CLASS NOTES ACCORDING LESSON WISE

Pharmaceutical Analysis

It involves a series of process for identification, determination, quantification, purification of a substance

Separation of components from a mixture solution

Determination of structure of compound

Ex: The substance may be simple, single compound, mixture of compounds and may be in of the dosage form.

The substance used as pharmaceuticals are animal, plants, micro-organisms, minerals and various synthetic products

The sample to be analyzed is called "**Analyte**" and on the basis of size of the sample, they can be classified as

Macro ---------- > 0.1 gm

Semi micro--------0.01-0.1 gm

Micro ----------0.001-0.01 gm

Sub micro---------0.0001-0.001 gm

Ultra-micro-------100-10000ppm

Trace analysis:

The development of pharmaceutical brought a revolution in human health. There pharmaceutical would serve their if they are free from impurities and administered in appropriate amount.

To make drugs serve their purpose, various chemicals and instrumental methods were developed at regular intervals which are involved in estimation of drugs

Types of chemical analysis:

Qualitative analysis: In this, which analyte is present in the sample is to be determined or to identify a compound / mixture

Quantitative Analysis: In this how much amount of analyte is present in the sample is to be determined

Types of quantitative Analysis:

1.chemical methods

a. volumetric/titrimetric method

b. gravimetric method

c. gasometric method

2.electrical method

3.instrumental method

4.bilogical and microbiological

1. **Chemical method:**

a. **volumetric / titrimetric method**: It is a method of analysis in which a solution of the substance of unknown concentration is treated with a solution of a suitable reagent of known concentration. The reagent is added to the substance until the amount is equivalent to the amount of substance to be determined

various types of volumetric methods

acid base titration

non-aqueous titration

oxidation-reduction

complexometric titration

precipitation titration

b) **gravimetric method**: In this a substance to be determined is converted into an insoluble precipitate in the purest form, then it is collected and weighed. It is a time-consuming process. In electrogravimetry, electrolysis of the sample is carried out in the electrodes is weighed after drying

Electrogravimetry: Analyte solution is electrolyzed. Electrochemical reduction causes the analyte to be deposited on the cathode. The cathode is weighed before and after the experiment and the weight difference is used to calculate the amount of analyte in the original solution

Thermogravimetry: Records the change in weight. It continuously measures mass while the temperature of a sample is changed overtime

Differential thermal analysis: Records the difference in temperature between test and reference material

Differential scanning calorimetry: Energy needed to establish a zero-temperature difference between a test and reference material.

c**) Gasometric Analysis**: It involves measurement of volume of gas evolved or absorbed in a chemical reaction.

Examples of some gases which are determined by gasometry N02, cyclopropane etc..

2. **Electrical method:**

It involves the measurement of electrical current, voltage or resistance in relation to the concentration of some species in solution

Electrical method of analysis includes:

1.potentiometry
2.conductometry
3.polarometry
4.voltometry
5.ampherometry

Potentiometry measures electrical potential of an electrode in equilibrium with an ion to be determined

Conductometry measures electrical conductivity of an electrode with a reference electrode

Polarography, voltmetry, and ampherometry measures electrical current at micro electrode

3. **Instrumental method of analysis**:

It measures physical properties of the compound and employed for the determination of trace concentration of element in the sample. Instrumental methods are preferred due to their selectivity, high speed, accuracy and simplicity of analysis. Any change in properties of system is detected by measurements of absorbance, specific rotation, refractive index, change in mass

Spectroscopic method:

This analysis involves measurement and interpretation of electromagnetic radiation (absorbed/emitted)

Methods which include absorption of radiation are uv, visible, IR, atomic absorption, NMR etc.

Emission methods involve heating or electrical treatment of the sample so that the atoms are raised to excited state to emit the energy and the intensity of the emitted energy is measured.

Example: Emission spectroscopy, flame photometry

Chromatography technique and electrophoretic method are separation of mixture of components but also apolize for identification of compounds

4. **Microbiological methods:**
They are based upon a comparison of the inhibition of growth of bacteria by a measured concentration of antibiotics to be examined with that produced by known concentration of standard preparation of the antibiotics having a known activity
5. **Biological method**: biological standardization on bioassay are the procedure by which the potency or the nature of the substance is estimated by studying its effect on living matter
Bioassays are generally done using animal tissue or organ as in case of use of guinea pig ileum for the estimation of histamine or using the intact animal as in case of insulin using mouse
The precision, reliability and reproductivity as a bioassay depends on proper selection of the tissue or method with highest selectivity and sensitivity for the drug
Bioassays are designed to measure the relative potency of two preparations, usually a standard and an unknown solution
The observed response of the unknown would be always relative to the effect that produced by a standard substance
The standard substance is pure substance and in official bio assays it refers to pharmaceutical standards

Methods of expressing concentration:
Different ways of expressing concentration
1.Normality
2.Molarity
3.Molality
4.Formal concentration
5.Percent solution
6.Parts per million(ppm)
1.**Normality:** Number of gram equivalents of solute in one liter of solution. Indicated by N
Equivalent weight = gram equivalent weight of solute

$$\frac{\text{gram equivalent weight of solute}}{\text{No of replaceable H+ and OH-}}$$

Example:
Preparation of 1N NaOH
Molecular weight of NaOH
Atomic weight of Na=23
Atomic weight of O=16
Atomic weight of H=1

$$\frac{}{40 \text{ gm}}$$

1N =40 gm of NaOH in 1 lit/1000 ml of water
0.1N= 4 gm of NaOH in 1 lit/1000 ml of water
0.01N=0.04 gm in NaOH in 1 lit/1000 ml of water

2.**Molarity:**
Number of molecular weight of the substance in one liter of solution. Indicated by M
M= gram molecular weight of solute

1000 ml of solution
Example: 1M NaOH
Molecular weight = 23+16+1
= 40 gm
1M=40 gm ----------→ 1 lit of solution
0.1M=4 gm----------→ 1 lit of solution
HCl = 1+35.5=36.5 gm of HCl in 1 lit of solution
3.**Molality:** gram molecular weight of the substance in 1 kg of solution. Denoted by m
M= number of molecular weight of substance

1000 gm of solution
NaOH=23+16+1=40 gm of NaOH in 1000 gm of water
4.**Formal concentration**:
Some substances do not exist in molecular form, they remain in ionic form in solid state as well as in solution. In such cases grams of molecular weight ; formula weight is used in preparation of solution and its concentration is expressed in terms of formality
F= weight of solute in grams

Volume of solution in liter
* formula weight

5**. Percent solution**:
Sometimes concentration is expressed in percent (parts per hundred) composition of a solution can expressed as

1.**percent W/W** = weight of the solute

Weight of the solution
*100

2.**percent V/V**= volume of the solute
---*100
Volume of solution
3.**percent W/V**= weight of the solute
---*100
Weight of the solution
a) Percent W/W frequently employed to express the concentration of commercial aqueous reagent
b) Percent V/V used to specify the concentration of a solution prepared by diluting a pure liquid with another liquid
c) percent W/V employed to indicate the composition of dilute aqueous solution of solid reagents

6. **parts per million and parts per billion** (ppm and ppb)
Parts per million is frequently employed to express the concentration of very dilute solution and is expressed as PPM
Concentration in PPM= Mass of solute
----------*106 ppm
Mass of solvent
Ppm and ppb are used to express the concentration of impurities in pharmaceuticals

Error: It is defined as the difference between true value and observed mean value
Absolute error =true value-observed mean value
Types of errors:
It is of two types.
1.Determinate error:
As the name indicates these errors are determinable and can be either avoided or corrected
2.Indeterminate error:
These errors are random and cannot be avoided or corrected by the use of high purity reagents or calibrated equipment
Types of determinate errors:
1.Operational or personal errors: These are associated with individual analyst and not associated with the procedure or method
Ex: wrong observation, wrong transferring
2.Instrumental errors:
These errors occur due to improper functioning of the instruments or due to the use of uncalibrated equipment or instruments
3.Reagent error:
These errors occur due to the use of reagent supplied in impure form or substandard form
4.Additive or constant error:
These errors are constant throughout the analysis
5.Proportional error:
These errors will be proportional throughout the analysis
6.errors in method:
These errors occur due to the wrong selection of procedure or method
Indeterminate errors:
They cannot be pin-pointed to any specific well-defined resources
They are random in nature and take place in several successive measurements performed by the same analyst under the same conditions and identical experimental parameters
Personal
Ex: some persons are unable to judge color changes sharply in visual titrations, which may result in a slight overtopping of the end point
An analyst may use the instrument incorrectly
Under washing or over washing of precipitate

Primary and secondary standard solutions:

Standard solution: In pharmaceutical analysis, the word standard means a material containing a substance with known concentration

Functions of standard solution:

1.To provide a reference for determining the concentration of unknown concentration
2.Stanadization of volumetric solution
3.To calibrate an instrument
4.Preparation of secondary standard

Primary standard:

It is a reagent which is very pure generally representative of the number of moles of the substance containing and easily weighed. It should satisfy the following requirements.

1.Easy to obtain, to purify, to dry, and to preserve in a pure state
2.The substance must be unaltered in air during weighing
(i.e. non-hygroscopic non-oxidized)
3.The total amount of impurities should not exceed 0.01-0.02%
4.It should have a high equivalent so that the weighing errors may be negligible
5.The primary standard should be readily soluble under the condition in which it is employed
6.The titration error should be negligible or easy to demonstrate accurately by experiment

The substances commonly employed as primary standards examples of acid-base titration, oxidation-reduction titration

Secondary standard:

It is a chemical which is standardized against a primary standard for use in a specific analysis
It follows that a secondary standard solution is a solution in which the concentration of dissolved solute has not been determined from the weight of the compound dissolved but by reaction of a volume of the solution against a measured volume of primary standard solution.
Example: most of the alkali hydroxides NaOH, KOH.

STANDARD SOLUTION:

The solution of accurately known strength is called standard solution

EQUIVALENCE POINT:

The point in a titration where the reaction is just completed /Theoretical end point/stoichiometric end point

INDICATOR:

The regent employed in titration to get locate the end point

ACCURACY:

It is defined has the closeness of the measured value to the true value. It depends on the minimization of the errors

PRECISION:

It refers to the agreement among a group of measured values
The errors in measurement can be broadly classified as systematic errors, random errors and gross errors

PREPARATION AND STANDARDISATION OF 0.1M SODIUM HYDROXIDE SOLUTION

AIM: To prepare and standardize 0.1M sodium hydroxide solution.
Requirements:
Apparatus: Conical flask, Burette, Pipette, Water Bath, Burner, Measuring cylinder, Beaker, Dropper, Glass rod, etc.
Chemicals: Sodium hydroxide pellets, Potassium hydrogen phthalate, Phenolphthalein, Distilled Water.
Principle: Potassium hydrogen phthalate, (KHC8H4O4) is a non-hygroscopic, crystalline, solid that behaves as a monoprotic acid. It is a water soluble and available in high purity. Because of its high purity, we can determine the number of moles of KHP directly from its mass and is referred as primary standard. Primary standard is used to determine the concentration of sodium hydroxide solution.
Neutralization reaction takes between sodium hydroxide and known amount of acid in the flask. End point is determined when all the acids has been neutralized and solution composition changes from excess acid to excess base. Phenolphthalein acts as an indicator to determine the endpoint and gives colour change.

$KHC_8H_4O_4 + NaOH \rightarrow KNaC_8H_4O_4(aq) + H_2O_2$

Titration: Acid base titration
Titrant: 0.1M Sodium hydroxide
Indicator: Phenolphthalein
Endpoint: Appearance of pale pink Primary Standard: Potassium hydrogen Phthalate.

Procedure:
Preparation of 0.1M sodium hydroxide:
Weigh accurately 4.0 gm of sodium hydroxide and transfer it to 100ml distilled water in a beaker with continuous stirring. Make up the volume to 1000ml with distilled water. Keep the solution for at least an hour and them carry out standardisation
Standardization of 0.1M NaOH:
* Weigh accurately 0.5 gm of KHP and transfer into a conical flask.
* Add total volume of 50-75 ml of water. Dissolve the sample properly.
* Add 2-3 drops of phenolphthalein indicator to the flask and titrate it against 0.1M NaOH until it gives pale pink colour as end point.
Each 1ml of 0.1M NaOH = 0.0204 gm of KHP

PREPARATION AND STANDARDISATION OF 0.1 N SODIUM THIOSULFATE

AIM: To prepare and standardise 0.1N sodium thiosulfate.

Requirements: Apparatus: Conical flask, Burette, Pipette, Water Bath, Burner, Measuring cylinder, Beaker, Dropper, Glass rod, etc.

Chemicals: Sodium thiosulfate, Potassium dichromate, Potassium iodide, sulphuric acid, Distilled Water.

Principle:

Iodometry (Iodometric titration) is a method of volumetric chemical analysis. A redox titration where appearance of elementary iodine indicates end point. Sodium thiosulphate a reducing agent is standardised by a primary standard potassium dichromate. A known amount of excess potassium iodide is added which oxidises to iodine in acidic medium. The liberated iodine is titrated with sodium thiosulphate using starch as an indicator.

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 \rightarrow 4K_2SO_4 + 7H2O + 3I_2$$

Titration: Redox titration
Titrant: 0.1N Sodium thiosulphate
Indicator: Starch solution
Endpoint: Appearance of pale blue
Primary Standard: Potassium dichromate.

Procedure:

Preparation of 0.1N Potassium dichromate:

Weigh accurately about 1.227 gm of Potassium dichromate in 250ml Volumetric flask and makeup to volume with distilled water. Preparation of 0.1N Sodium thiosulphate (Na2S2O3.5H2O): Dissolved accurately about 25g of Sodium thiosulphate in 1000ml of freshly boiled distilled water. Improve its stability by adding 0.1g of Sodium carbonate, stored the solution overnight and filter.

Standardization of 0.1N Sodium thiosulphate with potassium dichromate:

10ml of 0.1N Potassium dichromate solution is taken in iodine flask.
To this solution add 5ml of potassium iodide solution (10%) and add 5ml of 1M H2SO4 Cover the iodine flask with stopper and keep the solution in dark for 10minutes.
The liberated iodine is titrated with 0.1N Sodium thiosulphate until the solution becomes pale yellow. Introduce 5drops of starch indicator and titrate with constant stirring till the appearance of blue colour

1ml of 0.1N Sodium thiosulphate ≈

S. No	Content of flask	Burette reading		Volume of 0.1N $Na_2S_2O_3$Consumed	Indicator used	Endpoint
		Initial	Final			

$$M = \frac{\text{Weight of } K_2Cr_2O_7 * \text{Expected normality}}{\text{Volume of } H_2SO_4}$$

Report: 0.1N Sodium thiosulphate solution was prepared and standardised. Concentration of the solution was found to be _____N.

PREPARATION AND STANDARDISATION OF 0.1M SULPHURIC ACID SOLUTION

AIM: To prepare and standardise 0.1M sulphuric acid solution.
Requirements: Apparatus: Conical flask, Burette, Pipette, Measuring cylinder, Beaker, Dropper, Glass rod, etc.
Chemicals: Sulphuric acid, Sodium carbonate, Methyl red, Distilled Water.

Principle: It involves neutralisation reaction between sulphuric acid and sodium carbonate. (primary standard) Sulphuric acid reacts with sodium carbonate and forms sodium sulphate with water molecule. End point is seen when excess of methyl red indicator reacts with excess acid in the flask giving faint pinkish red colour.

$Na_2SO_3+H_2SO_4 \rightarrow Na_2SO_4+H_2O+CO_2$

Titration: Acid base titration
Titrant: 0.1M sulphuric acid
Indicator: methyl red
Endpoint: Appearance of faint pinkish red
Primary Standard: sodium carbonate

Procedure:
Preparation of 0.1M sulphuric acid:
Add 6ml of concentrated sulphuric acid to about 800 ml distilled water. Make up to volume 1000 ml with distilled water and cool the solution to 25°C
Standardisation of 0.1M sulphuric acid:
Weigh accurately 0.2gm of anhydrous sodium carbonate previously heated at 270°C for 1hr Dissolve it in 100 ml of water and add 0.1 ml of methyl red solution. Add acid slowly from burette with continuous stirring, until the solution becomes faint pink. Heat the solution to boiling, cool and continue the titration. Heat again to boiling and titrate further as necessary until faint pink colour is no longer affected by boiling.
1 ml of 0.1M sulphuric acid = 0.0106 gm of Sodium carbonate

Standardization of 0.1 M Sulphuric acid :

s.no	Content of flasks	Burette reading	Volume of 0.1M Sulphuric acid formation	Indicator used	End point

M = $\frac{\text{Weight of } Na_2SO_3 * \text{Expected molarity}}{0.0106 * \text{volume of 0.1 M } H_2SO_4}$

Report:
0.1M sulphuric acid solution was prepared and standardised. Concentration of the solution was found to be _____M.

PREPARATION AND STANDARDISATION OF 0.1 N POTASSIUM PERMANGANATE

AIM: To prepare and standardise 0.1N potassium permanganate

Requirements:

Apparatus: Conical flask, Burette, Pipette, Water Bath, Burner, Measuring cylinder, Beaker, Dropper, Glass rod, etc.

Chemicals: Oxalic acid, sulphuric acid, Potassium permanganate.

Principle:

Potassium permanganate (KMnO4) is a strong oxidising agent. Permanganate is intense dark purple colour. Reduction of purple permanganate ion to the colourless Mn+2 ion the solution will turn to faint pink from dark purple colour at the equivalence point No additional indicator is needed for the titration as KMn04 acts as self-indicator. The reduction of permanganate requires strong acidic medium.

In this permanganate is reduced by oxalate in acidic condition Oxalate reacts very slowly at room temperature so to enhance it the solution is heated.

$$2KMnO_4 + 3H_2C_2O_4 + 5H_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O$$

Titration: Redox titration

Titrant: 0.1N Potassium permanganate

Indicator: Self indicator

Endpoint: Appearance of pale pink

Primary Standard: Oxalic acid

Procedure:

Preparation of 0.1N Potassium permanganate:

Weigh accurately 3.2gm of Potassium permanganate transferred to 250ml beaker containing cold water and stir thoroughly.

Decant and makeup the volume to 1000ml.

