. Tetracyclines can also be determined polarographically. Analgesics and Antipyretics can be calculated in nitrate solution after diluting with a buffer solution with the help of polarography.

MULTIPLE CHOICE QUESTIONS

Q.1 Polarograph is

a. Current v/s Volt graph
b. DME
c. Instrument
c. None of these

Q.2 Entire polarography is carried out in absence of..... gas.

a. Nitrogen
b. Carbon dioxide
c. Moisture
d. Oxygen

Q.3 Diffusion current can be correlated with different conditions by

a. Nernst equation
b. Bragg's equation
c. Illkovic's equation
c. Beer's equation

Q.4 Residual current in polarography is due to

a. Oxidisable impurity
b. Reducible impurity
c. Analyte
d. All of these

FILL IN THE BLANKS

1. In polarography, migration current can be blocked by adding.....
2. Commonly used polarographic maxima supresor is .....
3. In polarography, supporting electrode must have.....
4. Diffusion current and concentration of analyte have ..... relationship.

VERY SHORT ANSWER QUESTIONS

Q.1 What is polarography ?

Q.2 Define diffusion current.

Q.3 Define migration current.

Q.4 What is residual current?

LONG ANSWER QUESTIONS

Q.1 Give detail about polarography, its principle and instrumentation.

Q.2 Give detail about the electrodes used in polarography.

Q.3 Give detailed applications of polarography

MULTIPLE CHOICE QUESTIONS

1. a 2. d 3. c 4. d

FILL IN THE BLANKS

1. KCl 2. Gelatin 3. Low reduction potential 4. Directrly proportional