Standardization of 0.1N Potassium permanganate:

Weigh accurately 6.3gm of Oxalic acid and transfer it a 1000ml graduated flask and makeup the volume with water. Pipette out 20ml of this solution and add 10ml of diluted sulphuric acid and warm to about 70°c.Add KMn04 solution from burette until pink colour appears. Wait until the colour disappears and continue until it persists faint pink colour for about 30seconds.

Standardization of 0.1N Potassium permanganate:

s.no	Contents of flask	Burette reading		Volume of 0.1 N $KMNO_4$ consumed	Indicator	Endpoint
		initial	final			

Each 1ml of 0.1N KMnO4 = 0.00063 gm of Oxalic acid

M = Weight of oxalic acid * Expected molarity
0.0063 * volume of 0.1 M $KMnO_4$

Report:
0.1N Potassium permanganate solution was prepared and standardised. Concentration of the solution was found to be _____N.

PREPARATION AND STANDARDISATION OF 0.1 M CERRIC AMMONIUM SULPHATE

AIM: To prepare and standardise 0.1 M cerric ammonium sulphate

Apparatus: Conical flask, Burette, Pipette, Water Bath, Burner, Measuring cylinder, Beaker, Dropper, Glass rod, etc.

Chemicals: Ceric ammonium sulphate, Arsenic trioxide, sodium hydroxide and sulphuric acid.

Principle:

Ceric ammonium sulphate is a powerful oxidising agent in acidic solution. It is bright yellow in colour and corresponding cerium salt form by reduction is colourless strong solution are self-indicating. However since dilute solutions are used so indicators are used for observation of end point. Aresnic trioxide used as primary standard in presence of sulphuric acid and osmic acid using ferroin sulphate as an indicator.

$$AS_2O_3 + NaOH \rightarrow NaAso_2$$
$$NaAsO_2 + H_2O \rightarrow NaH_2AsO_4 + 2H + 4e$$
$$4\ (Ce^{4+} + e \rightarrow Ce^{3+})$$

PROCEDURE:

Preparation of ceric ammonium sulphate:

66gm ceric ammonium sulphate was dissolved with gentle heat. Mix 30ml of sulphuric acid and 500ml of water. Cool and filter the solution if turbid and dilute to 100ml with water.

Standardisation of 0.1M ceric ammonium sulphate:

Weigh accurately 0.2gm of arsenic trioxide previously dried at 105°C for 1hr and transferred to a 500ml conical flask.

Wash down the flask with 25ml of 8% w/v solution of sodium hydroxide, swirl to dissolve, add 100ml of water and mix.

Add 30ml of dilute sulphuric acid, 0.1ml of ferroin sulphate solution.

Titrate with ceric ammonium sulphate until pale blue colour appears from pink colour.

Standardisation of 0.1M ceric ammonium sulphate:

s.no	Contents of flask	**Burette reading**		Volume of 0.1 M Ceric ammonium sulphate consumed	Indicator used	Endpoint
		initial	final			

\

Each 1ml of 0.1M Cerric ammonium sulphate = 49.46 gm of As_2O

M = Weight of As2O3 *** Expected molarity**
0.0063 * volume of ceric ammonium sulphate consumed

Report:
0.1M Ceric ammonium sulphate solution was prepared and standardised. Concentration of the solution was found to be _____M.

UNIT-II

Titration: it is defined as adding of titrant to titrand

Non-aqueous titrations: Most of the drugs or pharmaceuticals agents are weakly acidic or weakly basic in nature. These substances should be titrated by using non-aqueous solvents to get sharp end point. Most of the drugs are truly soluble in water.

Arrhenius acid-base concept:

According to Arrhenius acid base concept the substance ready to donate H+ ion is called as an acid, and the substance ready to donate OH- is a base.

Bronsted-Lowry theory:

The concept is based on protons.
Any substance ready to donate proton is acid
Any substance ready to accept proton is base

Lewis acid-base concept

It is based on electron pair
Any substance having rich of electrons and ready to donate is based
Any substance having lack of electron and seeking electron is called acid

H2SO4 + H2O ----------→ H30+ + HSO4-
Strong acid strong base weak acid weak base

Criteria for non-aqueous solvents

The non-aqueous solvents should be non -toxic and should be available in liquid form. The organic non-aqueous solvents should have appropriate dielectric constant and easily undergo ionization

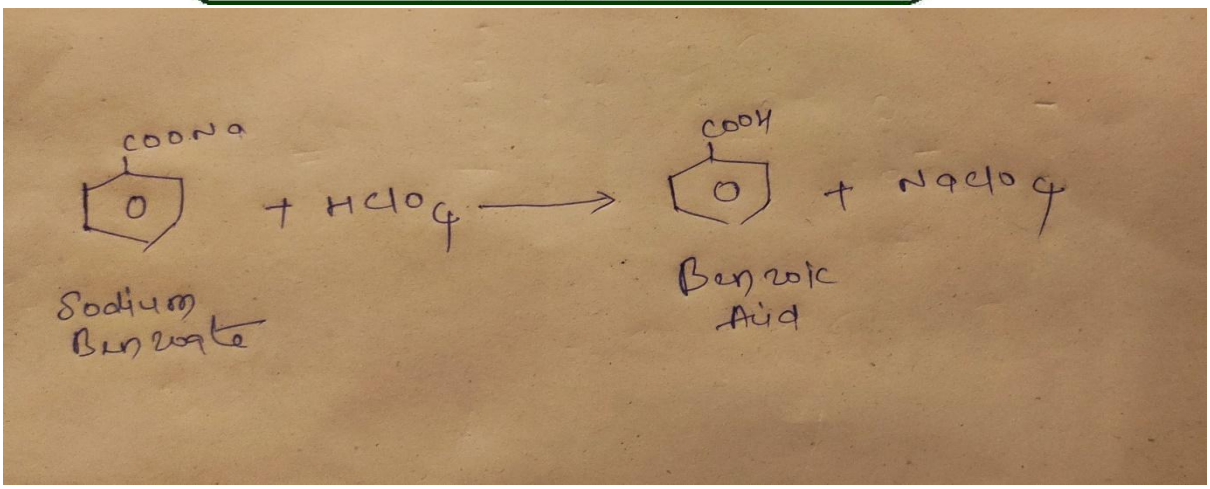
Role of solvents:

HCl + H2O ----------→ strong acid ↑

HCl + CH3COOH----------→ weak acid↓
CH3COOH+ H2O ----------→ weak acid↓
CH3COOH+NH3----------→ strong acid ↑

The solvent has an important role which influences the acidic properties of certain compounds. Water as a solvent increase acidity for HCl whereas Acetic acid decreases the acidity of HCl as a solvent. Water as a solvent decreases acidity of acetic acid while ammonia as a solvent increases acidity of acetic acid

Types of solvents:
1.Aprotic solvents
2.Protic solvents
3.Protpohilic solvents
4.Amphiprotic/ Amphoteric solvents
Aprotic solvents: These solvents are chemically inert having low dielectric constant and will not go easy for ionization
Examples: benzene, chlorobenzene, acetonitrile, carbon tetra chloride, toluene, chloroform
Protogenic solvents: these solvents are undergo easy ionization having more dielectric constant. All acids are acting as protogenic solvents
Examples:
$H_2SO_4 \leftrightarrow H^+ + so_4^-$
$CH_3COOH \leftrightarrow H^+ + CH_3COO^-$
$HClO_4 \leftrightarrow H^+ + ClO_4^-$
Protophilic solvents: protophilic solvents are basic in nature and having tendency to attract protons from strong acids and as well as weak acids and this effect is known as Levelling effect
Differentiating solvents: these solvents are having tendency to attract proton from strong acids only and this effect is known as differentiating effect
Strong acids can be considered as levelling solvents because of it gives proton to strong base as well as weak base
Examples: liq.Ammonia, pyridine, dimethyl formaldehyde, acetone and ether
Amphiprotic / amphoteric solvents: these solvents having both characteristic features of protophilic and protogenic solvents
Examples: H_2O, alcohol, acetic acid
$HClO_4 \leftrightarrow H^+ + ClO_4^-$
$CH_3COOH \leftrightarrow H^+ + CH_3COO^-$
Estimation of sodium benzoate:
Sodium benzoate is white crystalline powder or flakes
It is hygroscopic in nature and is used as pharmaceutical aid
Principle:
It is based on non-aqueous acidimetry titration. Sodium benzoate is acting as weak base, to strengthen this basicity add acetic acid. Thymol blue indicator is added to get completion of reaction by color change



Procedure: To 0.25 gm of sodium benzoate add 20 ml of glacial acetic acid in a clean dried conical flask. Mix thoroughly and add 2-3 drops of thymol blue indicator and titrate the contents of the conical flask with 0.1M perchloric acid which is taken in burette.
Each ml of 0.1M HClO4 =0.0144 gm of sodium benzoate

Estimation of Ephedrine HCl
Ephedrine HCl is acting as a sympathomimetic drug and also used to treat asthma as a bronchodilator and also used as a hypotension during spinal anesthesia
Principle:
It is based upon non-aqueous acidimetry titration. The chloride ions in Ephedrine makes weak base unable to accept proton properly, to strengthen the basic property had mercuric acetate
Figure:

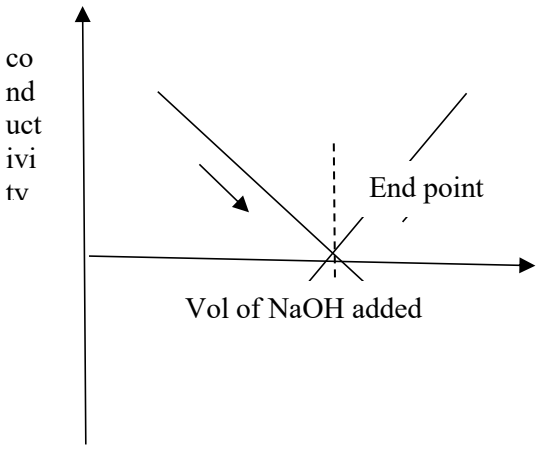
Procedure:
Add 0.17 gm of Ephedrine HCl in 10ml of mercuric acetate in a dried conical flack. To this add 50 ml of acetone and add 2 to 3 drops of methyl orange indicator
Each ml of 0.1M HClO4 =0.0207gm of Ephedrine HCl

Acid – Base Titrations.

1.Strong acid vs strong base
HCl is a strong acid and it completely dissociates into $\mathbf{H^+}$ and Cl^-

$$\mathbf{HCl \rightarrow H^+ + Cl^-}$$

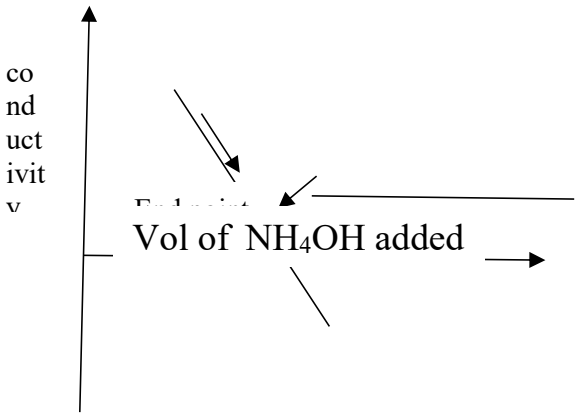
$\mathbf{H^+}$ ions moves to cathode and $\mathbf{Cl^-}$ ions move to anode. And the conductivity is more at initial stage, this is known as initial conductivity.
When NaOH is added from burette, OH^- ions of NaOH reacts with $\mathbf{H^+}$ of HCl and convert into water, so that the conductivity gradually decreases.
Once the total available $\mathbf{H^+}$ ions are converted into water, it indicates the completion of reaction or endpoint. Further addition of NaOH causes the increase in conductivity because of Na^+ and OH^- ions move to electrodes and increase conductivity.
Therefore we get '**V**' shaped graph, where two lines joined, is the endpoint.



2.Strong acid vs Weak base.

HCl completely dissociates and we get maximum conductivity. Once NH_4OH is added, the conductivity is decreased by conversion of $\mathbf{H^+}$ from HCl and OH^- from NH_4OH to water. Once the endpoint reaches, further addition of NH_4OH, it is not completely dissociates and conductivity will be neither increases nor decreases, so that we get the graph like below.

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

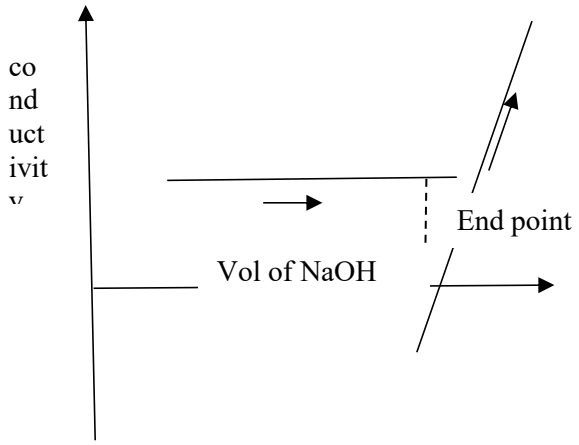


3. Weak acid VS Strong base

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

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

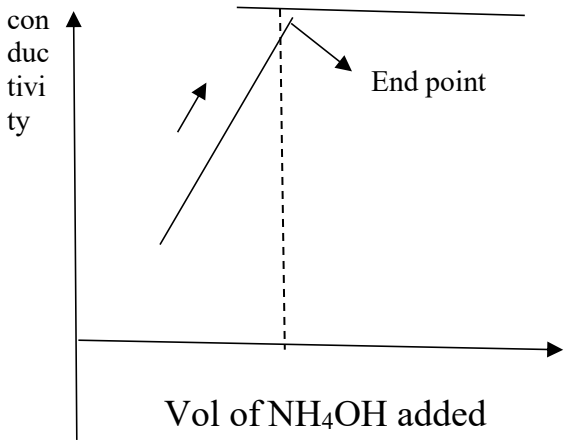
Acetic acid is weak acid and it is partially ionized to acetate and H^+ ions. Being a weak acid, conductivity is less, so that we get plateau or straight line. Once the endpoint reaches excess of Sodium hydroxide is ionized to Na^+ and OH^- ions. Because of more conductance of OH^- ion, the conductivity will be increased.



4.Weak acid VS Weak base.

$CH_3COOH + NH_4OH \rightarrow CH_3COONH_4 + H_2O$

when the reaction between weak acid like acetic acid and weak base like NH_4OH takes place, we get ammonium acetate which is having good conductance hence conductivity is increased. Once the endpoint reaches further addition of ammonium hydroxide will not change the conductivity, so that we get the straight line.



Theories of indicators: An **indicator** is a substance which show characteristic change in its colour when comes in contact with acid or base and thus it is used to determine **dictators** the degree of acidity or basicity of any solution. For example, litmus solution or litmus paper.

Role of indicators in chemistry is very important. They are used are also used to find out the end point in a titration.

In acid-base **titrations**, organic substances (weak acids or weak bases) are generally used as **indicators**.

Indicators change their colour within a certain pH range.The colour change and the pH range of some common **indicators used** are tabulated below:

Indicator	pH Range	Colour of Acidic Solution	Colour of Basic Solution
Methyl Orange	**3.2-4.5**	**Orange**	**Yellow**
Methyl Red	**4.4 – 6.5**	**Red**	**Yellow**
Bromothymol blue	**6.0 -7.8**	**Yellow**	**Blue**
Phenolphthalein	**8.3- 10.0**	**Colourless**	**Pink**
Alizarin Yellow	**10.1 – 12.1**	**Yellow**	**Red**
Litmus	**5.5-7.5**	**Red**	**Blue**
Phenol red	**6.8-8.4**	**Yellow**	**Red**

There are two theories which explain the change of colour **indicators** with change in pH.

Ostwald's Theory

According to Ostwald's theory

- The colour change of any indicator is due to its ionisation. The unionised form of indicator has different colour than its ionised form.
- An indicator is either a weak acid or base, so its ionisation is highly affected in acids and bases. If an **indicator** is a weak acid, its ionisation would be very much low in acids due to common H^+ ions while it is fairly ionised in alkalies. In the same way, if the **indicator** is a weak base, its ionisation is large in acids and low in alkalies due to common OH^- ions.

Let's take examples of two important indicators **phenolphthalein** which is a weak acid and **methyl orange** which is a weak base.

1. Phenolphthalein

It is represented as HPh. This indicator being a weak acid ionises in solution to a small extent as follows:

$HPh \rightleftharpoons H^+ + Ph^-$

Colourless Pink

Applying law of mass action, we get

$K = [H^+][Ph^-]/[HPh]$

The undissociated molecules of **phenolphthalein** are colourless while the Ph^- ions are pink in colour. In presence of an acid , ionisation of HPh is practically negligible as the equilibrium shifts to left hand side due to high concentration of H^+ ions. Thus, the solution would remain colourless. On addition of alkali, hydrogen ions are removed by OH^- ions in the form of water molecules and the equilibrium shifts to right hand side. Thus, the concentration of Ph^- ions increases in solution and they impart pink colour to the solution.

2. Methyl Orange

It is a very weak base and can be represented as MeOH. It is ionized in solution to give Me^+ and OH^- ions.

$MeOH \rightleftharpoons Me^+ + OH^-$

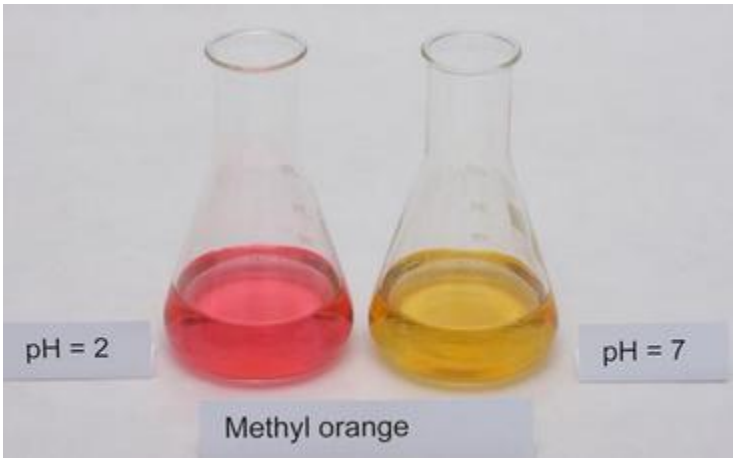
Yellow Red

Applying law of mass action,

$K = [Me^+][OH^-]/[MeOH]$

In presence of an acid, OH^- ions are removed in the form of water molecules and the above

equilibrium shifts to right hand side. Thus, sufficient Me^+ ions are produced which impart red colour to the solution. On addition of alkali, the concentration of OH^- ions increases in the solution and the equilibrium shifts to left hand side, i.e., the ionisation of MeOH is practically negligible. Thus, the solution acquires the colour of unionised **methyl orange** molecules, i.e., yellow.



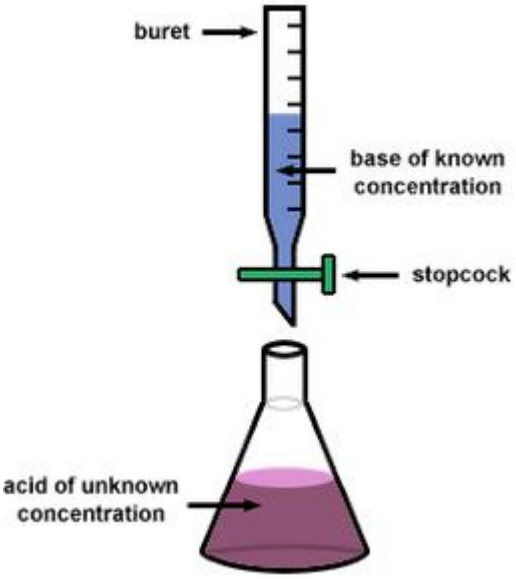
This theory also explains the reason why **phenolphthalein** is not a suitable **indicator** for **titrating** a weak base against strong acid. The OH^- ions furnished by a weak base are not sufficient to shift the equilibrium towards right hand side considerably, i.e., pH is not reached to 8.3. Thus, the solution does not attain pink colour. Similarly, it can be explained why **methyl orange** is not a suitable **indicator** for the **titration** of weak acid with strong base.

- **Quinonoid theory**

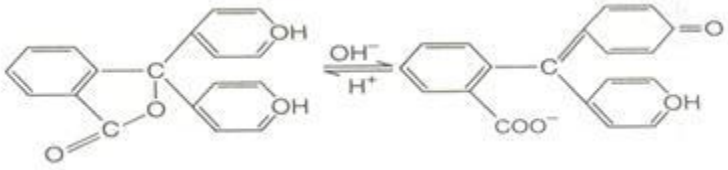
According to quinonoid theory, an **acid-base indicator** exists in two tautomeric forms having different structures which are in equilibrium. One form is termed benzenoid form and the other quinonoid form.

The two forms have different colours. The colour change is due to the interconversion of one tautomeric form into other. One form mainly exists in acidic medium and the other in alkaline medium.

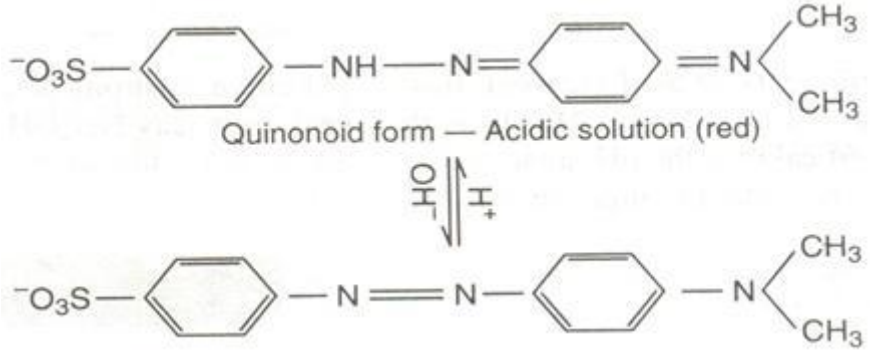
Thus, during **titration** the medium changes from acidic to alkaline or vice-versa. The change in pH converts one tautomeric form into other and thus, the colour change occurs.



Phenolphthalein has benziod form in acidic medium and thus, it is colourless while it has quinonoid form in alkaline medium which has pink colour.



Methyl orange has quinonoid form in acidic solution and benzenoid form in alkaline solution. The colour of benzenoid form is yellow while that of quinonoid form is red.



Common-ion effect:

The **common-ion effect** refers to the decrease in solubility of an ionic precipitate by the addition to the solution of a soluble compound with an ion in common with the precipitate.[1] This behaviour is a consequence of Le Chateliar principle for the equilibrium reaction of the ionic association/dissociation. The effect is commonly seen as an effect on the solubility of salts and other weak electrolytes. Adding an additional amount of one of the ions of the salt generally leads to increased precipitation of the salt, which reduces the concentration of both ions of the salt until the solubility equilibrium is reached. The effect is based on the fact that both the original salt and the other added chemical have one ion in common with each other.

Dissociation of hydrogen sulphide in presence of hydrochloric acid.

Hydrogen sulphide (H_2S) is a weak electrolyte. It is weakly ionized in its aqueous solution. There exists an equilibrium between unionized molecules and the ions in an aqueous medium as follows:

$$H_2S = 2H^+ + S^{2-}$$

By applying the law of mass action, we have

To the above solution of H_2S, if we add hydrochloric acid, then it ionizes completely as

$$HCl = H^+ + Cl^-$$

This makes H^+ a common ion and creates a common ion effect. Due to the increase in concentration of H^+ ions, the equilibrium of dissociation of H_2S shifts to the left and keeps the value of K_a constant. Thus, the ionization of H_2S is decreased. The concentration of unionized H_2S is increased. As a result, the concentration of sulphide ions is decreased.

acidimetry - volumetric analysis using standard solutions of acids to measure the amount of a base present volumetric analysis - quantitative analysis by the use of definite volumes of standard solution

alkalimetry - volumetric analysis using standard solutions of alkali to measure the amount of acid present volumetric analysis - quantitative analysis by the use of definite volumes of standard solution

UNIT - III

Mohr's method:

Mohr method of determination of chlorides by titration with silver nitrate is one of the oldest titration methods still in use - it was researched and published by Karl Friedrich Mohr in 1856.

The idea behind is very simple - chlorides are titrated with the silver nitrate solution in the presence of chromate anions. End point is signalled by the appearance of the red silver chromate.

Intense yellow color of chromate may make detection of first signs of formation of red silver chromate precipitation difficult. As some excess of silver must be added before precipitate starts to form, if concentration of titrant is below 0.1M, we may expect singificant positive error. To correct for this error we can determine a blank, titrating a solution of the indicator potassium chromate with standard silver nitrate solution. To make result more realistic we can add small amount of chloride free calcium carbonate to the solution to imitate the white silver precipitate.

Solution during titration should be close to neutral. In low pH silver chromate solubility grows

due to the protonation of chromate anions, in high pH silver starts to react with hydroxide anions, precipitating in form of AgOH and Ag_2O. Both processes interfere with the determination accuracy.

Exactly the same approach can be used for determination of bromides. Other halides and pseudohalides, like I^- and SCN^-, behave very similarly in the solution, but their precipitate tends to adsorb chromate anions making end point detection difficult.

reaction

Reaction taking place during titration is

$$Ag^+ + Cl^- \rightarrow AgCl(s)$$

sample size

Assuming 0.1M titrant concentration and 50 mL burette, aliquot taken for titration should contain about 0.12-0.16 g chloride anion (3.5-4.5 millimoles).

end point detection

Before titration small amount of sodium or potassium chromate is added to the solution, making its slightly yellow in color. During titration, as long as chlorides are present, concentration of Ag^+ is too low for silver chromate formation. Near equivalence point concentration of silver cations rapidly grows, allowing precipitation of intensively red silver chromate which signals end point. See precipitation titration end point detection page for more detailed, quantitative discussion.

solutions used

To perform titration we will need titrant - 0.1 M silver nitrate solution, indicator - potassium chromate solution, and some amount of distilled water to dilute sample.

procedure

- Pipette aliquot of chlorides solution into 250mL Erlenmeyer flask.
- Dilute with distilled water to about 100 mL.
- Add 1 mL of 5% potassium chromate solution.
- Titrate with silver nitrate solution till the first color change.

result calculation

According to the reaction equation

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

silver nitrate reacts with chloride anion on the 1:1 basis. That makes calculation especially easy - when we calculate number of moles of $AgNO_3$ used it will be already number of moles of Cl^- titrated.

Limitations:
This method is used for the solutions which are having PH range 6 to 10 if more than 10 we get silver oxide and silver hydroxide ppt instead of silver chloride and silver bromide
It is not carried out in the presence of reducing agent
This method is not carried out in the presence of anions
Due to adsorption effect, it is not used to quantitative analysis of iodides and thiocyanides
In acidic medium , there is a need of excess of silver which leads for large errors

Volhard method:

It is not always possible to use Mohr method to determine concentration of chlorides. For example, Mohr method requires neutral solution, but in many cases solution has to be acidic, to prevent precipitation of metal hydroxides (like in the presence of Fe^{3+}). In such cases we can use Volhard method, which is not sensitive to low pH.

In the Volhard method chlorides are first precipitated with excess silver nitrate, then excess silver is titrated with potassium (or sodium) thiocyanate. To detect end point we use Fe^{3+} cations, which easily react with the thiocyanate, creating distinct wine red complex.

There is a problem though. Silver thiocyanate solutility is slightly lower than solubility of silver chloride, and during titration thiocyanate can replace chlorides in the existing precipitate:

$$AgCl(s) + SCN^- \rightarrow AgSCN(s) + Cl^-$$

To avoid problems we can filtrate precipitated AgCl before titration. However, there exist much simpler and easier procedure that gives the same result. Before titration we add some small volume of a heavy organic liquid that is not miscible with water (like nitrobenzene, chloroform or carbon tetrachloride). These liquids are better at wetting precipitate than water. Once the precipitate is covered with non polar liquid, it is separated from the water and unable to dissolve.

Precipitate solubility is not a problem during determination of I^- and Br^-, as both AgBr and AgI have much lower solubilities than AgSCN.

reaction

There are two reactions, as this is a back titration. First, we precipitate chlorides from the solution:

$$Ag^+ + Cl^- \rightarrow AgCl(s)$$

Then, during titration, reaction taking place is:

$$Ag^+ + SCN^- \rightarrow AgSCN(s)$$

sample size

In back titrations sample size is more difficult to calculate than during normal, direct titrations. For best accuracy excess of silver should be titrated with about 40-45 mL of titrant (assuming - as we usually do - that we are using 50 mL burette). However, that usually means we should use relatively large initial volume of silver solution. Assuming we will start with 50 mL of pipetted silver nitrate and we will titrate excess with about 25 mL of thiocyanate solution, and finally assuming both solutions used are 0.1M, aliquot taken for titration should contain about 0.09 g chloride anion (2.5 millimoles).

Note, that silver nitrate can be added not using single volume pipette, but from burette. If the amount of chlorides is approximately known, this way it is possible to control excess of silver nitrate and volume of the thiocyanate titrant.

end point detection

End point is detected with the use of iron (III) thiocyanate complex, which have very distinct and strong wine color.

solutions used

To perform titration we will need 0.1M silver nitrate solution to precipitate chlorides, titrant - 0.1M potassium thiocyanate solution, nitric acid (1+1) to acidify solution, ammonium ferric sulfate solution that will be used for end point detection, nitrobenzene, and some amount of distilled water to dilute sample.

procedure

- Pipette aliquot of chlorides solution into 250mL Erlenmeyer flask.
- Add 5 mL of 1+1 nitric acid.
- Dilute with distilled water to about 100 mL.
- Add 50 mL of 0.1M silver nitrate solution.
- Add 3 mL of nitrobenzene.
- Add 1 mL of iron alum solution.
- Shake the content for about 1 minute to flocullate the precipitate.
- Titrate with thiocyanate solution till the first color change.

result calculation

As in every back titration, to calculate amount of substance we have to subtract amount of titrated excess from the initial amount of reactant used. In the case of argentometry calculations are easy, as all substances used react on the 1:1 basis.

First we have to calculate number of moles of silver nitrate initially added to the chlorides sample. Assuming it was 50 mL of 0.1 M solution, it contained 5 millimole of silver. Then, excess was titrated according to the reaction equation:

$$Ag^{+} + SCN^{-} \rightarrow AgSCN(s)$$

Modified Volhard's method:

Caldwell J.R and Mayer V.H modified this Volhard method by introducing wetting agent.

In this method Nitrobenzene is acting as a wetting agent and forms an insoluble protective layer over AgCl which minimizes the solubility of AgCl, hence we accurate end point.

Fajan's method:

Titrant: AgNO3

Analyte: Halides

Indicator: Adsorption indicator

Fluorescein

Dichloro-fluorescein

Eosin

Red Bengal

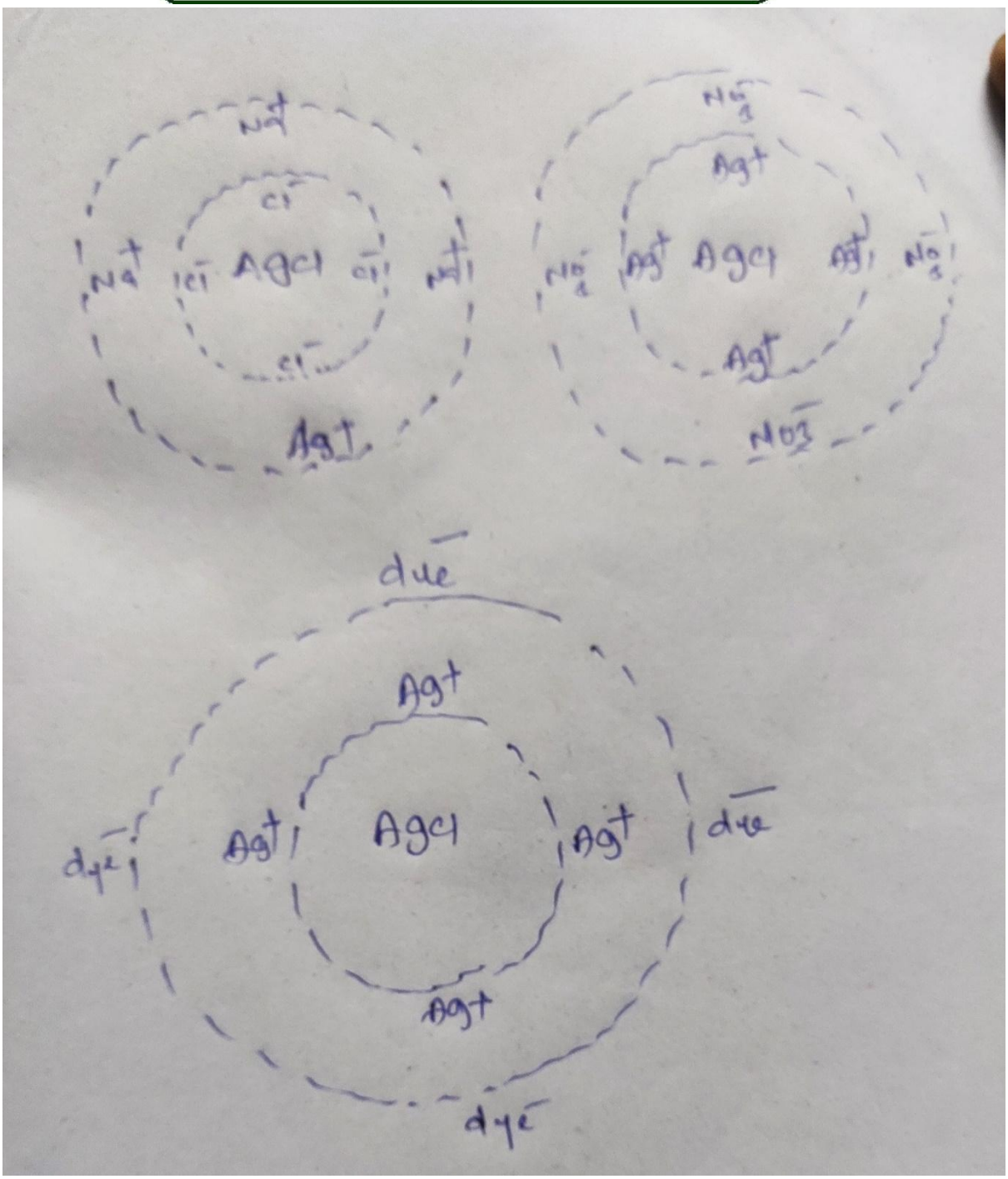
Principle:

It is based upon the Adsorption mechanism

$AgNO_3 + NaCl \text{ -------} \rightarrow AgCl + NaNO_3$

The indicator forms a layer over silver chloride precipitate and forms pink colour, indicates the completion of reaction

Adsorption indicators are acidic/basic dyes



Estimation of 1.0M NaCl [Mohr's method]

Preparation of 0.1M AgNO3:

Take 10 gm of silver nitrate which is previously dried at 120°C for 2 hrs and cool in a desiccator. Then take 8.49 gm of AgNO3 and mix in sufficient water to produce 500 ml which is equivalent to 0.1 M

Preparation of 0.1M NaCl:

Take 2.922 gm of sodium chloride and mix in sufficient water to produce 500ml which is equivalent to 0.1M NaCl

Principle:

$AgNO_3 + NaCl \text{ ----------} \rightarrow AgCl + NaNO_3$

$AgNO_3 + K_2SO_4 \text{ ----------} \rightarrow Ag_2CrO_4 + KNO_3$

Method:

Take 10ml of 0.1M NaCl in conical flask. Add few drops of potassium chromate as an indicator. Burette is filled with 0.1M $AgNO_3$.start the titration, silver nitrate is reacting with sodium chloride and forms white ppt of AgCl. Silver nitrate reacts with indicator and form silver chromate which gives brick red colour indicates the end point
Report the process for three times to get accurate end point. Take the average value, go for necessary calculation
Each ml 0.1M $AgNO_3$ =0.005845 gm of NaCl

Metal ion-indicators:

A **complexometric indicator** is an ionochromic dye that undergoes a definite color change in presence of specific metal ions. It forms a weak complex with the ions present in the solution, which has a significantly different color from the form existing outside the complex. Complexometric indicators are also known as pM indicators.

In analytical chemistry, complexometric indicators are used in complexometric titration to indicate the exact moment when all the metal ions in the solution are sequestered by a chelating agent (most usually EDTA). Such indicators are also called **metallochromic indicators**.

The indicator may be present in another liquid phase in equilibrium with the titrated phase, the indicator is described as **extraction indicator**.

Some complexometric indicators are sensitive to air and are destroyed. When such solution loses color during titration, a drop or two of fresh indicator may have to be added.

Complexometric indicators are water-soluble organic molecules. Some examples are:

- Calcein with EDTA for calcium
- Patton-Reeder Indicator with EDTA for calcium with magnesium
- Curcumin for boron, that forms Rosocyanine, although the red color change of curcumin also occurs for pH > 8.4
- Eriochrome Black T for aluminium, cadmium, calcium and magnesium
- Fast Sulphon Black with EDTA for copper
- Hematoxylin for copper
- Murexide calcium and rare earths
- Xylenol orange for gallium, indium and scandium

Masking agents:

A masking agent is a reagent used in chemical analysis which reacts with chemical species that may interfere in the analysis. In sports a masking agent is used to hide or prevent detection of a banned substance or illegal drug like anabolic steroids or stimulants. Diuretics are the simplest form of masking agent and work by enhancing water loss via urine excretion and thus diluting the urine, which results in lower concentrations of the banned substance as more of it is being excreted from the body making it more difficult for laboratories to detect

Masking agents:

tri ethanol amine---------- iron, aluminium

triglycerol -------copper

potassium/sodium cyanide-----heavy metals

ammonium fluoride------iron, aluminium

Demasking agents:

Demasking agent is the agent which dissociates the masking agent and metal ion and makes the metal ion free. Now the metal ion is going to be titrated with concern titrant for estimation metal ions

Examples: formaldehyde, chloral hydrate

Techniques of demasking agents:

By altering PH

By changing oxidation state of metal ions in the complex

By voltasation of complex

By replacement of metal ion from the complex with another metal ion

Complexometric titrations

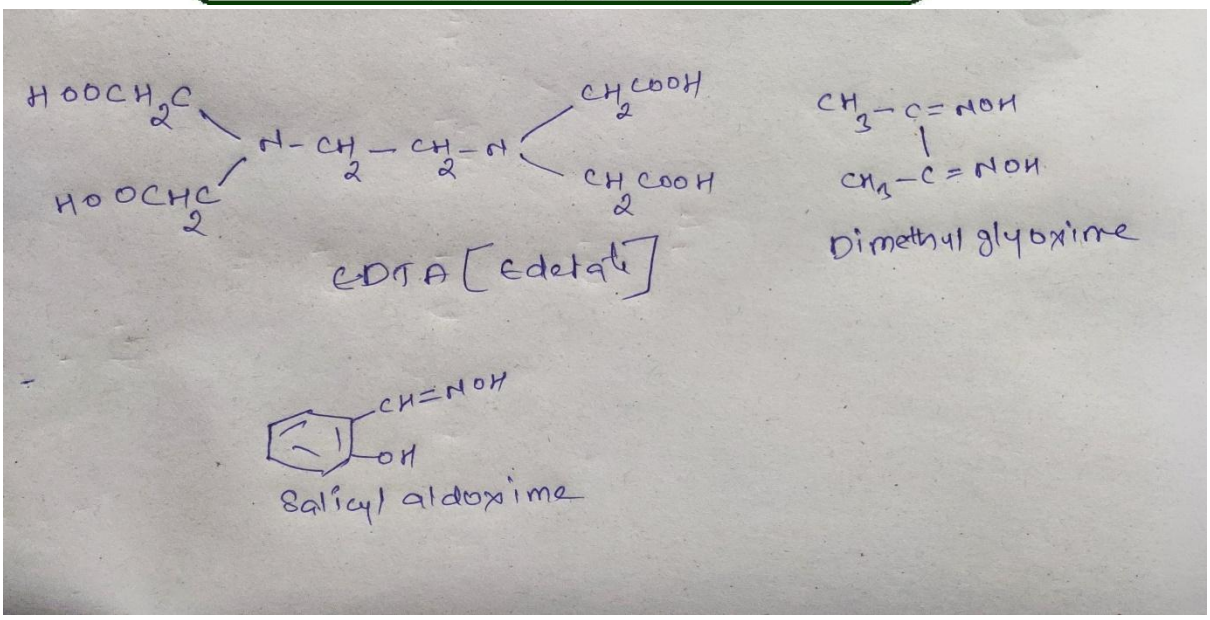
Metal ions analysis is carried out by complexometric titrations. Titrations involves the reaction between metal ion sample and complexing agent and with the help of metal ion indicators. Metal ions includes monovalent, divalent, trivalent and tetra valent and poly valent. Complexing agents are electron donor and form covalent bonds with the respective metal ions. If any complexing agent forms a single bond with metal ion is known as unidentate[ligand]. If the complexing agent forms no of covalent bonds with metal ion and that is known as polydentate or chelating agent

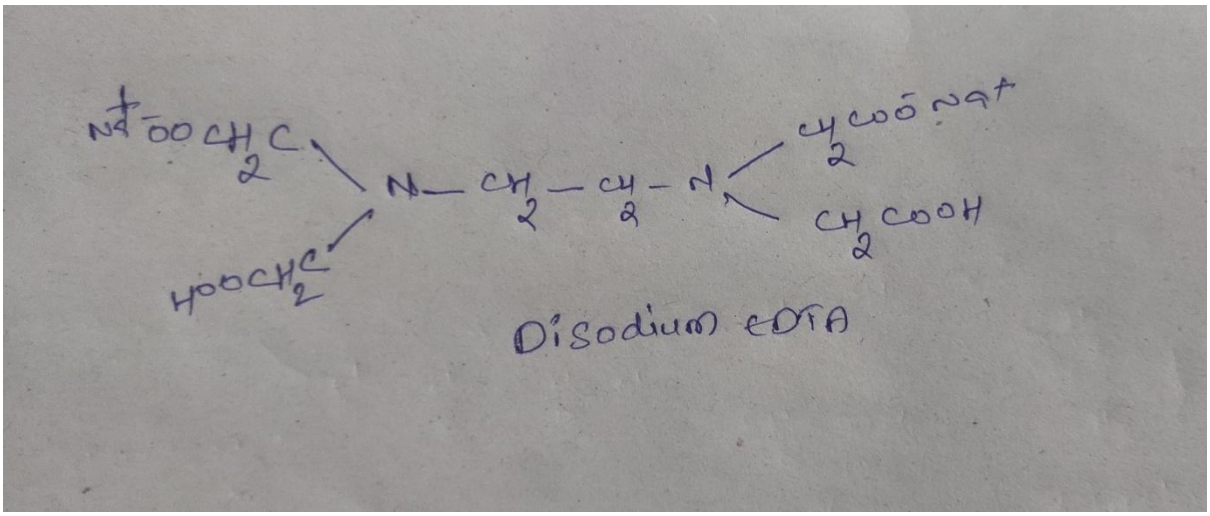
Example: EDTA -Ethylene Diamine Tetra Acetate

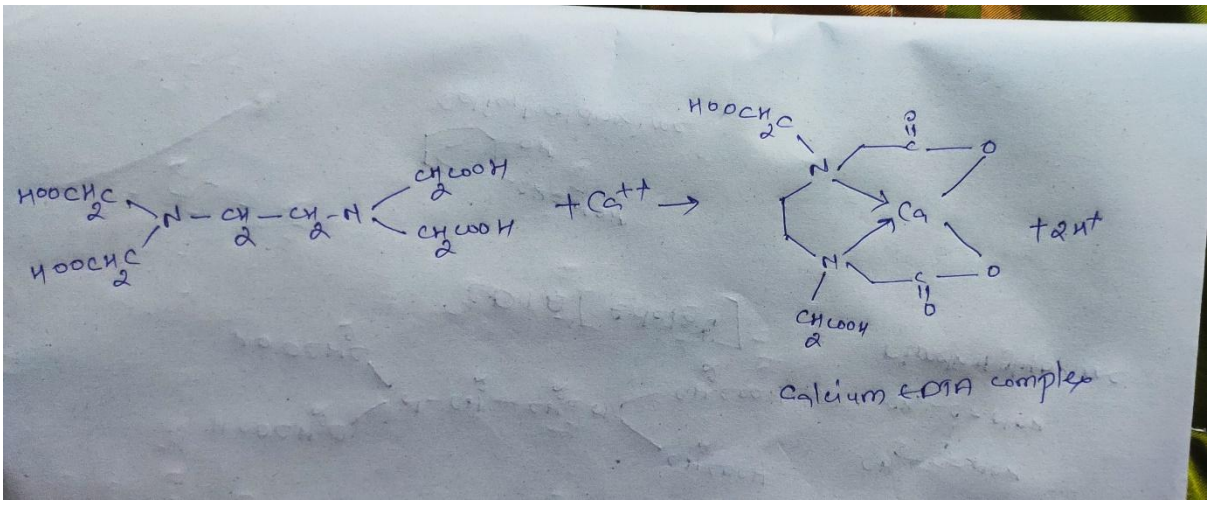
Salicyl aldoxime

Dimethyl glyoxime

Fig


EDTA [Edetate]
Dimethyl glyoxime
Salicyl aldoxime


Disodium EDTA


Calcium EDTA complex

Classification of complexometric titrations:
1.Direct complexometric titrations
2.Indirect/back complexometric titrations
3.Replacement complexometric titrations
4. Alkalimetric titrations of metal

1.**Direct complexometric titrations**:
Take the sample of metal ions and mix with the buffer solution and mordant black-II indictor and add an auxiliary agent to prevent precipitation and standardise with standard EDTA solution which is taken in burette
Perform blank titration[without sample] by omitting the sample.
Ex: zinc oxide, calcium chloride, magnesium sulphate

2.**Indirect complexometric titrations**:
The conditions by which back titrations favours
Insolubility of sample
Stability of complex being formed is slow
Formation of precipitate by reacting with alkali of buffer solution
Low reactivity of sample

Procedure:
Take a conical flask and add enough standard EDTA solution. And add buffer solution. And add mordant black-II indicator and go for heat to get proper metal ion complex. And then cool, go for titration with standard zinc sulphate or magnesium sulphate which is taken in burette
Example: aluminium hydroxide gel, dried aluminium hydroxide gel

3.**Replacement complexometric titrations:**

Ca +2 + Mg-EDTA----------→Ca-EDTA + Mg+2
Mg+2 + EDTA ----------→ Mg-EDTA

When there is no option to form direct and indirect titrations, we go with these replacement complexometric titrations. In this method, the metal ion form metal ion complex is replaced by introducing the same amount of different metal ion and then the liberated metal ion is titrated with standard EDTA solution
Ex: lead compounds
Mercuric compounds
Calcium compounds

4.**Alkalimetric titrations of metal ion**:

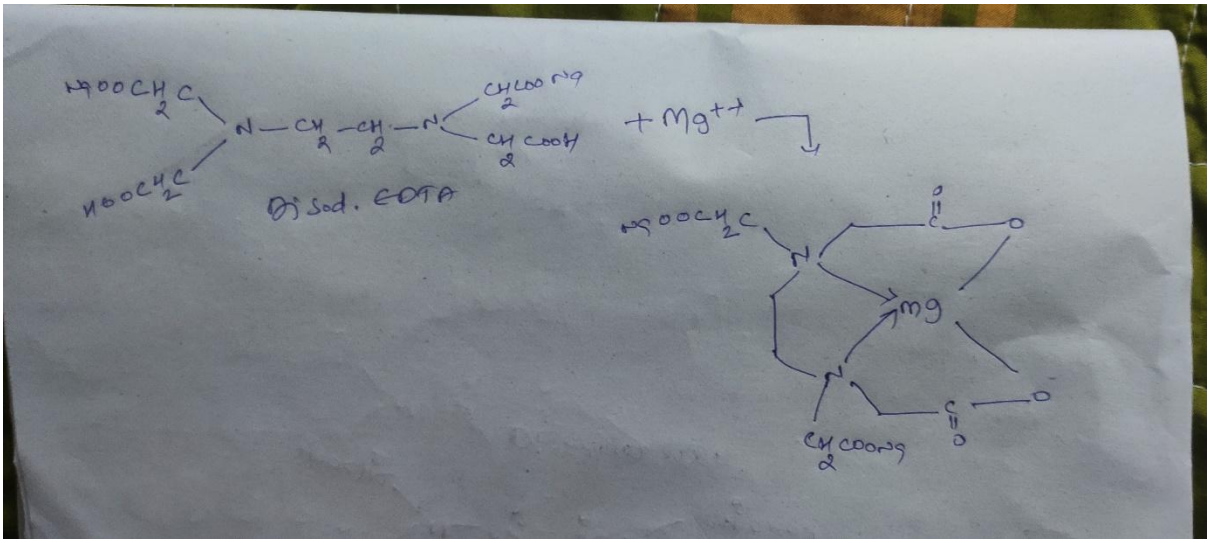
M+ + H4Y ----------→ MY + 4H+

This titration should be carried out without buffer solutions. When the reaction proceeds, we get liberation of H+ ions. Furtherly the protons form an acid and this acid is titrated with alkali substance which is taken in burette

Estimation of Magnesium Sulphate

Principle:

It involves direct titration. The required amount of magnesium reacts with EDTA and form Mg-EDTA complex with the help of mordant black-II indicator in the presence of buffer solution



Procedure:

Take 0.3 gm of MgSO4 and dissolve in 50 ml of distilled water in conical flask. Take standard 0.05M disodium EDTA in burette. Add 10 ml of ammonia-ammonium chloride buffer solution in conical flask and add 2 drops of mordant black -II indicator. Repeat the process for 3 times and get mean value to avoid errors and to get precise value and perform blank titration. And end point is pale pink to blue colour

Each ml of 0.05M disodium EDTA =0.00605 gm of MgSO4

Estimation of Calcium Gluconate

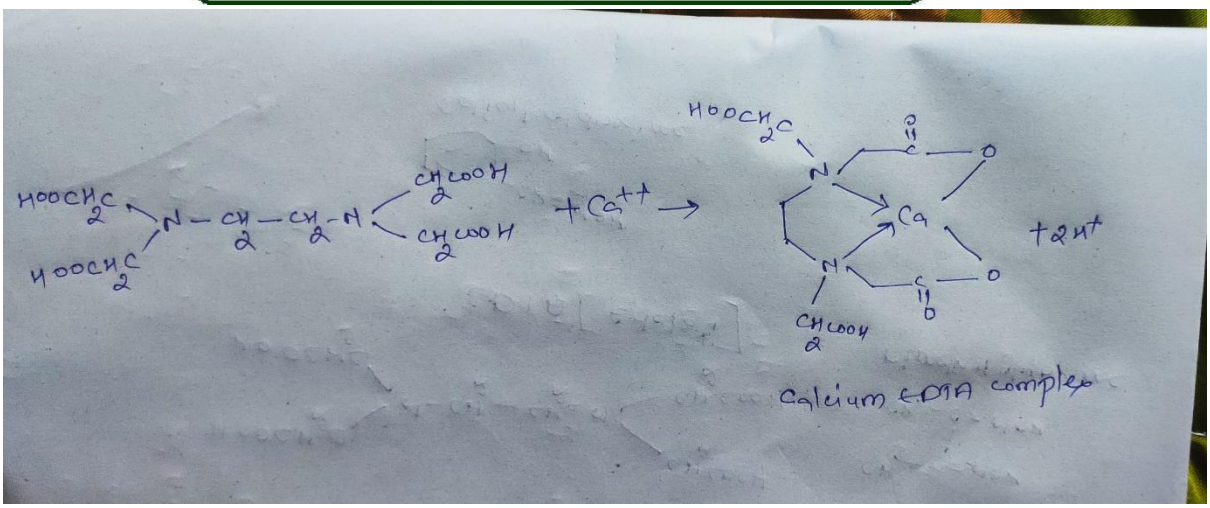
Principle:

It is replacement type of titration. Magnesium sulphate reacts with indicator and form a coloured magnesium indicator complex

Mg + In- ----------→ Mg-In

Coloured-1(mg-indicator complex)

Calcium reacts with standard disodium EDTA and forms calcium disodium EDTA complex



After fully utilisation of calcium, a single drop of disodium EDTA breaks/ dissociates magnesium indicator complex and liberates magnesium and indicator with colour which gives information about the completion of reaction

Mg-In + EDTA ----------→ Mg-EDTA + In-

Coloured -II (end point)

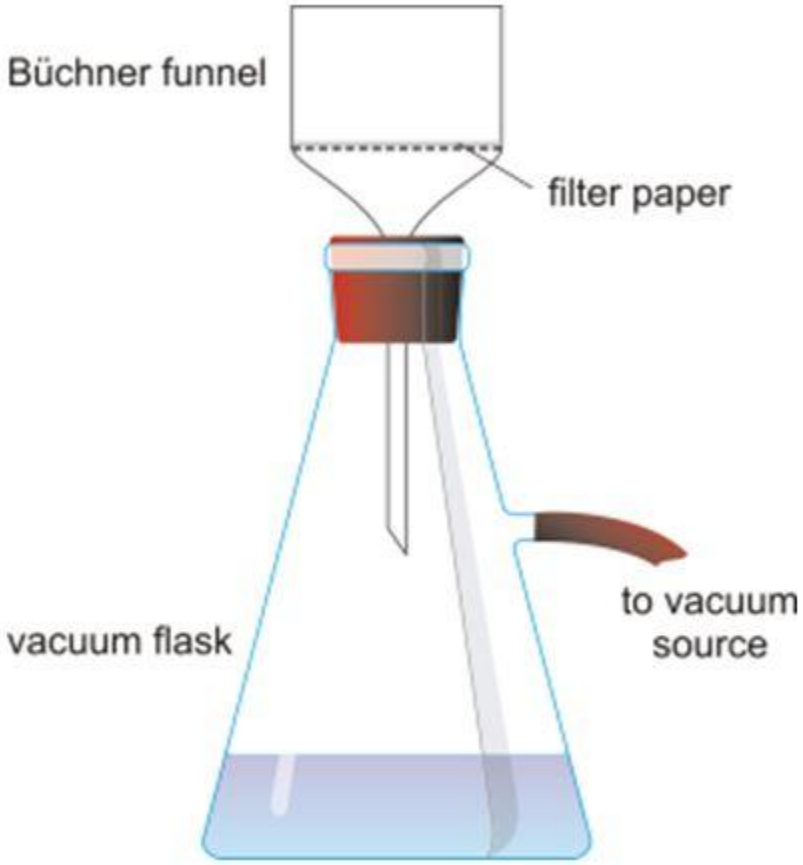
Procedure:

Take 0.5 gm of Calcium gluconate and dissolve in 50 ml warm distilled water, allow it to cool and then add 5ml of 0.05M magnesium sulphate. Then add 10 ml of NH3-NH4Cl buffer solution and add 2drops of mordant black -II indicator.

Repeat the process for three times to get precise value and perform blank titration

Each ml of 0.05 M disodium EDTA = 0.02242 gm of calcium gluconate

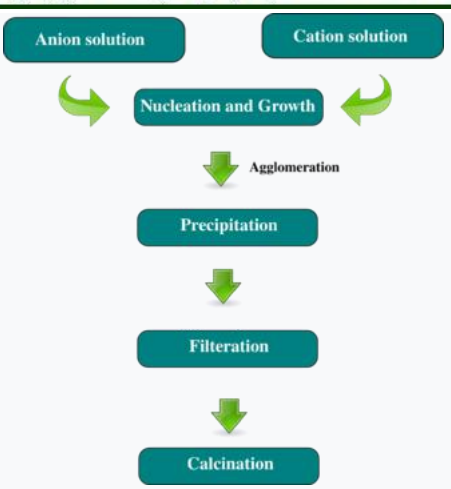
Gravimetric analysis: it describes a set of methods used in analytical chemistry for the quantitative determination of an analyte (the ion being analyzed) based on its mass. The principle of this type of analysis is that once an ion's mass has been determined as a unique compound, that known measurement can then be used to determine the same analyte's mass in a mixture, as long as the relative quantities of the other constituents are known.



The four main types of this method of analysis are *precipitation*, *volatilization*, *electro-analytical* and *miscellaneous physical method*. The methods involve changing the phase of the analyte to separate it in its pure form from the original mixture and are quantitative measurements.

coprecipitation (**CPT**) or **co-precipitation**:is the carrying down by a precipitate of substances normally soluble under the conditions employed.[1] Analogously, in medicine, coprecipitation is specifically the precipitation of an unbound "antigen along with an antigen-antibody complex".

Coprecipitation is an important issue in chemical analysis, where it is often undesirable, but in some cases it can be exploited. In gravimetric analysis, which consists on precipitating the analyte and measuring its mass to determine its concentration or purity, coprecipitation is a problem because undesired impurities often coprecipitate with the analyte, resulting in excess mass. This problem can often be mitigated by "digestion" (waiting for the precipitate to equilibrate and form larger, purer particles) or by redissolving the sample and precipitating it again.



Typical co-precipitation method for micro and nano particle synthesis

On the other hand, in the analysis of trace elements, as is often the case in radiochemistry, coprecipitation is often the only way of separating an element. Since the trace element is too dilute (sometimes less than a part per trillion) to precipitate by conventional means, it is typically coprecipitated with a *carrier*, a substance that has a similar crystalline structure that can incorporate the desired element. An example is the separation of francium from other radioactive elements by coprecipitating it with caesium salts such as caesium perchlorate. Otto Hahn is credited for promoting the use of coprecipitation in radiochemistry.

There are three main mechanisms of coprecipitation: inclusion, occlusion, and adsorption. An **inclusion** occurs when the impurity occupies a lattice site in the crystal structure of the carrier, resulting in a crystallographic defect; this can happen when the ionic radius and charge of the impurity are similar to those of the carrier. An **adsorbate** is an impurity that is weakly bound (adsorbed) to the surface of the precipitate. An **occlusion** occurs when an adsorbed impurity gets physically trapped inside the crystal as it grows.

Besides its applications in chemical analysis and in radiochemistry, coprecipitation is also "potentially important to many environmental issues closely related to water resources, including acid mine drainage, radionuclide migration in fouled waste repositories, metal contaminant transport at industrial and defense sites, metal concentrations in aquatic systems, and wastewater treatment technology".

Coprecipitation is also used as a method of magnetic nanoparticle synthesis.

Post-precipitation:
After conversion of analyte into precipitate during digestion period, whatever the impurities or soluble substances present in mother liquid form a precipitate layer over the primary precipitate of analyte. This phenomenon is known as post-precipitation.
Ex: In the determination of calcium, we get calcium oxalate precipitate. Besides this magnesium is also present in the form of impurity and convert into magnesium oxalate precipitate over the layer of calcium oxalate primary precipitate layer

Steps in a gravimetric analysis

After appropriate dissolution of the sample the following steps should be followed for successful gravimetric procedure:

1. **Preparation of the Solution**: This may involve several steps including adjustment of the pH of the solution in order for the precipitate to occur quantitatively and get a precipitate of desired properties, removing interferences, adjusting the volume of the sample to suit the amount of precipitating agent to be added.

2. **Precipitation**: This requires addition of a precipitating agent solution to the sample solution. Upon addition of the first drops of the precipitating agent, supersaturation occurs, then nucleation starts to occur where every few molecules of precipitate aggregate together forming a nucleus. At this point, addition of extra precipitating agent will either form new nuclei or will build up on existing nuclei to give a precipitate. This can be predicted by Von Weimarn ratio where, according to this relation the particle size is inversely proportional to a quantity called the relative supersaturation where

Relative supersaturation = (Q – S)/S

The Q is the concentration of reactants before precipitation, S is the solubility of precipitate in the medium from which it is being precipitated. Therefore, to get particle growth instead of further nucleation we must make the relative supersaturation ratio as small as possible. The optimum conditions for precipitation which make the supersaturation low are:

a. Precipitation using dilute solutions to decrease Q b. Slow addition of precipitating agent to keep Q as low as possible c. Stirring the solution during addition of precipitating agent to avoid concentration sites and keep Q low d. Increase solubility by precipitation from hot solution e. Adjust the pH to increase S, but not too much increase np as we do not want to lose precipitate by dissolution f. Usually add a little excess of the precipitating agent for quantitative precipitation and check for completeness of the precipitation

3. **Digestion of the precipitate**: The precipitate is left hot (below boiling) for 30 min to one hour for the particles to be digested. Digestion involves dissolution of small particles and reprecipitation on larger ones resulting in particle growth and better precipitate characteristics. This process is called Ostwald ripening. An important advantage of digestion is observed for colloidal precipitates where large amounts of adsorbed ions cover the huge area of the precipitate. Digestion forces the small colloidal particles to agglomerate which decreases their surface area and thus adsorption. You should know that adsorption is a major problem in gravimetry in case of colloidal precipitate since a precipitate tends to adsorb its own ions present in excess, Therefore, forming what is called a primary ion layer which attracts ions from solution forming a secondary or counter ion layer. Individual particles repel each other keeping the colloidal properties of the precipitate. Particle coagulation can be forced by either digestion or addition of a high concentration of a diverse ions strong electrolytic solution in order to shield the charges on colloidal particles and force agglomeration. Usually, coagulated particles return to the colloidal state if washed with water, a process called peptization.

4**. Washing and Filtering the Precipitate**: It is crucial to wash the precipitate thoroughly to remove all adsorbed species that would add to the weight of the precipitate. One should be careful nor to use too much water since part of the precipitate may be lost. Also, in case of

colloidal precipitates we should not use water as a washing solution since peptization would occur. In such situations dilute nitric acid, ammonium nitrate, or dilute acetic acid may be used. Usually, it is a good practice to check for the presence of precipitating agent in the filtrate of the final washing solution. The presence of precipitating agent means that extra washing is required. Filtration should be done in appropriate sized Gooch or ignition filter paper.

5. **Drying and Ignition**: The purpose of drying (heating at about 120-150 oC in an oven) or ignition in a muffle furnace at temperatures ranging from 600-1200 oC is to get a material with exactly known chemical structure so that the amount of analyte can be accurately determined.

6. ***Precipitation from Homogeneous Solution***: To make Q minimum we can, in some situations, generate the precipitating agent in the precipitation medium rather than adding it. For example, to precipitate iron as the hydroxide, we dissolve urea in the sample. Heating of the solution generates hydroxide ions from the hydrolysis of urea. Hydroxide ions are generated at all points in solution and thus there are no sites of concentration. We can also adjust the rate of urea hydrolysis and thus control the hydroxide generation rate. This type of procedure can be very advantageous in case of colloidal precipitates.

Estimation of Barium Sulphate:

The amount of sulphate is determined quantitatively as barium sulphate, $BaSO_4$ by gravimetric analysis.

This determination consists of slowly adding a dilute solution of barium chloride to a hot solution of the sulphate slightly acidified with concentrated HCl.

$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4$

The white precipitate is filtered off, washed with water, dried in the oven, and weighed as barium sulphate. The percentage of sulphate is calculated from the weight of barium sulphate.

PROCEDURE

(a) Preparation of porcelain Gooch crucible

1. Dry the porcelain, Gooch crucible in the oven at 110o - 120oC for 30 minutes.

2. Cool it in the desiccator.

3. Weigh the crucible, together with a piece of filter paper.

4. Repeat the above until constant weights are obtained.

Caution: Do not place the hot crucible directly on the bench top.

(b) Precipitation of $BaSO_4$

1. Pipette 25.0 mL of the given sulphate solution into a 250 mL beaker.

2. Add 5 drops of concentrated HCl and about 50 mL of water.

Caution: Concentrated HCl is very corrosive, add in the fume hood.

3. Heat to boiling and, with vigorous stirring, add dropwise from a measuring cylinder 10 mL of 10% barium chloride solution.

4. Cover the beaker with a watch glass and digest (heat to just below boiling) for 20 minutes.

5. Test for complete precipitation by adding a few drops of $BaCl_2$ to the clear supernatant liquid.

(c) Washing and Filtration of $BaSO_4$ precipitate

1. Decant the clear supernatant by filtration (use a weighed filter paper) at the vacuum pump, using a pre-weighed crucible.

2. Wash and swirl the precipitate with about 20 mL of warm deionised water.

3. Use a 'rubber-policeman' to dislodge any particles on the beaker.

4. Allow to settle.

5. Decant the liquid through the filter paper.

6. Repeat the washing and decanting at least 2 more times.

7. Discard the filtrate.

(d) Drying and weighing of $BaSO_4$ precipitate

1. Dry the crucible in the oven at 150oC for about 1/2 hour.

2. Cool the crucible with $BaSO_4$ precipitate in a desiccator for about 10 minutes.

3. Weigh the crucible when it is cooled down.

4. The difference between this weight and the empty crucible (plus filter paper) is the weight of $BaSO_4$ precipitate. (Note: You may repeat Steps 1 to 4 until a constant weight of the precipitate is obtained.

When you dissolve ionic compounds in water, there is a "battle of attraction" between the water molecules and the ions. If ions like water more than they like each other, then the compound dissolves, if the ions like each other more then the compound is said to be insoluble.

When you combine two soluble compounds, there is always the possibility that ions from

different solutions will be attracted to each other more than to the water. That is the case of Ba^{2+} and SO_4^{2-}. The attraction for each other is greater than their attraction to water.

CO2 in the air dissolves in water to form carbonates and bicarbonates, barium also forms precipitates with carbonates. In the procedure you heat the solution and add HCl to minimize the presence of carbonates.

The repeat washings makes sure that you get rid off any ions from the original solutions that may be present. Any water that may remain is boiled off during the drying procedure.

The testing of the decanted liquid for more precipitate allows you to make sure that you precipitated all of the sulfate.

1) By keeping the solution acidic you reduce the chance of dissolved CO2 from the air reacting with the Barium to form barium carbonate.

2) The higher the concentrations of Ba+2 and SO4-2 ions, the more BaSO4 will precipitate.

3) Since you started with BaCl2 and Na2SO4 the only other possible substance might be NaCl, you could test for that by washing the BaSO4 crystals, and then after decanting it, test it with AgNO3, if any NaCl was present in the BaSO4 it should dissolve and cause a precipitate of AgCl in the wash water.

4) Increase the number of washings.

UNIT-IV

Oxidation: It is a part of oxidation and reduction, when electron is lost or the oxidation state will be increased

The combination of a substance with oxygen.

A reaction in which the atoms of an element lose electrons and the valence of the element is correspondingly increased.

A substance is oxidized if it gains oxygen, loses hydrogen, or loses electrons.

A chemical reaction involving loss of electrons. In the human body, oxidation occurs when breathed-in oxygen combines with molecules in food to produce energy, water, and carbon dioxide.

Reduction: It is a part of oxidation -reduction reaction, where electron is gained as the oxidation state, the valency will be decreased.

Oxidizing agents are substances containing the elements that accept electrons, allowing other elements to oxidized by accepting electrons

it is a substance which oxidizes other substances and itself it undergoes reduction

Example: KMnO4, KBrO3, KIO3, Iodine

Reducing agents are substances which reduces other substances and itself it undergoes oxidation

Example: FeSO4, Oxalic acid, Ferric ammonium sulphate

Reducing agents are substances containing the elements that donate electrons, allowing other elements to be reduced

Oxidation:

$SO_2 + (O)$ ----------→ SO_3 addition of oxygen

$H_2S + (O)$----------→ $S + H_2O$ removal of hydrogen

Fe^{+2}----------→ Fe^{+3} loss of electrons

Reduction:

$C_2H_4 + H_2$ ----------→ C_2H_6 addition of hydrogen

$CuO + 2H$ ----------→ $Cu + H_2O$ removal of oxygen

Mn^{+7} ----------→ Mn^{+2}

Types of redox titrations:

1. Permanganometry titration
2. Dichrometry titration
3. Cerimetry titration
4. Iodo/iodimetry titration
5. Bromatometry titration
6. Titrations with potassium iodate

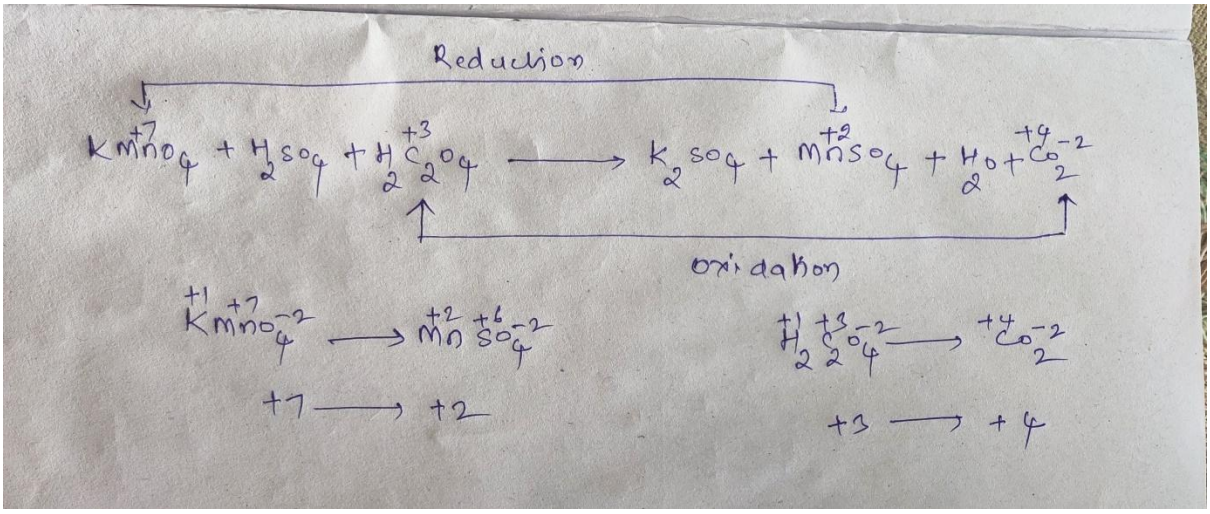
1.**Permanganometry titration:**

Such type of reactions where we use $KMnO_4$ such type of reactions is known as permanganometry titrations. The $KMnO_4$ should be standardized with primary standard like Oxalic acid

Principle: $KMnO_4$ is strong oxidizing agent. In the presence of acidic medium, it reduces itself and oxidizes other substances. It is acting as a self-indicator because of intense color

Standardization of 0.1M $KMnO_4$

Take 20 ml of 0.1N oxalic acid in a conical flask and add 5 ml of 1N H_2SO_4 and heat up to 70° and then titrates with $KMnO_4$ which is taken in burette until permanent pink color appears



Limitations:

$KMnO_4$ is not available in pure form and it contains manganese dioxide as an impurity if we use ordinary water and that manganese dioxide is responsible for decomposition of $KMnO_4$

Remedy:

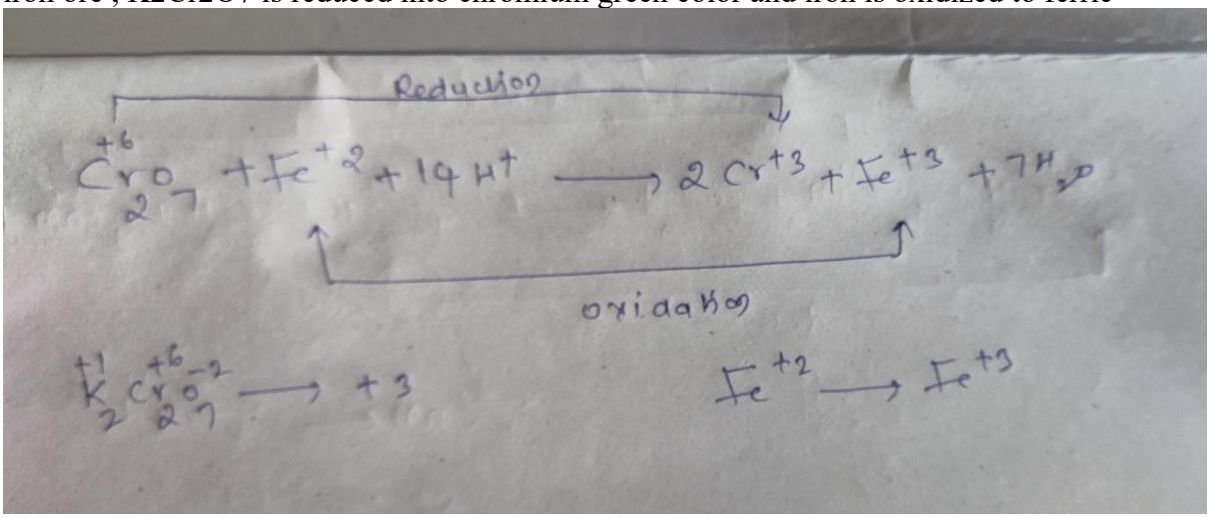
KMnO4 is prepared and heated for 1 hour and transfer to amber colored bottle and keep aside for 2 days

2.Dichrometry titrations:

When we use potassium dichromate K2Cr2O7 such types of redox titrations are known as dichrometry titrations

Principle:

K2Cr2O7 is a moderate oxidizing agent and available in pure state and less expense. At ordinary temperature, K2Cr2O7 is used for the determination of Iron. In the determination of Iron from iron ore , K2Cr2O7 is reduced into chromium green color and iron is oxidized to ferric



Applications:

Used for the determination of iron from iron ore

Used to determine FeSO4

3.Cerimetry/Ceriometry:

Principle:

Cerric ammonium sulphate Ce(SO4)2 2(NH4)2 SO4.2H2O is strong oxidizing agent and can be replaced with $KMnO_4$ in such type of titrations where we can use ceric ammonium sulphate as a titrant that titrations are known as cerimetry/ceriometry titrations.

Preparation of 0.1M ceric ammonium sulphate:

Take 66 gm of cerric ammonium sulphate and dissolve in the mixture of H_2SO_4 and water with the ratio of 30:500 by gentle heat then cool and filter if any turbid is present and dilute to 1000 ml with distilled water

Standardization of Cerric ammonium sulphate:

Dissolve 0.2 gm of As2O3 which is previously dried at 105° for 1 hour in 25 ml of 8% w/v NaOH and add 30ml H2SO4 make up to 100ml with distilled water. Add 0.1ml ferroin solution and 0.15ml osmium tetroxide in a dried conical flask. All the contents of the conical flask are titrated with ceric ammonium sulphate until pale pink color turns to blue. This indicates the completion of the reaction

As2O3 + NaOH ----------→NaAsO2 + H2O (sodium arsenite)

NaAsO2 + H2O----------→ NaH2AaO4 (sodium dihydrogen arsenate)

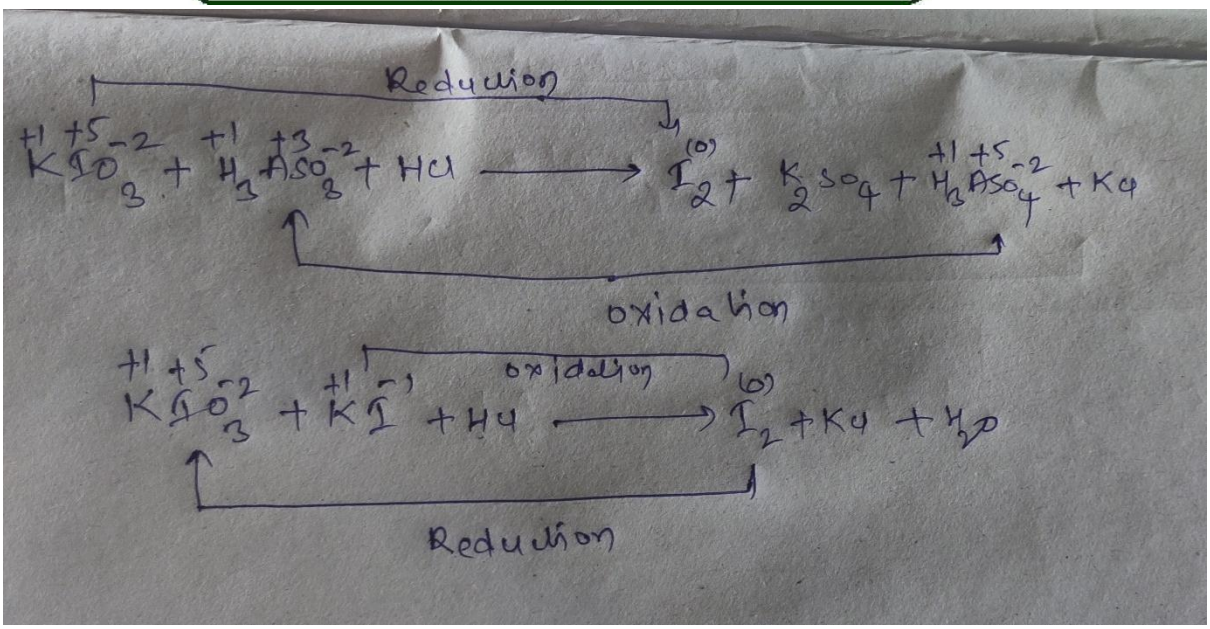
4[Ce+4 +e- ----------→Ce+3]

Ceric ammonium sulphate is reduced to Ce+3 to Ce+4 by gain of electrons
Applications:
It is used for the determination of following compouds
Ferrous fumarate
Ferrous gluconate
Ferrous sulphate
Ascorbic acid
Paracetamol

4.**iodometry/ iodimetry:**
Both the types of reactions come under oxidation and reduction reaction. In both cases iodine is acting as a mild oxidizing agent, and oxidizes other substances and undergo reduction.
Iodometry indicates using of iodine from other sources. The liberated iodine is titrated with standard solution.
In other hands iodimetry type of titration involves by using of direct iodine where iodine is reduced to iodide and that iodide is titrated against standard solution
$Sn^{+2} + I_2 \longrightarrow Sn^{+4} + 2I^-$
$S_2O_4^- + I_2 \longrightarrow S_4O_6 + 2I^-$
$H_3AsO_3 + I_2 \longrightarrow H_3AsO_4 + 2I^-$
In iodimetry type of titration, iodide form is converted into iodine and that iodine is titrated with standard titrant.
$CuSO_4 + KI \longrightarrow CuI_2 + K_2SO_4$ [cupric iodide]
$CuI_2 \longrightarrow Cu_2I_2 + I_2$ [liberated iodine]
$I_2 + Na_2S_2O_3 \longrightarrow NaI + Na_2S_4O_6$
Applications for Iodimetry:
It is used to determine ascorbic acid
It is used determine stannous chloride, sodium thio sulphate and arsenious oxide
Applications for Iodometry:
It is used to determine $KMnO_4$, H_2O_2, $CuSO_4$, KIO_3

5.Bromatometry:
Such type of titrations where we use potassium bromate are known as bromatometric type of oxidation-reduction titrations.
$kBrO_3$ is a mold oxidizing agent in presence of acid, it is reduced to bromide at the end point bromide is converted in free bromine and form yellow color, which indicates the end point
$BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + H_2O$
$BrO_3^- + Br^- + H^+ \longrightarrow Br_2 + H_2o$
In this type of oxidation-reduction titrations, two methods we have, direct and indirect
In direct method, we use direct bromine and in indirect method we use the source of bromine
Applications:
It is used to determine the metals like aluminium, Co, Zn, Nickel etc
It is used to determine phenols
It is used to determine hydroxyl amines

6.Titration with potassium iodate:
Principle: potassium iodate is a strong oxidizing agent in moderate acidic conditions where iodides/ Arsenic oxidizes are converted into iodine. That liberated iodine is titrated with sodium thio sulphate



Applications:
It is used for the determinations of arsenic
It is used for the determination of hydrazine sulphate
It is used to determine copper compounds

UNIT-V

Conductometry

Determination of concentration of an electrolyte solution by conductometer is called conductometry.

The ions bearing charges have mobility to concern electrodes.

Cations migrate towards cathode and anions migrate towards anode.

The conductance of ions is the basic principle for conductometric titrations.

In this type of titrations where there is no need of indicators or such type of titrations not required indicators.

Conductivity cell:

It is made up of fine glass quartz having two electrodes that is cathode and anode.it can available in three types

1.the conductivity cell having wide mouth with cork which is having holes for the passing of electrodes

2.the conductivity cell has a fixed lid with holes by which the burette and stirrer can be introduced

3.the conductivity cell consists of a wide glass bore at the tip of glass bore two platinum electrodes are present

the cell constant can be determined by using 0.02 KCl at 25°c or 0.01 KCl at 18° c

determination of cell constant at 25°c = $\frac{2765}{\text{Conductivity of 0.02 KCl MMhos}}$

Determination of at 18° c = $\frac{1221}{\text{Conductivity of 0.01 KCl M Mhos}}$

Conductometry is a measurement of electrolytic conductivity to monitor a progress of chemical reaction. Conductometry has notable application in analytical chemistry, where **conductometric titration** is a standard technique. In usual analytical chemistry practice, the term *conductometry* is used as a synonym of *conductometric titration*, while the term **conductimetry** is used to describe non-titrative applications. Conductometry is often applied to determine the total conductance of a solution or to analyze the end point of titrations that include ions

Conductometric titration is a type of titration in which the electrolytic conductivity of the reaction mixture is continuously monitored as one reactant is added. The equivalence point is the point at which the conductivity undergoes a sudden change. Marked increase or decrease in conductance are associated with the changing concentrations of the two most highly conducting ions—the hydrogen and hydroxyl ions.[5] The method can be used for titrating coloured solutions or homogeneous suspension (e.g.: wood pulp suspension[5]), which cannot be used with normal indicators.

Acid-base titrations and redox titrations are often performed in which common indicators are used to locate the end point e.g., methyl orange, phenolphthalein for acid base titrations and starch solutions for iodometric type redox process. However, electrical conductance measurements can also be used as a tool to locate the end point.

Example: titration of an HCl solution with the strong base NaOH. As the titration progresses, the protons are neutralized to form water by the addition of NaOH. For each amount of NaOH added equivalent amount of hydrogen ions is removed. Effectively, the mobile H^+ cation is replaced by the less-mobile Na^+ ion, and the conductivity of the titrated solution as well as the measured conductance of the cell fall. This continues until the equivalence point is reached, at which one obtains a solution of sodium chloride, NaCl. If more base is added, an increase in conductivity or conductance is observed, since more ions Na^+ and OH^- are being added and the neutralization reaction no longer removes an appreciable amount of H^+. Consequently, in the titration of a

strong acid with a strong base, the conductance has a minimum at the equivalence point. This minimum can be used, instead of an indicator dye, to determine the endpoint of the titration. The conductometric titration curve is a plot of the measured conductance or conductivity values as a function of the volume of the NaOH solution added. The titration curve can be used to graphically determine the equivalence point.

For reaction between a weak acid and a weak base in the beginning conductivity decreases a bit as the few available H+ ions are used up. Then conductivity increases slightly up to the equivalence point volume, due to contribution of the salt cation and anion. (This contribution in case of a strong acid-strong base is negligible and is not considered there.) After the equivalence point is achieved the conductivity increases rapidly due to the excess OH- ions.

Titrations:

Acid-base titrations

Strong acid vs strong base:

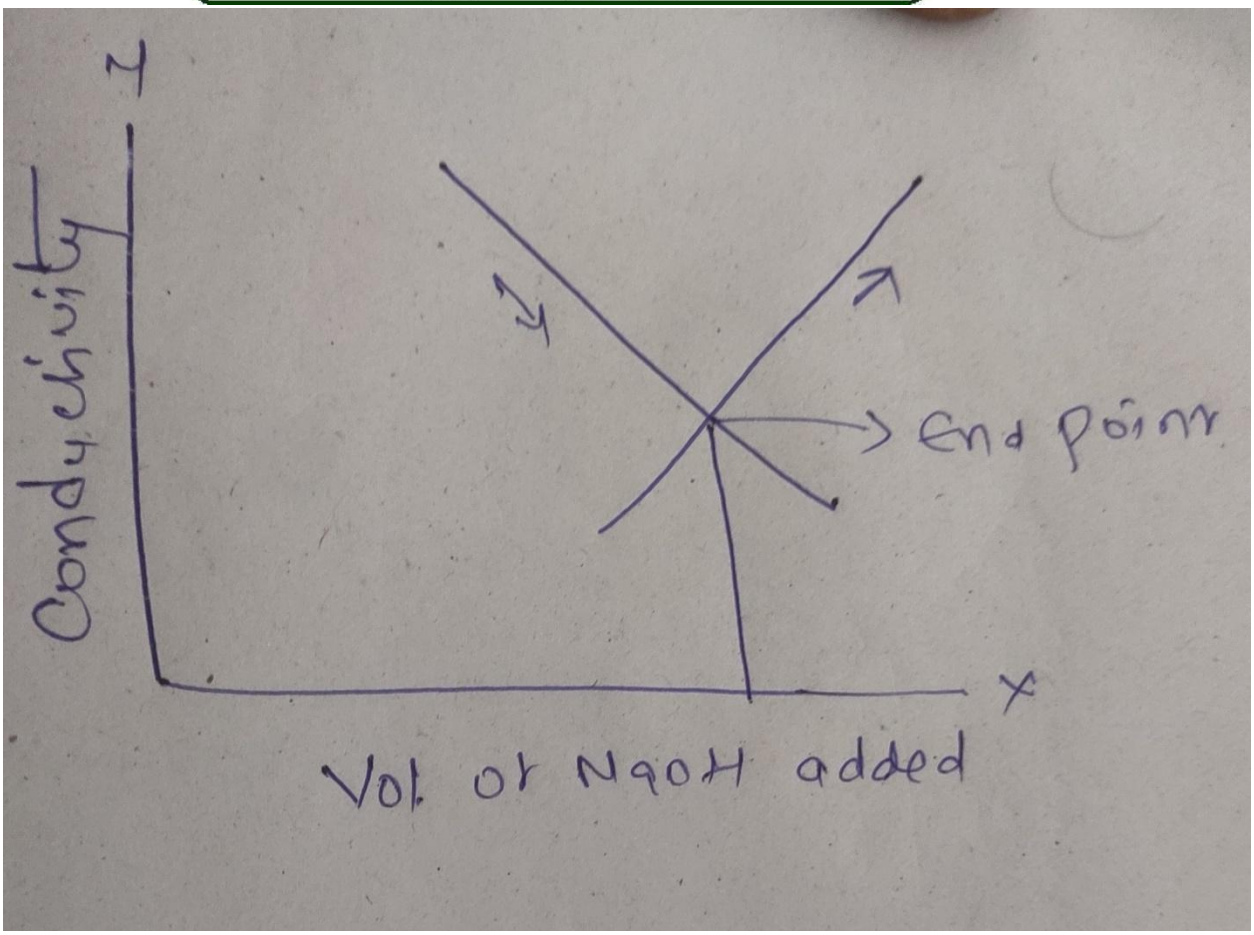
HCl is strong acid and it completely dissociates into H+ and Cl-

HCl ----------→ H+ + Cl-

H+ ions move to cathode and Cl- ions move to anode and the conductivity is more at initial stage and this is known as initial conductivity

When NaOH is added from burette, OH- of NaOH reacts with H + of HCl and convert into water so that the conductivity gradually decreased. Once the total available H+ ions are converted into water indicates completion of reaction or end point. Further addition of NaOH causes increase in the conductivity because of Na+, OH- move to electrodes and increase the conductivity. Therefore we get V shaped graph, where two lines joined is the end point.

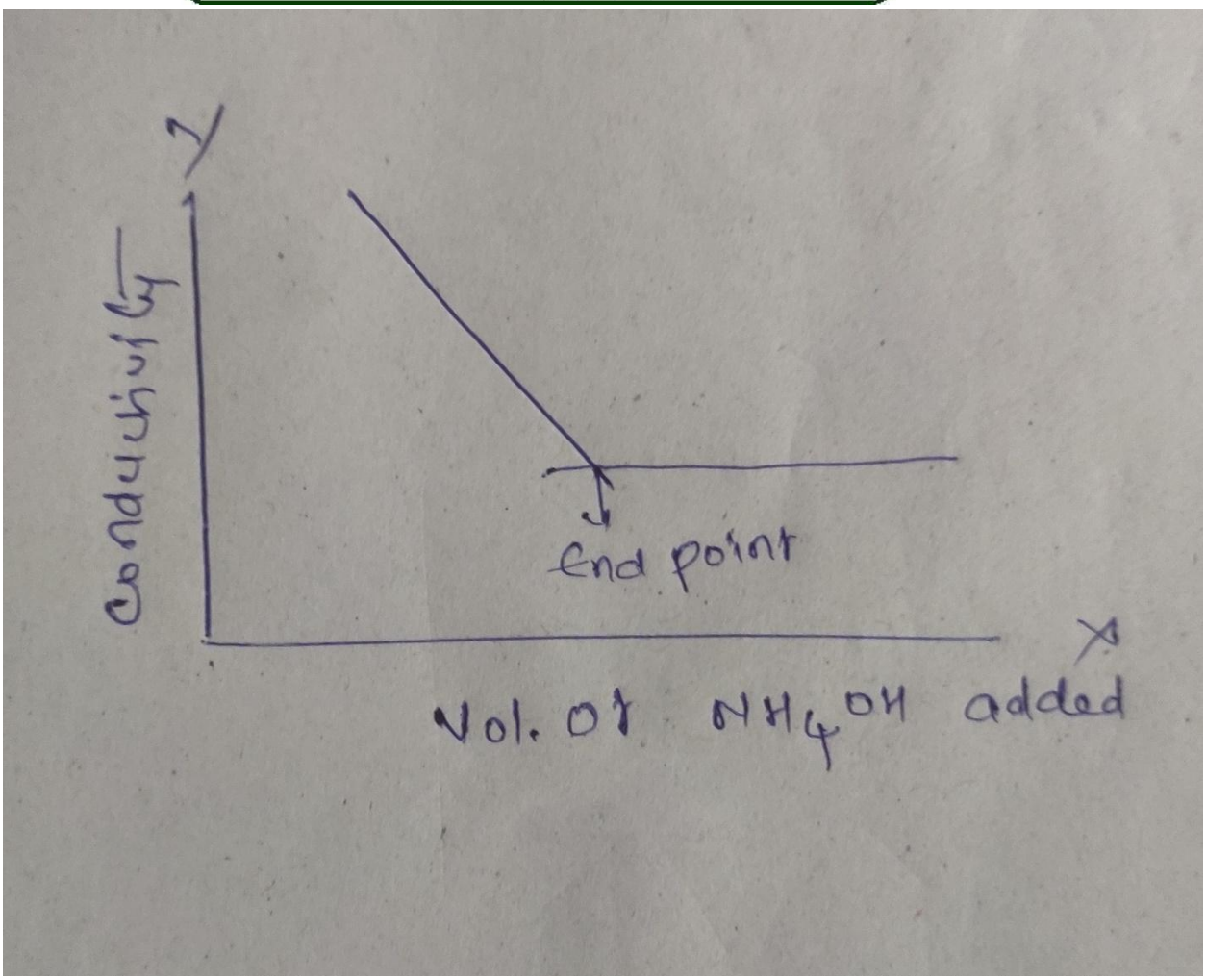
Fig



Strong acid vs weak base:

HCl is completely dissociates and we get maximum conductivity. Once NaOH is added the conductivity is decreased by conversion of H+ from HCl and OH- from NH4OH to water. Once the end point reaches, further addition of NH4OH it is not completely dissociates and conductivity will be neither decreased or increased. So that we get the graph like below

NH4OH ……..> NH4+ + OH-

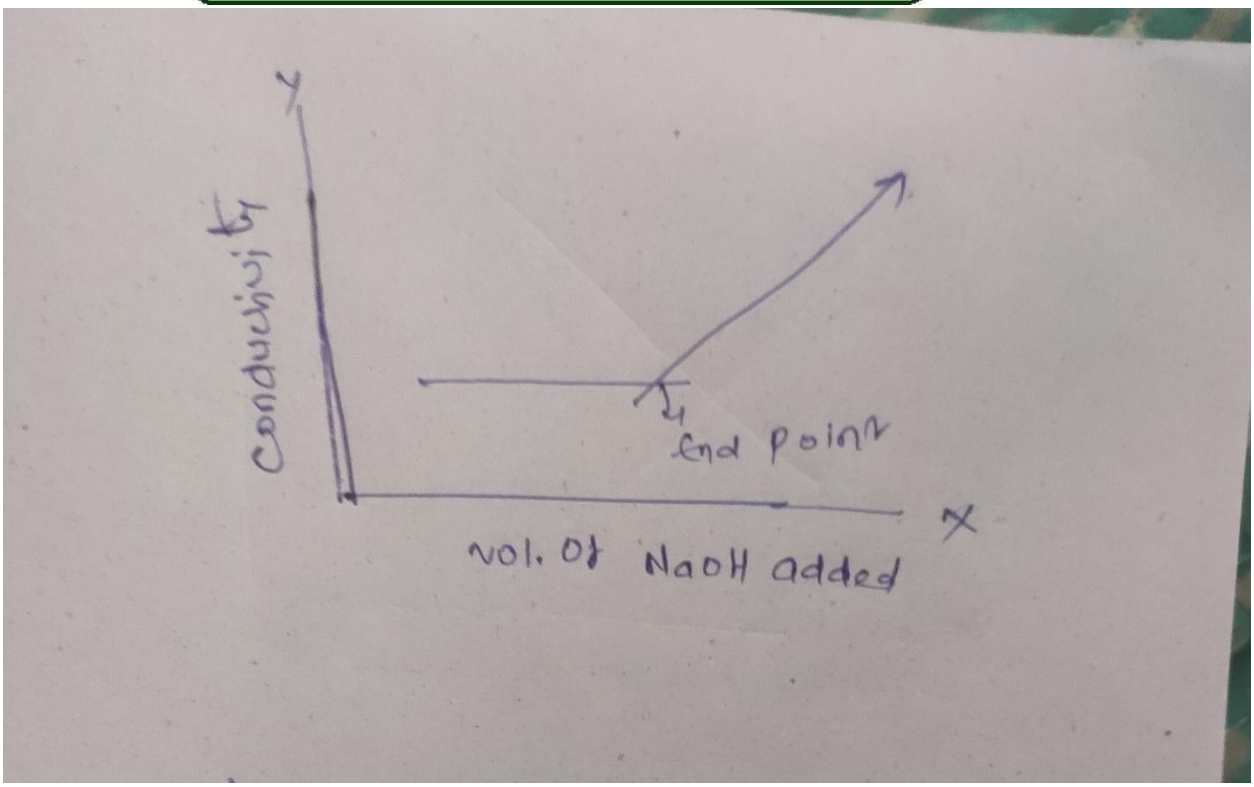


Weak acid vs strong base

Acetic acid is weak acid and it is partially ionised to acetate and H+ ions. Being a weak acid , conductivity is less so that we get plateau or straight line. Once the end point reaches excess of sodium hydroxide is ionized to Na+ and OH- ions. Because of more conductance of OH- ion, the conductivity will be increased so that if we plot the graph we grt as below

CH3COOH ----------→ CH3COO- + H+

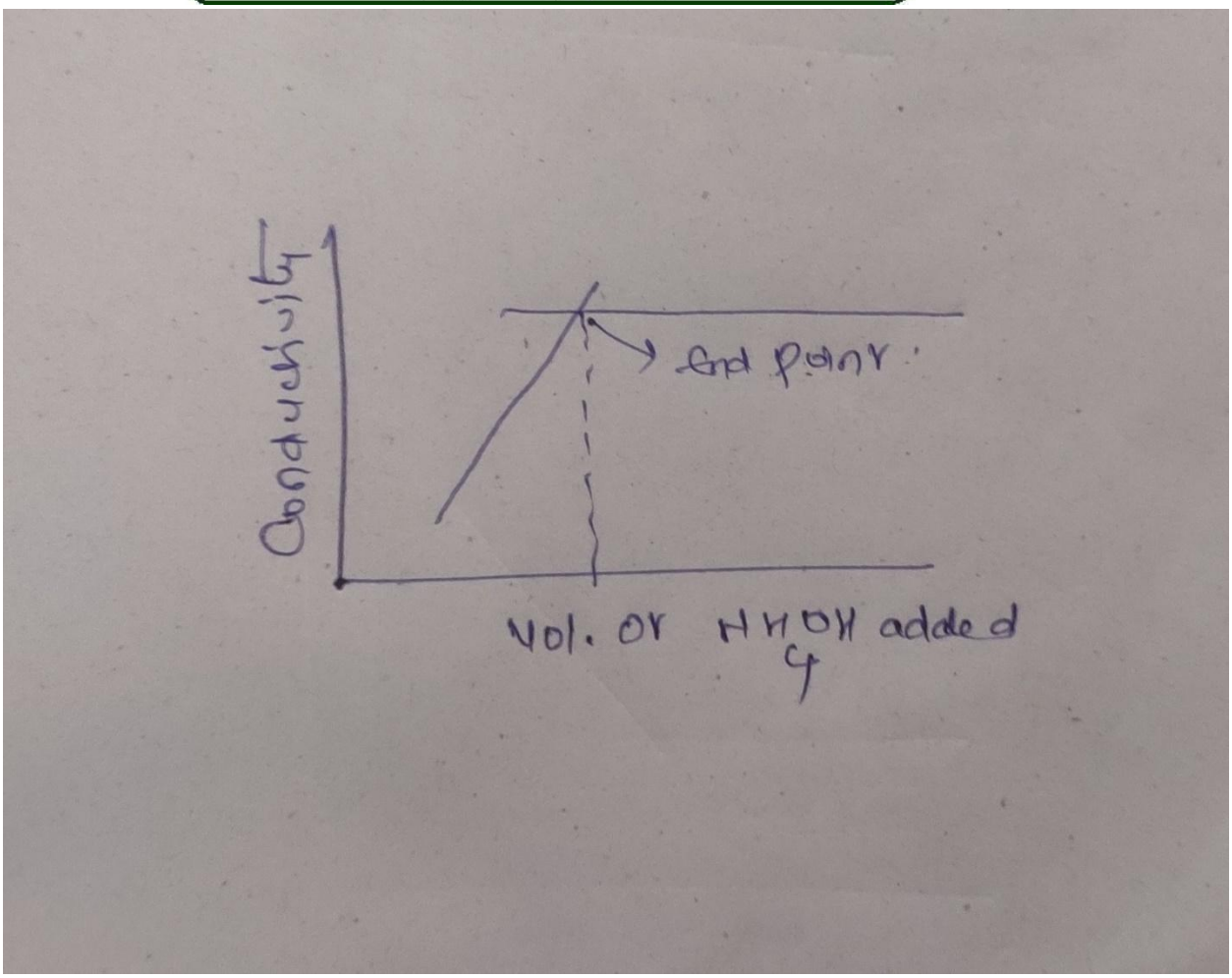
CH3COOH + NaOH ----------→ CH3COONa + H2O



Weak acid vs weak base

The titration between weak acid like acetic acid and wea base like NH4OH takes place and we get ammonium acetate which is having good conductance hence conductivity is increased. Once the end point reaches further addition of ammonium hydroxide will not change the conductivity, so that we get straight line

CH3COOH+ NH4OH ----------→ CH3COONH4 +H2O



Polarography

Principle:

When negative potential or electrode potential or voltage is applied to a beaker containing analyte solution which is equipped with cathode and anode, migration or diffusion of ions takes place which in turn give flow of current. That is known as diffusion current.

The amount of diffusion current is directly proportional to the concentration of analyte. This is the basic principle of polarography.

The ideal polarogram is having sigmoid shape of curve

Residual current

Migration current

Diffusion current

Limiting current

Residual current:

In polarography method we use dropping mercury electrode [DME] which is polarisable and acting as cathode. Mercury pole is non polarisable electrode and acting as anode. Lead sample

solution is taken as analyte with supporting electrolyte like KCl.

Residual current is the combination of current produced by impurities and the current produced by potassium layer at DME

Ir = if + ic

Where,

if is current produced by impurities

ic is current produced by potassium double layer at DME

AB is residual current

Migration current:

It is because of migration of potassium ions towards cathode electrode. Migration current of analyte is negligible. Migration of analyte is less towards anode because of large surface area

Diffusion current:

When voltage is applied whatever the sample present or analyte ex: lead being cation reaches to or diffused to DME through double layer of potassium. Due to potential difference some amount of current is produced this is known as diffusion current. This is directly proportional to concentration of the analyte. Diffusion current can be expressed by Ilkovic equation

$$id = 607\ n\ D^{1/2}\ C\ m^{2/3}\ t^{1/6}$$

where,

id = diffusion current

n = no of electrons transferred

C =concentration of analyte

D = diffusion co-efficient

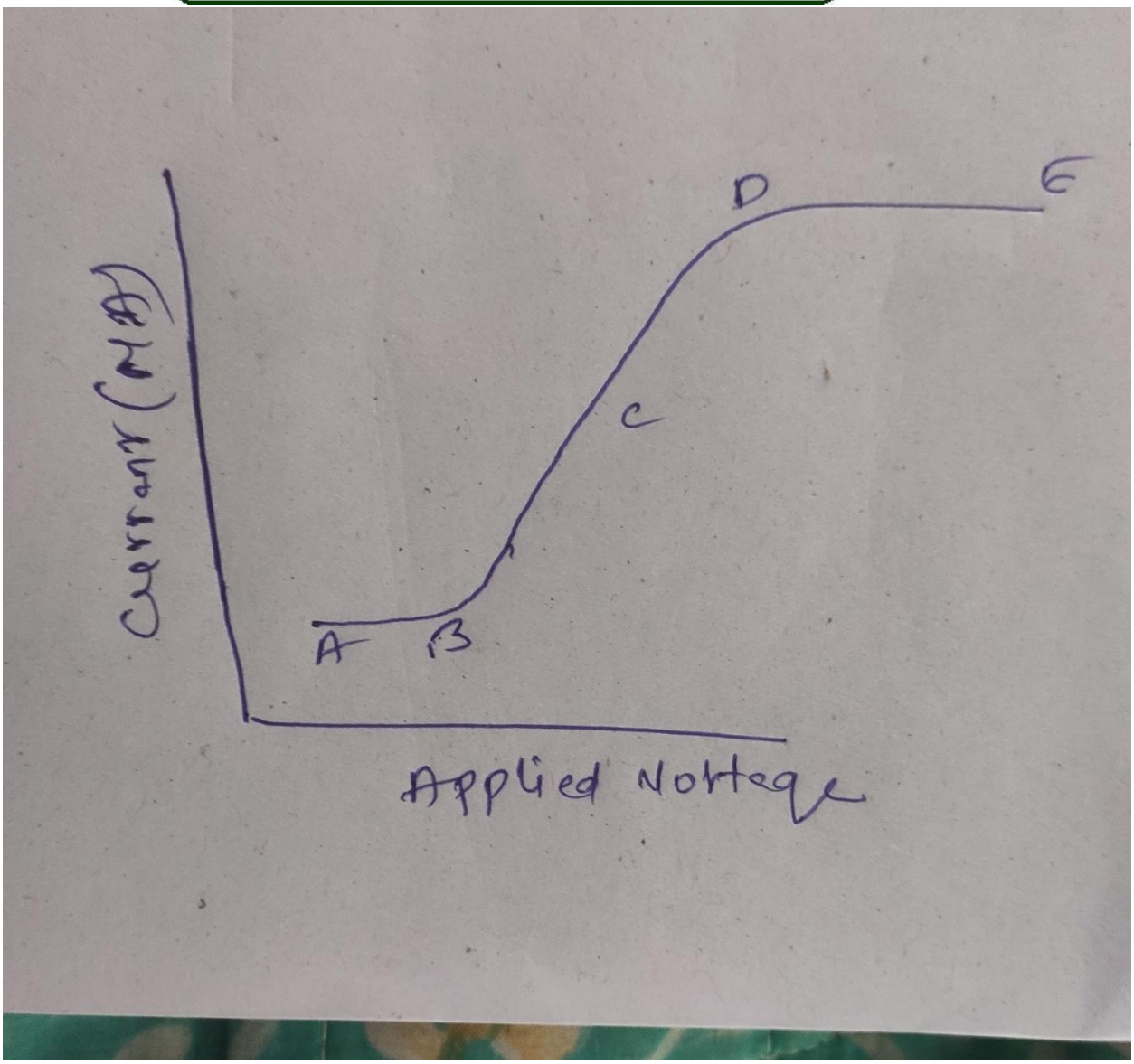
m= mass of mercury drop flow rate

t= time of mercury drop formation

Limiting current:

Lead is reduced and gives some amount of current is known as limiting current

$Pb^{+2} + 2e^- \longrightarrow Pb^0$



Polarography:

Polarography is a voltammetric measurement whose response is determined by only diffusion mass transport. The simple principle of polarography is the study of solutions or of electrode processes by means of electrolysis with two electrodes, one polarizable and one unpolarizable, the former formed by mercury regularly dropping from a capillary tube. Polarography is a specific type of measurement that falls into the general category of linear-sweep voltammetry where the electrode potential is altered in a linear fashion from the initial potential to the final potential. As a linear sweep method controlled by convection/diffusion mass transport, the current vs. potential response of a polarographic experiment has the typical sigmoidal shape. What makes polarography different from other linear sweep voltammetry measurements is that polarography makes use of the dropping mercury electrode (DME) or the static mercury drop electrode.

A plot of the current vs. potential in a polarography experiment shows the current oscillations corresponding to the drops of Hg falling from the capillary. If one connected the maximum current of each drop, a sigmoidal shape would result. The limiting current (the plateau on the sigmoid), called the diffusion current because diffusion is the principal contribution to the flux of

electroactive material at this point of the Hg drop life.

Limitations:

There are limitations in particular for the classical polarography experiment for quantitative analytical measurements. Because the current is continuously measured during the growth of the Hg drop, there is a substantial contribution from capacitive current. As the Hg flows from the capillary end, there is initially a large increase in the surface area. As a consequence, the initial current is dominated by capacitive effects as charging of the rapidly increasing interface occurs. Toward the end of the drop life, there is little change in the surface area which diminishes the contribution of capacitance changes to the total current. At the same time, any redox process which occurs will result in faradaic current that decays approximately as the square root of time (due to the increasing dimensions of the Nernst diffusion layer). The exponential decay of the capacitive current is much more rapid than the decay of the faradaic current; hence, the faradaic current is proportionally larger at the end of the drop life. Unfortunately, this process is complicated by the continuously changing potential that is applied to the working electrode (the Hg drop) throughout the experiment. Because the potential is changing during the drop lifetime (assuming typical experimental parameters of a 2 mV/s scan rate and a 4 s drop time, the potential can change by 8 mV from the beginning to the end of the drop), the charging of the interface (capacitive current) has a continuous contribution to the total current, even at the end of the drop when the surface area is not rapidly changing. As such, the typical signal to noise of a polarographic experiment allows detection limits of only approximately 10^{-5} or 10^{-6} M.

Ilkovic equation:

The Ilkovic equation is a relation used in polarography relating the diffusion current (I_d) and the concentration of the depolarizer (c), which is the substance reduced or oxidized at the dropping mercury electrode. The Ilkovic equation has the form

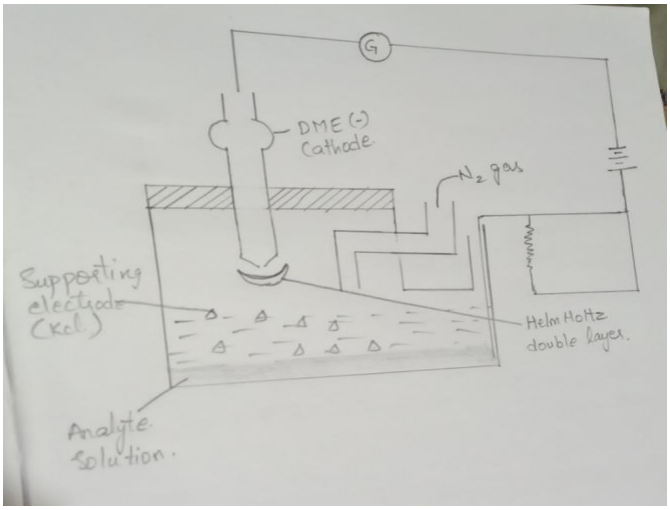
or

$$id = 607\ n\ D^{1/2}\ C\ m^{2/3}\ t^{1/6}$$

where k is a constant which includes π and the density of mercury, and with the Faraday constant F has been evaluated at 708 for maximal current and 607 for average current, D is the diffusion coefficient of the depolarizer in the medium (cm^2/s), n is the number of electrons exchanged in the electrode reaction, m is the mass flow rate of Hg through the capillary (mg/s), t is the drop lifetime in seconds, and c is depolarizer concentration in mol/cm^3.

The equation is named after the scientist who derived it, the Slovak chemist Dionýz Ilkovič (1907–1980).

Dropping mercury electrode



Construction:

It is acting as cathode and sometimes acting as anode**.**

It consists of long capillary tube of 15-20cm long and 20-50mm internal diameter and that capillary tube is connected with Mercury reservoir.

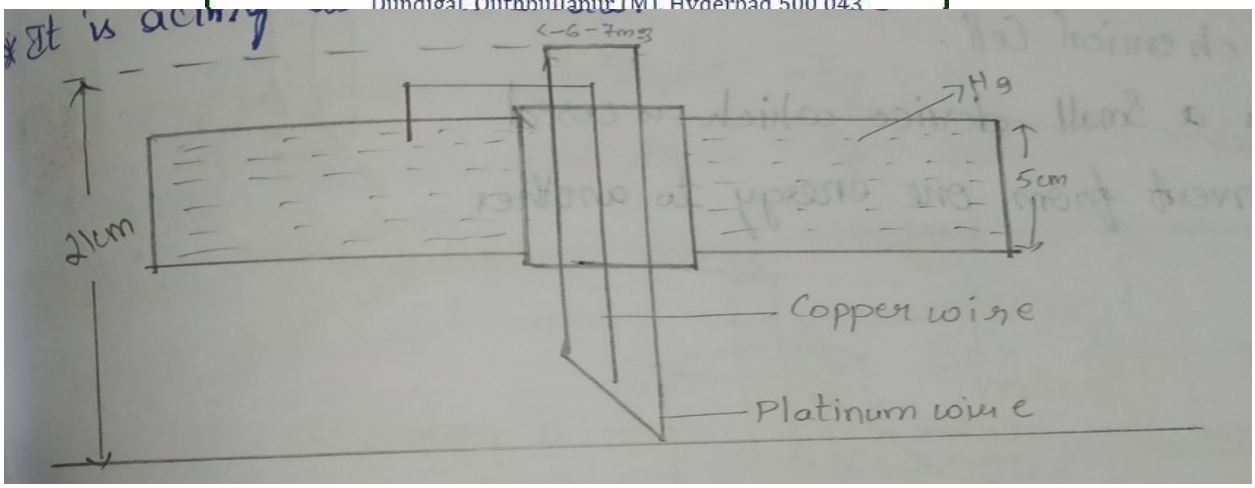
2-12 seconds takes the time to form a mercury droplets.

20-30 droplets can be formed in a minute and all the mercury droplets form mercury pool at the bottom and acting as counter electrode.

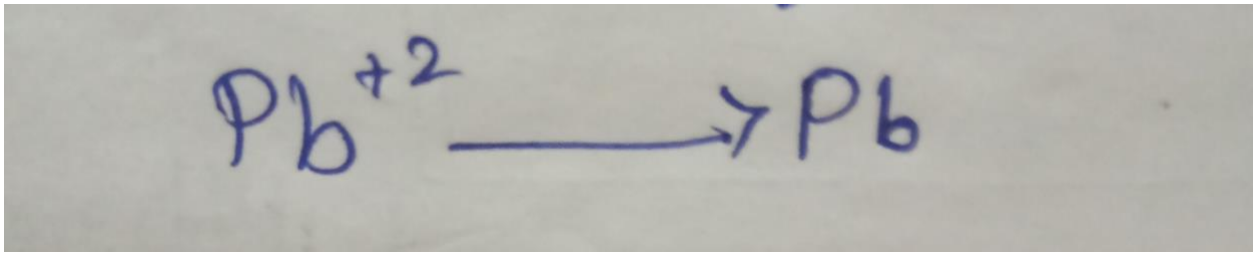
The potential can be applied for DME is +0.4 to -1.8 volts.

Working:

1. The sample analyte is taken in a beaker along with 50-100 times of supporting electrolyte i.e.,Kcl.
2. Nitrogen gas is introduced into the beaker to remove the dissolved oxygen.
3. Dropping mercury electrode and mercury pool are connected to battery and external potential is applied.
4. The sample analyte is taken in a beaker along with 50-100 times of supporting electrolyte i.e.,Kcl.
5. Nitrogen gas is introduced into the beaker to remove the dissolved oxygen.
6. Dropping mercury electrode and mercury pool are connected to battery and external potential is applied.



4. The potassium cation reaches to cathode that is DME and form Helm Holtz double layer after that the sample Pb+2 reaches to the cathode surface by passing through potassium double layer and reduced their.



5. Due to the potential difference current is produced because of diffusion of ions which is directly proportional to concentration of analyte.

Rotating platinum electrode

This is used when more positive potential is applied.

Steady electrode if we use, we get slow diffusion current .so that we use rotating platinum electrode which gives sharp and accurate result.

it consists of 21cm long mercury platinum wire consists of 5-6 mm length and 0.5mm diameter.

The total electrode is covered with glass tube which rotated 600 rpm speed.

It is acting as a indicated electrode.

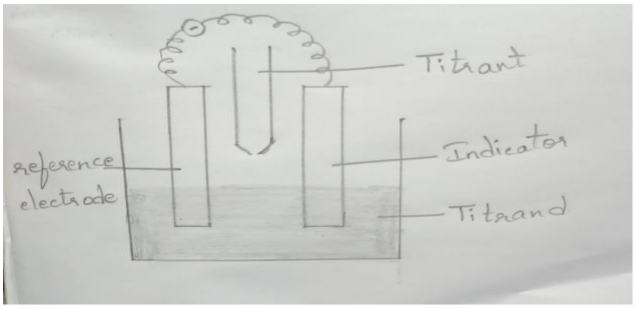
Polarography graph is known as polarogram

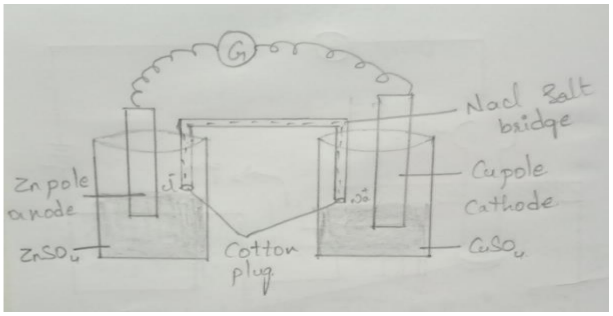
Application:

.It is used for determination of quantitative analysis.
2.It is used for determination of qualitative analysis.
3.It is used for determination of dissolved oxygen.
4.It is used for determination of organic and inorganic compounds

Potentiometry

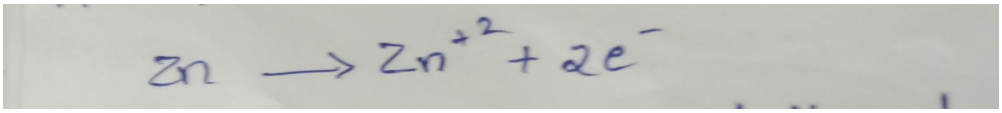
Electro chemical cell

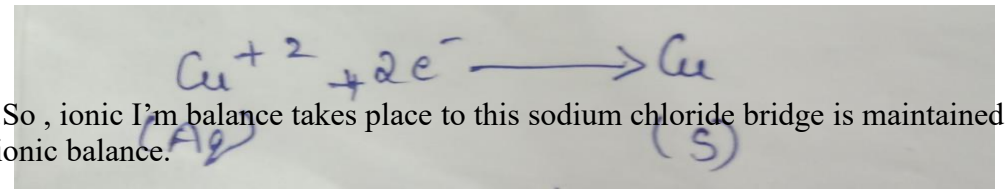




Cell is a small device which is used to convert from one energy to another energy.
At anode, Oxidation takes place

At cathode, Reduction takes place





.So , ionic I'm balance takes place to this sodium chloride bridge is maintained ionic balance.

.chlorides move to anode and sodium move towards cathode.

.We have two types of electrodes in potentiometric titrations i.e.,

(1) Reference electrode

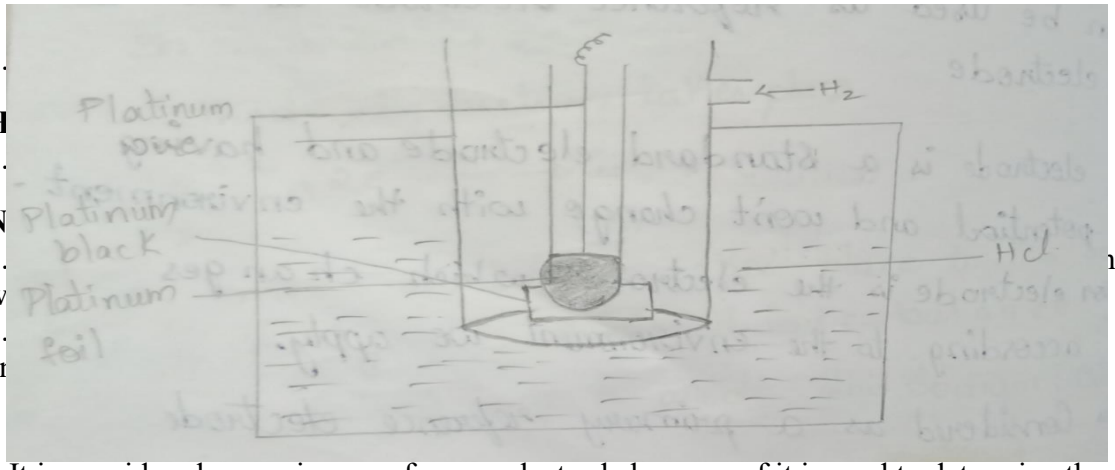
(2) Indicator electrode

Reference electrode:

1.Primary reference electrode Eg:Hydrogen.
2.Secondary reference electrode Eg : Saturated calomel electrode, silver- silver chloride electrode, Mercury-mercury sulphate electrode.

(2) Indicator electrode:

1.



H
1.

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e

3.It is considered as a primary reference electrode because of it is used to determine the potential of other electrodes.

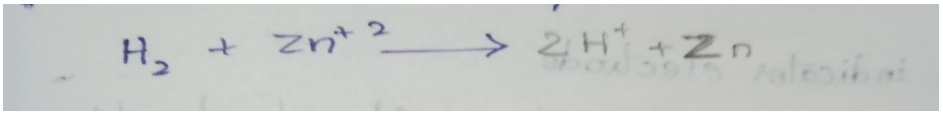
4.It is acting as Indicator electrode when dip in analyte or sample solution.

5.It is acting as reference electrode when it is dip in standard electrode solution.

Construction and Working:

1.It consists of a tube and a hole at bottom.
2.It consists of another tube which is having a platinum or copper wire with platinum foil which is marked with platinum black.
3.Through this glass hydrogen gas is introduced where hydrogen is converted into ions . Hence the name is hydrogen Electrode.

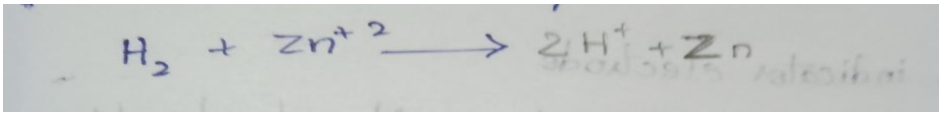
The reaction takes place



Saturated calomel Electrode

Construction and Working
It consists of inner jacket and outer sleeve and in inner jacket platinum wire is connected with mercury and in turn connected with calomel and potassium chloride .
2.Tbe outer sleeve consists of saturated potassium chloride or 1N Kcl or 0.1N Kcl.
3. The tip of apparatus consists of potassium chloride and porous plug.

The reaction takes place



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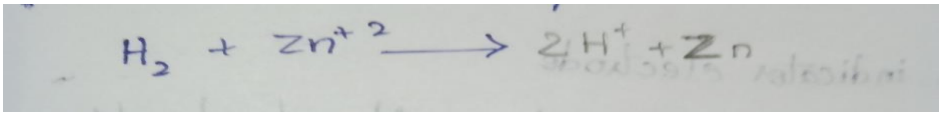

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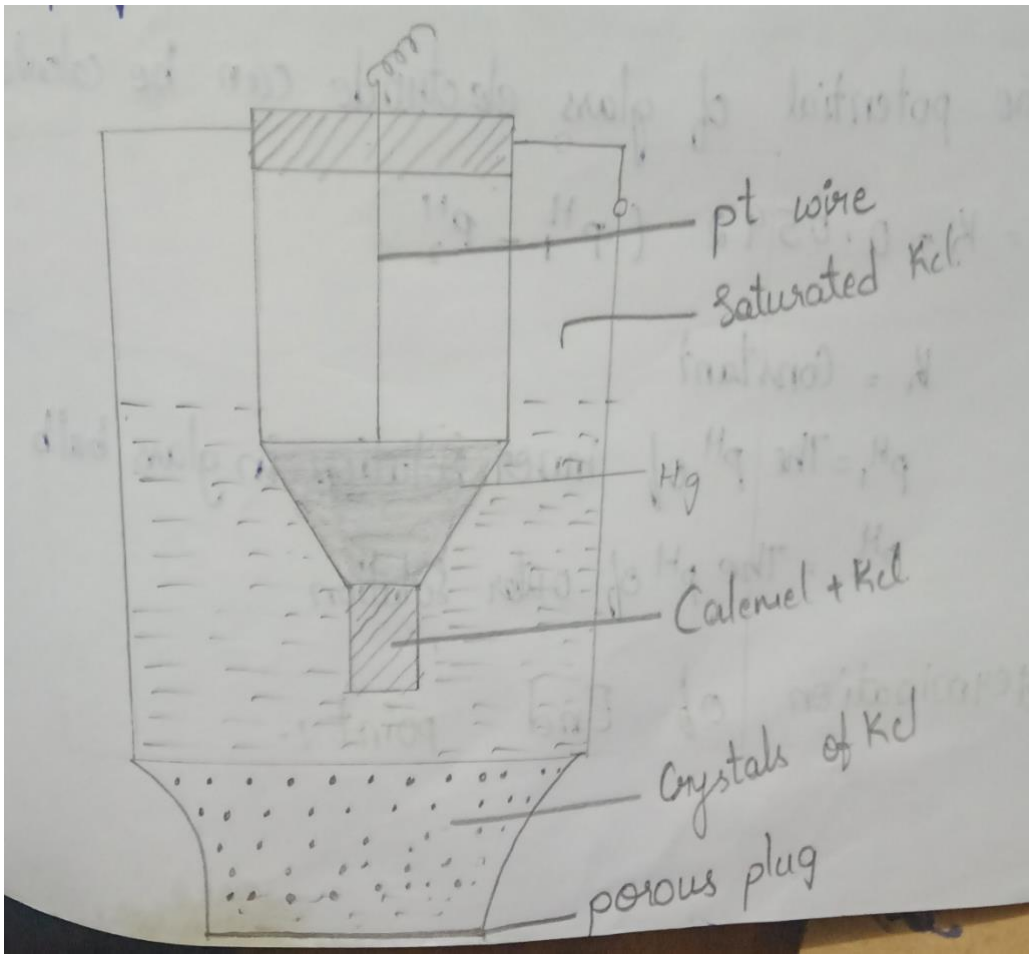
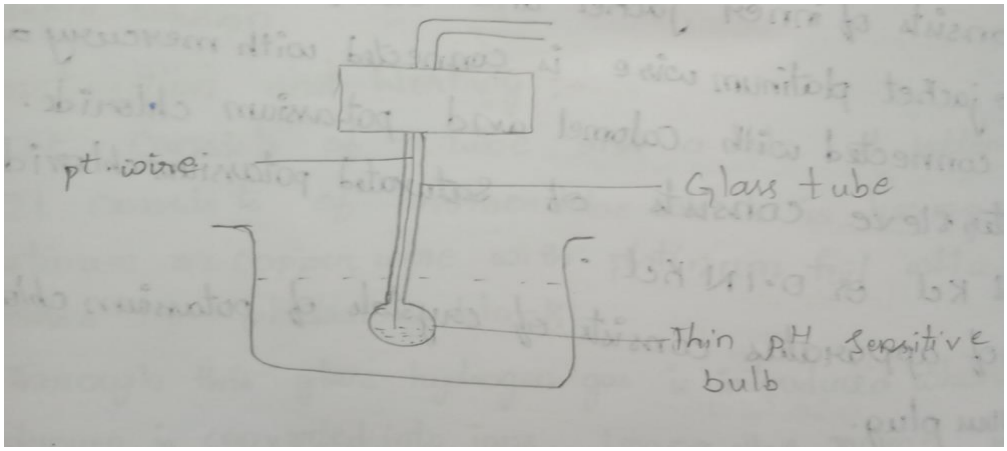
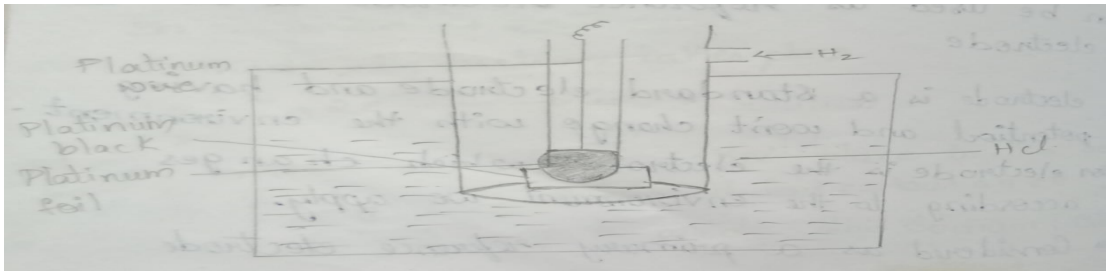

pt wire
Saturated Kcl
Hg
Calomel + Kcl
Crystals of Kcl
porous plug

Glass Electrode





It is acting as Indicator electrode.

2.This is widely used Indicator it consists of glass tube with platinum or silver wire .

3.The glass tube is having a thin ph sensitive bulb.

4. The potential of glass electrode can be calculated by